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PERCHLORATES: A REVIEW OF THEIR THERMAL DECOMPOSITION AND COMBUSTION, WITH AN APPENDIX ON PERCHLORIC ACID

by

G. S. Pearson

OCTOBER 1968

MINISTRY OF TECHNOLOGY, LONDON, W.C.2

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SUMMARY

The thermal decomposition and combustion of both non-metallic and metallic perchlorates are reviewed. Particular attention is given to those perchlorates that have been considered for use in solid propellents including ammonium, hydrazine, hydroxylamine, nitrosyl, nitronium, lithium and potassium perchlorates. Previous reviews on ammonium perchlorate and on perchloric acid have been brought up-to-date. The previous review* on perchloric acid is included as an appendix.

Common features in the behaviour of the perchlorates are ascertained and comparative data tabulated. Areas for future study are indicated.

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* Previously issued as R.P.E. Technical Memorandum 352.

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1 INTRODUCTION

Perchlorates have been used extensively as oxidizers in explosives. More recently, they have found an increasing use as oxidizers in solid propellents. In particular, ammonium perchlorate is used in composite propellents in which the oxidizer crystals are incorporated in a polymeric fuel binder.

In recent years the search for more energetic solid propellents has stimulated the revival of interest in other perchlorates, and especially in non-metallic perchlorates, as possible propellent ingredients. This review collates the available data on a wide range of perchlorates, and attempts to ascertain the common features in the behaviour of these perchlorates. The previous reviews on perchloric acid[1] and ammonium perchlorate[2] are supplemented by material recently published*. The final section tabulates and discusses comparative data for the perchlorates reviewed. Indications are given of areas where future research would be valuable.

2 NITROSYL PERCHLORATE, $NOClO_4$

2.1 General

Nitrosyl perchlorate was first prepared by Hofmann and von Zedtwitz[3] in 1909 by passing a mixture of NO and NO_2 into 72% perchloric acid:

$$2HClO_4 + NO + NO_2 \longrightarrow 2NOClO_4 + H_2O \quad . \qquad (1)$$

The nitrosyl perchlorate was precipitated in the form of colourless crystals. A much improved yield was obtained by Cruse et al.[4] by passing nitrogen oxides into a mixture containing concentrated sulphuric acid and sodium perchlorate in the ratio 1:7.

High purity nitrosyl perchlorate (99.7%) has recently been prepared[5] by reaction of cold 70% perchloric acid with excess nitrogen tetroxide in 99% nitric acid at -5 to -10°C. The crystalline nitrosyl perchlorate separates out and is dried. A similar method[6] reacts chlorine heptoxide with anhydrous nitric acid or RFNA in excess at -78°C in the presence of a dehydrating agent.

---

* The literature survey for the present review was completed on 1 March 1968.

Nitrosyl perchlorate is stable at room temperature but is decomposed by heat to yield nitrogen oxides. Some general properties[7-10] are summarized in Table 1. Other properties are described in a report[11] in which its use as a solid propellent was considered. It is readily hydrolysed to nitrous and perchloric acids:

$$NOClO_4 + H_2O \longrightarrow HNO_2 + HClO_4 \quad . \qquad (2)$$

It is extremely hygroscopic; consequently a protective coating is required where atmospheric moisture is present. Since nitrosyl perchlorate has been found not to react with vinyl chloride polymers, these have been used for such coatings.

The reactions of nitrosyl perchlorate with some organic compounds are generally vigorous and frequently result in explosion[11]. In particular, a solution of 25% by volume of aniline in ethyl alcohol ignited readily on contact with nitrosyl perchlorate.

Nitrosyl perchlorate has also been used in a method[12] for preparing anhydrous metal perchlorates with simultaneous production of nitrosyl compounds.

2.2 Thermochemistry

The heat of formation was measured by Cruse et al.[13] from the heat of reaction of nitrosyl perchlorate with sodium hydroxide:

$$9NOClO_4 + 16NaOH = 9NaClO_4 + 6NaNO_2 + NaNO_3 + 2NO + 8H_2O \quad . \qquad (3)$$

The value initially derived[13] was -39.6 ±0.3 kcal mole^{-1} but this was later recalculated[14] using better auxiliary heats of formation to be -41.79 ±0.08 kcal mole^{-1}. However, these auxiliary heats of formation do not correspond well with the values given in the N. B. S. Circular 500 [15].

The discrepancy between the values obtained for the heat of formation of potassium perchlorate by Johnson and Gilliland[16] and by Vorob'ev et al.[17,18] has been described previously[1]. Recently, direct determinations of the heats of decomposition of sodium and silver perchlorates have been made by Gilliland and Wagman[19]. Solution calorimetry was then used to relate these heats of

decomposition to the heat of decomposition of potassium perchlorate. The heat of decomposition derived was

$$\Delta H = -1.41 \pm 0.20 \text{ kcal mole}^{-1}$$

which may be compared to the previous values of Johnson and Gilliland[16]

$$\Delta H = -0.96 \pm 0.08 \text{ kcal mole}^{-1}$$

and of Vorob'ev et al.[17,18]

$$\Delta H = -2.55 \pm 0.18 \text{ kcal mole}^{-1} .$$

These lead[1] to values for the heat of formation of perchloric acid in aqueous solution of -30.58, -31.03 and -29.93 kcal mole^{-1} respectively or a best mean value of -30.51 kcal mole^{-1}.

Recalculation of Cruse's data using later N.B.S. values[19-21] yields a value for the heat of formation of nitrosyl perchlorate of

$$\Delta H_f = -36.8 \pm 0.4 \text{ kcal mole}^{-1}.$$

2.3 Thermal decomposition

Cruse et al.[22] studied the thermal decomposition by heating a sample at a rate of about 3 deg C min^{-1}. Decomposition began below 100°C with the evolution of a yellow gas. A small explosion was observed at 115-120°C and a brown gas was evolved above 140°C. Analyses of the product gas suggested that the initial decomposition was:

$$2NOClO_4 \longrightarrow N_2O_5 + 2ClO_2 + \tfrac{1}{2}O_2 , \qquad (4)$$

followed by decomposition of the nitrogen and chlorine oxides corresponding to the overall reaction:

$$2NOClO_4 \longrightarrow N_2O_4 + Cl_2 + 3O_2 . \qquad (5)$$

Markowitz et al.[9] studied the decomposition of a 0.5 gm sample at 3-5 torr and 92°C and found that weight losses of 27, 61, 94 and 100% occurred after 3,

6, 9 and 12 hours respectively. At a higher temperature, 100°C, the losses were 65, 80 and 99% after 3, 6 and 9 hours respectively. Differential thermal analysis (DTA) experiments showed no sign of a crystallographic transition when samples were heated from 0 to 100°C at heating rates of 5 and 10 deg C per minute.

Later work by Rosolovskii[10,23] in which nitrosyl perchlorate was decomposed at 99°C at a pressure of 1 torr showed that nitronium perchlorate was present in the residue. Experiments were stopped at various stages and both the solid residue and the gaseous products were analysed. The presence of nitronium perchlorate was confirmed by the infrared spectrum of the solid.

The ratio of chlorine to nitrogen found in the product gases was close to unity and the presence of chlorine dioxide was shown by measuring the absorption spectrum of an aqueous solution of the product gases. The major nitrogen containing species was nitrogen dioxide. The proposed mechanism was:

$$2NOClO_4 \longrightarrow NO_2ClO_4 + NO_2 + ClO_2 \qquad (6)$$

followed by

$$NO_2ClO_4 \longrightarrow NO_2 + ClO_2 + O_2 \, . \qquad (7)$$

It was suggested that the chlorine found in the products results from pyrolysis of chlorine dioxide. The ratio NO_2ClO_4:$NOClO_4$ was found to increase throughout the decomposition, thus showing that the rate of pyrolysis of nitronium perchlorate is somewhat slower than that of nitrosyl perchlorate.

DTA curves at a heating rate of 3 deg C per minute showed[10,23] two resolved endothermic regions; the first at 100-125°C was ascribed to nitrosyl perchlorate decomposition and the second at 165-180°C to nitronium perchlorate decomposition. The effect of addition of cadmium or zinc oxide to nitrosyl perchlorate in a molar ratio of oxide:$NOClO_4$ of about 1:4 was examined[24] by DTA experiments. The endotherms at 100-125°C were again observed but that at 165-180°C was replaced by an endotherm at 255-260°C with cadmium oxide and at 260-270°C with zinc oxide. It was suggested that the endotherms at the higher temperatures corresponded to the decomposition of anhydrous cadmium and zinc perchlorates respectively. Infrared spectra confirmed that the solid residue

contained the metal perchlorate along with nitronium perchlorate. The almost pure (>99%) zinc perchlorate could be obtained by decomposing the nitronium perchlorate by prolonged heating in vacuo. The cadmium perchlorate was thermally unstable and could not be isolated in this way.

The formation of nitronium perchlorate by thermal decomposition of nitrosyl perchlorate has been confirmed[25] by X-ray examination of the residue from decomposition at 130-150°C in dry nitrogen at 1 atmosphere. The increase in nitronium perchlorate content of the residue was found to increase monotonically with the extent of decomposition of the nitrosyl perchlorate.

It is concluded that the mechanism indicated by equations (6) and (7) explains the observations so far made. No estimates have yet been obtained of the activation energy or the rate constant for the decomposition, although nitrosyl perchlorate clearly decomposes at a faster rate than nitronium perchlorate.

2.4 Combustion

Nitrosyl perchlorate has been little considered as a rocket propellent since it is less stable than nitronium perchlorate and also contains less oxygen. However, a proposal[11] was made in 1941 to use it as a propellent with ammonia as a fuel, since it was known that ammonia ignited spontaneously and burnt smoothly when passed over solid nitrosyl perchlorate. It was proposed to operate with an ammonia excess thereby reducing the combustion temperature to about 1500°C.

An ignition delay was observed when ammonia was passed over the solid perchlorate but immediate ignition was achieved when the perchlorate was preheated to 100°C. The burning rate of nitrosyl perchlorate in the form of 15.4 mm diameter rods in an ammonia flow of about 500 cm^3 sec^{-1} was generally about 1 mm sec^{-1} although values as high as 3 mm sec^{-1} were recorded. However the burning surface was usually conical in shape.

Mixtures of nitrosyl perchlorate and activated carbon powder burnt at atmospheric pressure. A 1:5 mixture tamped into a 13 mm diameter glass tube had a burning rate of 5 mm sec^{-1}. It was suggested that such a mixture could be used to vaporize the nitrosyl perchlorate which would then react fully with the ammonia.

The handling of such a reactive and hygroscopic material is formidable and no further combustion studies have been reported. The problems of handling

nitrosyl perchlorate are similar to those for nitronium perchlorate, which is also energetically a more attractive oxidizer.

3 NITRONIUM PERCHLORATE, NO_2ClO_4

3.1 General

Hantzsch[26,27] mixed anhydrous nitric and perchloric acids and obtained two distinct perchlorates, depending on the proportions of the acids, for which he proposed:

$$HNO_3 + HClO_4 \longrightarrow (H_2NO_3^+)\ (ClO_4^-) \qquad (8)$$

$$HNO_3 + 2HClO_4 \longrightarrow (H_3NO_3^{++})\ (ClO_4^-)_2 \ . \qquad (9)$$

However, no special precautions were taken to exclude moisture and samples used for analysis were freed from excess acid on porous tiles in the laboratory atmosphere. This work was repeated by Goddard et al.[28] taking care to reduce exposure to the atmosphere as much as possible and using as low a temperature as possible to minimise the thermal decomposition of the reactants. They found that the perchlorates proposed by Hantzsch ((8) and (9)) were not produced but that mixtures of nitronium perchlorate and perchloric acid monohydrate were formed.

However, the existence of the perchlorates postulated by Hantzsch has recently been re-examined by Rousselet[29-31], who studied the solid-liquid phase diagram for the binary system NO_2ClO_4 - $HClO_4.H_2O$. This was characterized by three invariants - one at -24.0°C corresponding to the crystal transition of perchloric acid monohydrate:

$$\underset{\alpha}{HClO_4.H_2O} \rightleftharpoons \underset{\beta}{HClO_4.H_2O} \ , \qquad (10)$$

the second at 38.6°C to a eutectic between perchloric acid monohydrate and a new compound, and the third at 51.0°C to the incongruent melting point of the new compound which decomposed to nitronium perchlorate and a liquid. The new compound was shown to be $HNO_3.2HClO_4$ which is equivalent to the perchlorate $(H_3NO_3^{++})\ (ClO_4^-)_2$ formed in reaction (9).

This compound was found to be formed readily by direct contact of perchloric acid monohydrate with nitronium perchlorate because the thermal effect,

as shown by a DTA curve, was virtually the same whether the reactants were mixed briefly or for a long period. It was also formed by reaction at 0°C of 2 moles of anhydrous perchloric acid with 1 mole of anhydrous nitric acid. The products were shown to be identical by X-ray spectra which were different from the X-ray spectra of perchloric acid monohydrate and of nitronium perchlorate.

Later work[31] has shown by infrared spectrometry that the compound is actually the double perchlorate $(H_3O^+)(NO_2^+)(ClO_4^-)_2$ and not $(H_3NO_3^{++})(ClO_4^-)_2$ as suggested by Hantzsch.

The ternary system $Cl_2O_7 - N_2O_5 - H_2O$ has recently been re-examined by Rosolovskii et al.[32] and Skorokhodov[33]. The crystalline compounds observed were

(i) $NO_2ClO_4 \cdot 2H_2O$ (or $HNO_3 \cdot HClO_4 \cdot H_2O$) ,

(ii) $NO_2ClO_4 \cdot H_3OClO_4$ (or $HNO_3 \cdot HClO_4 \cdot 2H_2O$) ,

(iii) $NO_2ClO_4 \cdot \frac{1}{3}H_2O$.

The stability of these compounds increases from (i) to (iii): (i) is stable at 0°C only in contact with the mother liquor, (ii) is stable up to 50°C, when it melts. It can be distilled without change at 30°C and 1 torr, and (iii) starts to melt at about 100°C and becomes yellow at 130°C. The structures of the observed compounds were not examined.

Nitronium perchlorate may be prepared by reaction of nitrogen pentoxide and anhydrous perchloric acid

$$N_2O_5 + HClO_4 \longrightarrow NO_2ClO_4 + HNO_3 \quad , \qquad (11)$$

which yields[28] a sample >99% pure. Nitrosyl perchlorate is an impurity present to the extent of about 0.2%. Other methods include the reaction of chlorine heptoxide with nitric acid in the presence of a dehydrating agent

$$Cl_2O_7 + HNO_3 \longrightarrow NO_2ClO_4 + HClO_4 \quad , \qquad (12)$$

or passing nitrogen pentoxide diluted with oxygen through a solution of chlorine heptoxide in carbon tetrachloride[30].

Nitronium perchlorate may also be prepared[34-36] by reaction of ozonized air, i.e. a mixture of ozone and nitrogen oxides, with chlorine dioxide:

$$2NO_2 + 2ClO_2 + 6O_3 \longrightarrow 2NO_2ClO_4 + 7O_2 \cdot \qquad (13)$$

It is a colourless crystalline compound stable at room temperature which decomposes on heating. Some properties[37-41] are presented in Table 2. It is extremely hygroscopic and absorbs water to produce nitric and perchloric acids,

$$NO_2ClO_4 + H_2O \longrightarrow HNO_3 + HClO_4 , \qquad (14)$$

although solution in water results in only moderate evolution of heat.

Raman[42,43], infrared[44] and X-ray[37,40,45] examinations of nitronium perchlorate have shown the structure to be $NO_2^+ClO_4^-$ with a monoclinic unit cell. The bond lengths are 1.464 ±0.007 Å for Cl-O and 1.10 ±0.01 Å for N-O.

Nitronium perchlorate reacts violently with many organic compounds, and ignition and explosion may result as was observed[34] with acetone, diethyl ether and benzene. However, its solution in nitromethane gently nitrates aromatic compounds[28].

Complex metal perchlorates of the type $NO_2Al(ClO_4)_4$ and $(NO_2)_3Al(ClO_4)_6$ have recently been prepared[46]. In general, they appear to be somewhat reactive and thermally unstable, although energetically they should be attractive as oxidizers for high energy solid propellents.

3.2 Thermochemistry

The heat of solution in water at 24.7°C was determined by Cordes[41] who obtained a value of -20.4 ±0.4 kcal mole^{-1} for solution of 1 mole of perchlorate in 10^4 moles of water:

$$NO_2ClO_4 + H_2O_{(aq)} \longrightarrow HNO_{3(aq)} + HClO_{4(aq)}, \quad \Delta H = -20.4 \pm 0.4 \text{ kcal mole}^{-1}. \qquad \ldots\ldots(14)$$

The thermochemical data then available[15] gave a heat of formation of 8.0 ±0.4 kcal mole^{-1} for crystalline nitronium perchlorate. Recalculation using later heats of formation[1,20] yields a value of 8.7 ±0.4 kcal mole^{-1}.

The heat of neutralization in potassium hydroxide was later determined by Gilliland[39] who obtained a heat of formation of 8.88 ±0.25 kcal mole^{-1} in good agreement with the recalculated value from the work of Cordes.

3.3 Thermal decomposition

Nitronium perchlorate was observed[28,34] to decompose without explosion at 120-135°C with the evolution of nitrogen dioxide.

The first comprehensive study was made by Cordes[47] who studied the decomposition of powder samples in vacuo at 70 to 112°C. The products were condensed in cold traps and then analysed by mass spectrometer. The main components were oxygen, nitrogen dioxide, chlorine, chlorine dioxide and NO_3Cl together with small amounts of nitrogen pentoxide. The analytical results were quite variable due to the different extents of reaction and decomposition of the products in the cold trap. The degree of decomposition was calculated from the rate of pressure increase. Rate constants were then obtained using Mampel's theory for the decomposition of uniform spherical particles which gave an excellent fit to the experimental data for 0.5% to 95% decomposition. The rate curves suggested that a first-order initiation of nuclei was followed by a three dimensional growth of these nuclei with rate constants

$$\text{Initiation} \quad : \quad k = 10^{12.6}\, e^{-28,500/RT} \ \text{sec}^{-1}$$

$$\text{Growth} \quad : \quad k = 10^{12.5}\, e^{-27,500/RT} \ \text{sec}^{-1}$$

and an induction time given by

$$\tau = 10^{-15.0}\, e^{+30,700/RT} \ \text{sec}^{-1} .$$

The mechanism for the decomposition was speculative, three stages being postulated:

(1) Reactions in the solid

$$\left.\begin{aligned} ClO_4^- &\longrightarrow ClO_4 + e , \\ e + NO_2^+ &\longrightarrow NO_2 . \end{aligned}\right\} \qquad (15)$$

(2) Desorption

$$\left.\begin{array}{l} ClO_{4(ads)} \rightarrow ClO_{4(g)}, \\ NO_{2(ads)} \rightarrow NO_{2(g)} \cdot \end{array}\right\} \quad (16)$$

(3) Reactions in the gas phase

$$\left.\begin{array}{l} ClO_4 \rightarrow ClO_2 + O_2 , \\ NO_2 + ClO_2 \rightarrow NO_3 + ClO , \\ NO_2 + ClO \rightarrow NO_3Cl , \\ 2ClO \rightarrow Cl_2 + O_2 , \\ NO_2 + NO_3 \rightleftharpoons N_2O_5 \rightarrow N_2O_4 + \tfrac{1}{2}O_2 \cdot \end{array}\right\} \quad (17)$$

The solid residue was not analysed. The rate constants were independent of sample size which indicated that the product gases had little effect on the decomposition under these conditions.

Marshall and Lewis[48] re-examined the thermal decomposition and found that it began at 50°C and that the stability appeared to be related to the purity. They showed that, at 65°C in sealed tubes, nitrosyl perchlorate was a major decomposition product. Moreover, nitrogen tetroxide in the liquid phase was shown to convert nitronium perchlorate to nitrosyl perchlorate, quantitatively.

Decomposition in vacuo at 65°C was found to proceed in four stages:

(1) an immediate deposit of sublimate on heating the sample to 65°C,

(2) an induction period of 24-40 hours during which no gas evolution was observed,

(3) an initially slow but rapidly increasing production of oxygen which reached a maximum at about 100 hours with simultaneous appearance of a yellow condensate in a trap at -196°C and finally,

(4) a gradual slow decrease in the rate of oxygen evolution.

The amount of oxygen liberated per gram weight loss varied from 15.5 to 6.5 moles indicating a change in the mechanism or the increasing importance of a secondary reaction. Analysis of the solid residue by X-ray, Raman and wet analysis techniques showed that nitrosyl perchlorate was present in substantial quantities. The maximum rate of formation of nitrosyl perchlorate was found to coincide with the maximum rate of decomposition of nitronium perchlorate. Further, the nitrosyl perchlorate appeared to decompose faster than the nitronium perchlorate (cf. section 2.3).

The sublimate was shown to be nitronium perchlorate and did not contain nitrosyl perchlorate. Sublimation was independent of the decomposition and occurred at an almost constant rate of about $\frac{1}{2}$ to $\frac{1}{3}$ of that of the decomposition.

The mechanism proposed for the decomposition was in two stages:

$$NO_2ClO_4 \longrightarrow NOClO_4 + \tfrac{1}{2}O_2 \qquad (18)$$

followed by

$$NOClO_4 \longrightarrow NO_2 + ClO_2 + \tfrac{1}{2}O_2 \,. \qquad (19)$$

Additionally, the following reaction would be required in the decomposition in sealed tubes

$$NO_2ClO_4 + N_2O_4 \longrightarrow NOClO_4 + N_2O_5 \,. \qquad (20)$$

It is concluded that decomposition is probably initiated by reaction (18) forming nitrosyl perchlorate, and that the instability of nitronium perchlorate arises from the particular NO_2^+ and ClO_4^- combination, since complex nitronium perchlorates such as $(NO_2)_3Al(ClO_4)_6$ and $NO_2Zn(ClO_4)_3$ are quantitatively prepared[46,49] at 125°C.

The various studies of nitronium perchlorate in which the X-ray, infrared and Raman spectra have been measured also indicate that something less than a truly ionic crystal lattice is present. This would be expected to facilitate the decomposition.

Recently, the photochemical and thermal decomposition of nitronium perchlorate have been examined by Maycock et al.[50,51]. In the photochemical

study a sample of about 500 mg was irradiated by an unfiltered high pressure mercury arc and the kinetics of gas evolution studied as a function of intensity, temperature in the range -40 to +25°C, and time of irradiation. The absorption spectrum of a single crystal showed nitronium perchlorate to be transparent in the visible region and to absorb below 3400 Å. The rate of evolution of oxygen and nitric oxide, after an initial period of acceleration and deceleration, remained constant with time. There was also a small but definite induction period. Gaseous products were shown not to affect the rate of gas evolution. An Arrhenius type plot of the temperature dependence of rate of gas evolution (gases not trapped by methanol-solid carbon dioxide) gave activation energies of 10.5 kcal mole^{-1} for irradiations of 2 and 6 minutes and of 8.25 kcal mole^{-1} for 30 minutes. Mass spectrometric analysis of an untrapped sample of product gas showed the presence of oxygen, nitric oxide, chlorine, nitrogen dioxide, chlorine dioxide and ClO (in order of decreasing abundance). The oxides of chlorine were minor constituents.

It was proposed[50] that two processes, releasing oxygen and nitric oxide, were taking place simultaneously. The first process occurred quite rapidly and resulted in the initial fast rate but was considered to be dependent on the existence of impurity or trapping centres. This process was postulated as

$$\left.\begin{aligned} ClO_4^- &\rightleftharpoons (ClO_4^-)^* , \\ (ClO_4^-)^* + T &\rightleftharpoons (TClO_4^-)^* , \\ (TClO_4^-)^* + (ClO_4^-)^* &\longrightarrow T + Cl_2 + 4O_2 + 2e^- , \\ 2NO_2^+ + 2e^- &\longrightarrow 2NO_2 + 2 \text{ cation vacancies} . \end{aligned}\right\} \quad (21)$$

The traps are thus associated with two anion vacancies and can no longer participate in the above process (21) which thus dies out to be replaced by the second process which does not depend on such centres. This was postulated as

$$\left.\begin{array}{c} NO_2^+ \overset{h\nu}{\rightleftharpoons} (NO_2^+)^* \ , \\ ClO_4^- \rightleftharpoons (ClO_4^-)^* \ , \\ (NO_2^+)^* + (ClO_4^-)^* \longrightarrow NO + ClO + 2O_2 \ . \end{array}\right\} \qquad (22)$$

No analyses were made of the solid residue after photolysis had been completed.

The thermal decomposition was studied[51] at 10^{-3} torr for the temperature range 100–160°C using isothermal constant volume techniques with mass spectrometric analysis. Such analysis of the decomposition products indicated the presence of oxygen, chlorine, chlorine dioxide, ClO and nitric oxide with no trace of NO_3Cl, nor of parent or fragment ions of nitrosyl perchlorate.

Pressure-time curves were obtained as were curves for the variation in peak height with time for oxygen, chlorine and nitric oxide. An induction period of a few minutes was found in contrast to that of several hours previously observed[47]. Analysis of the data for oxygen, chlorine and nitric oxide by the Prout-Tompkins equation:

$$\ln [\alpha/(1 - \alpha)] = kt + c \ , \qquad (23)$$

where α is the fractional decomposition in time t and k is the rate constant, yielded rate constants that agreed within experimental error.

Activation energies of 16.11, 14.43 and 15.14 kcal mole^{-1} were obtained from the oxygen, chlorine and nitric oxide data respectively, with a best line through all the points corresponding to 14.3 kcal mole^{-1}.

However, the validity of applying this equation was doubtful and consequently the data were re-analysed using the Jacobs-Kureishy method in which the activation energy of any reaction obeying a single equation of the form

$$F(\alpha) = kt \qquad (24)$$

can be obtained by finding the time for the fractional decomposition to proceed from $\alpha = \alpha_1$ to $\alpha = \alpha_2$.

The oxygen data when treated in this way gave an activation energy of 16.12 kcal mole^{-1}, in close agreement with the value found from the Prout-Tompkins equation for the same data.

It is concluded that the activation energy is 15 ±1 kcal mole^{-1}. Re-examination by Maycock and Pai Verneker[51] of Cordes data[47] suggested an activation energy of about 15 kcal mole^{-1} above 100°C and of about 25 kcal mole^{-1} below 100°C, rather than the value reported by Cordes[47] of 28-30 kcal mole^{-1}.

The mechanism proposed is

$$\left.\begin{aligned} ClO_4^- &\rightarrow ClO_4 + e^- \text{ (conduction band)} , \\ ClO_4 &\rightarrow ClO_2 + O_2 \text{ (in solid phase)} , \\ e^- + NO_2^+ &\rightarrow NO_2 . \end{aligned}\right\} \quad (25)$$

The resultant gases, NO_2, O_2 and ClO_2 then react in the gas phase

$$NO_2 + ClO_2 \rightarrow NO + O_2 + ClO , \quad (26)$$

$$2ClO \rightarrow Cl_2 + O_2 . \quad (27)$$

The overall reaction may be expressed as

$$2NO_2ClO_4 \rightarrow 5O_2 + Cl_2 + 2NO , \quad (28)$$

although the experimental data do not clearly show the formation of $NO:Cl_2$ in a 2:1 ratio.

It appears probable, as suggested by Maycock and Pai Verneker[51], that the mechanism changes at about 100°C. Below this temperature the activation energy is about 25 kcal mole^{-1} and nitrosyl perchlorate is a product and above this temperature the activation energy is 15 kcal mole^{-1}. It has yet to be established that nitrosyl perchlorate is not formed at these higher temperatures.

3.4 Combustion

Nitronium perchlorate not only contains the highest percentage of oxygen of all the simple inorganic perchlorates considered in this review but it is

also an endothermic compound. It has therefore attracted interest as a possible oxidizer for solid propellents. It has been considered as a hybrid propellent with aniline or unsymmetrical dimethylhydrazine as the fuel and the specific impulse has been calculated[38].

However, it is difficult to handle nitronium perchlorate safely because it is sensitive. The sensitivity can be reduced by encapsulating the nitronium perchlorate crystals with a thin film of polymer[52]. It is important that the nitronium perchlorate should be free from perchloric acid otherwise reaction will occur with the polymer coating, or with the polymer in the propellent if the perchlorate is not encapsulated[53].

The burning rate of strands of nitronium perchlorate propellents has been studied[54] for a range of fuels: polyisobutene, paraffin wax (m.pt. 91°C), synthetic wax (m.pt. 200°C) and tetramethyl ammonium chloride (m.pt. 425°C). The nitronium perchlorate was used either as received as a fine powder (23 μ) or as recrystallized from nitric acid (110 μ). In the latter case the strands were prepared by pressing and not by extrusion. Burning rates were in the range 0.5 to 5.0 inch sec^{-1} at 1000 psi. It was found that the burning rates for strands containing 70% weight nitronium perchlorate (23 μ) were much lower than those for strands with 60% by weight nitronium perchlorate (1100 μ). This is the reverse from that predicted by Summerfield's granular diffusion flame theory[55]. Photographs of strands burning at 1 atm show that nitronium perchlorate particles are ejected from the surface of nitronium perchlorate-paraffin wax strands. Such ejection was not observed under these conditions for ammonium perchlorate paraffin wax strands, although it has been found under other conditions for ammonium perchlorate propellents[2,56]. Nor was ejection observed for nitronium perchlorate-tetramethyl ammonium chloride strands in which the fuel has a much lower volatility. An ammonium perchlorate strand with the same fuel could not be ignited even at 1000 psi, which further emphasises the high reactivity of the nitronium perchlorate or of its decomposition products.

It was concluded that oxidizer-fuel reaction at the interface was extremely rapid, whilst the oxidizer particle appeared to decompose at a relatively slow rate governed by heat transfer from the surrounding diffusion flame. It is true that nitronium perchlorate, unlike ammonium perchlorate, cannot support a flame by self-decomposition and thus burn as a monopropellent.

Linear pyrolysis studies[54] of pure nitronium perchlorate have shown that it pyrolyses fairly slowly but smoothly. On the other hand, mixtures with 5% finely ground synthetic wax decomposed violently causing the porous metal hot plates to rupture. Further, the reactions appeared to be oscillatory, which was not observed with ammonium perchlorate-fuel mixtures. An estimated heat of vaporization for nitronium perchlorate was obtained of 175 cal gm^{-1} exothermic, but this was probably in error on account of reaction between the pyrolysis products and the stainless steel plate.

Experiments on T-burner firings with nitronium perchlorate indicated[54] that contamination with moisture resulted in explosion. However, even when great care was taken to exclude moisture, a transition to a high burning rate was observed within 200 msec after ignition.

4 HYDRAZINE MONOPERCHLORATE, $N_2H_5ClO_4$

Hydrazine forms two perchlorates - the monoperchlorate $N_2H_5ClO_4$ and the diperchlorate $N_2H_5ClO_4 \cdot HClO_4$. As their decomposition and combustion are quite different[57], the monoperchlorate is described in this section and the diperchlorate is discussed in section 5. Their general properties[58-66] have, however, been collected together in a single table (Table 3).

4.1 General

Hydrazine monoperchlorate (HP) was first prepared by Salvadori[67] in 1907 by neutralizing a dilute solution of hydrazine hydrate with perchloric acid followed by evaporation on a water-bath. Later preparations have followed the same route. Experimental details are given, for example, by Levy et al.[63] and by Batty and Martin[62]. The latter workers emphasized the need to avoid contact with metal of any kind since soluble metal salts cause decomposition of HP. An alternative route by reaction of hydrazine and ammonium perchlorate has been patented[68].

HP is a white crystalline solid which has been reported[59] to be more impact-sensitive than pentaerythritol tetranitrate. However, Levy et al.[63] did not experience any explosions during the careful handling of HP. Stern[68] has shown that the sensitivity depends markedly on the water content and that the hemihydrate is much less sensitive than anhydrous HP. Some general properties are summarized along with the properties of the diperchlorate in Table 3.

4.2 Thermochemistry

The heat of solution determined by Shidlovskii et al.[59] was 9.77 kcal mole^{-1} for a 1:1000 dilution in reasonable agreement with the earlier value[69] of 9.26 kcal mole^{-1} for a 1:600 dilution. The heat of solution[59] may be combined with values for the heat of formation of ClO_4^- and $N_2H_5^+$ ions of -30.48 and -1.8 kcal mole^{-1} respectively to yield:

$$\Delta H_f\ N_2H_5ClO_4\ (aq) = -32.28 \text{ kcal mole}^{-1},$$

$$\Delta H_f\ N_2H_5ClO_4\ (s) = -42.05 \text{ kcal mole}^{-1}.$$

Another value may be deduced from the heat of dissociation to hydrazine and perchloric acid obtained by Levy[63],

$$\Delta H_{vap}\ N_2H_5ClO_4\ (l) = 59.2 \text{ kcal mole}^{-1}$$

which, with values[1,19] for the heats of formation of perchloric acid and hydrazine of -1.20 and 12.10 kcal mole^{-1}, gives

$$\Delta H_f\ N_2H_5ClO_4\ (l) = -48.3 \text{ kcal mole}^{-1}.$$

The heat of fusion was determined to be 3.84 kcal mole^{-1} by Rathmann[61] and 1.68 kcal mole^{-1} by Batty[62]. The latter value was determined from the solubility curves for HP in ethanol which is unlikely to behave as an ideal solution. Consequently the former value is used to obtain

$$\Delta H_f\ N_2H_5ClO_4\ (s) = -44.46 \text{ kcal mole}^{-1}.$$

The agreement with that derived from Shidlovskii must be considered good in view of the difficulties of preparing and handling a pure sample of HP. The best value is considered to be that derived from the heat of solution, -42.05 kcal mole^{-1}.

The hemihydrate has been studied by Gilbert[65,69] who determined its heat of solution to be 11.170 kcal mole^{-1} for a dilution of 1:670 and its heat of dehydration to be -6.977 kcal mole^{-1}. The heat of solution may be combined with that for solution of HP (for consistency Gilbert's value is

used here) to yield a heat of hydration of -1.913 ± 0.02 kcal mole^{-1}. This in turn gives

$$\Delta H_f\ N_2H_5ClO_4 \cdot \tfrac{1}{2}H_2O\ (s) = -77.925 \text{ kcal mole}^{-1}.$$

The heat of dehydration gives a very similar value

$$\Delta H_f\ N_2H_5ClO_4 \cdot \tfrac{1}{2}H_2O\ (s) = -78.120 \text{ kcal mole}^{-1}.$$

More recently, Carlton and Lewis[70] obtained a value of -8.8 kcal mole^{-1} for the heat of dehydration of the hemihydrate which yields

$$\Delta H_f\ N_2H_5ClO_4 \cdot \tfrac{1}{2}H_2O\ (s) = -79.75 \text{ kcal mole}^{-1}.$$

The consistency of the earlier results is favoured and consequently a best value of -78.02 ± 0.10 kcal mole^{-1} is taken.

4.3 Thermal decomposition

Early statements indicated[58] that HP decomposed near its melting point of 142°C. The first comprehensive study was by Shidlovskii et al.[59] who studied the weight loss of HP when held at a given temperature for 6 minutes. Decomposition was measurable at 180°C (0.3%) and increased up to 240°C (5.4%); rapid combustion was observed at 250°C. Determination of the 'ignition point' by heating a 0.2 g sample from 100°C at a rate of 20 deg C min^{-1} gave a temperature of 277-283°C for HP as compared to 360°C for ammonium perchlorate. The thermal stability of HP is thus much less than that of ammonium perchlorate.

Catalytic additions of 5% manganese dioxide or cuprous chloride to HP reduced this ignition point to 254-259°C and to 170°C respectively.

Thermal decomposition at 150-230°C was examined by Hermoni and Salmon[71] who also analysed the products of the decomposition. The final products below 200°C were ammonium perchlorate, hydrazine hydrochloride, water, nitrogen and a very small amount of chlorine. The rate of decomposition was followed by the pressure increase in a constant volume vacuum system. The rate fitted a first order law and the temperature dependence of the rate constant gave values for the Arrhenius parameters of

$$E = 20 \pm 0.3 \text{ kcal mole}^{-1}, \quad A = 5.9 \pm 0.3 \text{ min}^{-1} \quad (\text{presumably } 10^{5.9}) .$$

The proposed mechanism was a rate determining step,

$$N_2H_5ClO_4 \longrightarrow NH_4ClO_4 + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2 , \tag{29}$$

followed by

$$4H_2 + N_2H_5ClO_4 \longrightarrow N_2H_5Cl + 4H_2O . \tag{30}$$

Analyses for N_2H_4, NH_4^+ and Cl^- were said to be in good agreement with those expected from these equations.

The decomposition at 140-200°C has also been studied by Grelecki and Cruice[64,72]. Analyses of the vapour phase were made mass spectrometrically and of the solid phase by conventional techniques. Their results were in general agreement with those of Hermoni and Salmon[71]. The overall stoichiometry could be represented by

$$N_2H_5ClO_4 \longrightarrow \tfrac{7}{8}NH_4ClO_4 + \tfrac{1}{8}NH_4Cl + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2O . \tag{31}$$

The rate accelerated during the first 10% of reaction and then remained constant for 10-70% decomposition. An activation energy was deduced for the 10-70% part of the decomposition to be 23.8 kcal mole^{-1}.

The mechanism proposed was proton transfer

$$N_2H_5ClO_4 \longrightarrow N_2H_4 + HClO_4 , \tag{32}$$

followed by decomposition of the perchloric acid to yield radicals which react with the HP:

$$HClO_4 \longrightarrow OH + ClO_3 , \tag{33}$$

$$OH + N_2H_5ClO_4 \longrightarrow H_2O + NH_4ClO_4 + \tfrac{1}{2}N_2 , \tag{34}$$

$$ClO_3 + 7N_2H_5ClO_4 \longrightarrow 3H_2O + 6NH_4ClO_4 + 3\tfrac{1}{2}N_2 + NH_4Cl + HClO_4 , \tag{35}$$

which agrees with the overall reaction (31). It was proposed that the rate controlling step was the perchloric acid pyrolysis.

The thermal decomposition of the hemihydrate has been examined by Jacobs and Russell-Jones[73,74] at the higher temperature range of 180-280°C. The hemihydrate is dehydrated[65] to anhydrous HP by heating at 60.5°C. Consequently, the thermal decomposition studied was actually that of HP. The rate of decomposition was studied both from pressure increase on decomposition in vacuo and by thermogravimetry at 1 atm. In both cases the rate decreased throughout and did not conform to any of the usual equations (see equations used for ammonium perchlorate decomposition in Ref.2). Consequently, rate constants were determined from the initial slopes. Activation energies obtained from pressure increase and thermogravimetry were 36.5 kcal mole^{-1} and 35.8 kcal mole^{-1} respectively. The rate of decomposition was significantly greater in silica than in Pyrex but had the same activation energy.

Thermogravimetry showed a point of inflexion at 33% decomposition. Infrared and X-ray spectra of the residue at this point in the decomposition showed the residue to be ammonium perchlorate. It was suggested that the mechanism involves proton transfer with vaporization of the products:

$$N_2H_5ClO_4 \longrightarrow N_2H_4 + HClO_4 \,, \qquad (32)$$

followed by heterogeneous decomposition of the perchloric acid and of the hydrazine, and oxidation of the hydrazine by decomposition products of the perchloric acid. The overall equation, from product analyses and thermogravimetry, was

$$2N_2H_5ClO_4 \longrightarrow 0.8\ NH_4ClO_4 + 0.7\ O_2 + 1.6\ N_2 + 0.6\ Cl_2 + 3.4\ H_2O \,. \qquad (36)$$

4.4 Sublimation

The vaporization products of HP have been shown[75,76], by a cold matrix isolation technique with infrared identification of the trapped species, to be hydrazine and perchloric acid:

$$N_2H_5ClO_4 \longrightarrow N_2H_4 + HClO_4 \,. \qquad (32)$$

However, other infrared bands were observed which were assigned to ammonia, water and hydrogen chloride. A series of experiments at 163-210°C showed that the intensity of the bands of the ammonia and water but not those of the hydrogen chloride increased more rapidly with increasing temperature than those of hydrazine and perchloric acid. At temperatures above 200°C bands in the 1050-1400 cm^{-1} region became evident. These bands suggest the presence of a chlorine oxide other than $HClO_4$, Cl_2O_7, ClO_2 or Cl_2O.

The rate of vaporization was determined at 180-235°C by Levy et al.[63] using a cold-finger sublimation apparatus. The rate of vaporization was related to the vapour pressure by assuming the evaporation coefficient to be unity and the mean molecular weight of the vapour to be 66 (average of that of hydrazine and perchloric acid). The temperature dependence can be expressed as

$$\log_{10} P_{(mm)} = 10.2 - \frac{6400}{T} \qquad (37)$$

which yields a heat of vaporization of 29.2 kcal $mole^{-1}$. Consequently, the heat of reaction for equation (32) is 58.4 kcal $mole^{-1}$. Both the residue and sublimate in these experiments were analysed and shown to contain 95-100% HP. 97-99% of the HP used in each experiment was recovered as such, clearly showing that at 180-235°C effectively no decomposition occurs in sublimation from the melt onto the cold finger. Thus, in thermal decomposition experiments reaction occurs not in the melt but in the gas phase or on the reaction vessel walls after evaporation.

4.5 Combustion

It is convenient to describe the combustion of HP in three sub-sections, the first on pure HP, the second on HP-fuel mixtures and the third on catalysed systems.

4.5.1 Pure hydrazine perchlorate

Salvadori[67] reported that HP burnt smoothly when ignited, but that it exploded when struck. However, Shidlovskii et al.[59] were unable to ignite samples of HP powder packed into glass tubes of 1.05 cm inside diameter using a white hot wire at atmospheric pressure. The perchlorate was observed to melt and ignite but only a surface layer of 1-2 mm was consumed before combustion ceased. Mixtures with ammonium perchlorate containing

from 30 to 60% HP burnt stably in such tubes at rates from 0.13 to 0.22 cm sec^{-1}. Ammonium perchlorate alone will not burn under these conditions without preheating[2].

A more extensive study has been made by Levy et al[63]. With pure hydrazine perchlorate the behaviour was found to be irreproducible. Smooth deflagration was observed at 0.24 to 4.3 atm for both tamped (ρ = 1.1 to 1.3 gm cm^{-3}) and pressed (ρ = 1.8 to 1.9 gm cm^{-3}) strands but strands prepared later in the same way did not burn smoothly. Preheating of these strands resulted in smooth deflagration at 2, 4 and 6 atm but again these results could not be reproduced. It was concluded that this erratic behaviour was due to the presence or absence of small amounts of impurities which could catalyse a condensed phase process. This process was considered to be essential for steady combustion but to be a relatively minor part of the whole combustion process.

It should be noted that Levy[57] has reported that if the deflagration of pure HP is attempted by prolonged application of a heat source, the material usually detonates.

4.5.2 Hydrazine perchlorate-fuel mixtures

Levy et al.[57] examined the combustion with gaseous fuels using pressed 8 mm diameter spheres of oxidizer using a technique first used for ammonium perchlorate combustion by Barrère and Nadaud[77]. The deflagration of HP in streams of methane or propane was many times faster than that for ammonium perchlorate. It was, however, observed that the hot ignition wire might remain in contact with the HP sphere for as long as 1 minute with no observable effect other than the melting of the HP at the point of contact. Ignition then occurred and was followed by rapid deflagration. The deflagration was also observed to be pulsating. Values were deduced for the constant k in the expression

$$D^2 = D_o^2 - kt , \qquad (38)$$

where D is the diameter at time t and D_o is the initial diameter, for ammonium perchlorate and both hydrazine mono- and di-perchlorate. However, accurate data were not readily obtained due to experimental difficulties such as the pulsing mentioned above.

Various solid fuels have been used[57,63] with HP to obtain mixtures which burn stably over a range of pressures. Paraformaldehyde and S-trioxane were unsuitable since they reacted with HP. However, a stabilized formaldehyde polymer, Delrin, was found to be compatible. 0.5% magnesium oxide was added to the Delrin mixtures since it was thought that the reaction in the fuel mixtures was due to the presence of acid in the HP. The magnesium oxide must also have exerted some effect as a catalyst. Other fuels that were used successfully were thiourea and naphthalene.

Deflagration rates were obtained for a range of pressures from 0.26 to 7.7 atm. A straight line, passing through the origin, could be drawn through the data for all the fuels. The burning rate thus depends not on the nature of the fuel but only on the ambient pressure:

$$\dot{r} = 0.22\ p \quad , \tag{39}$$

where $\dot{r}$ is the linear burning rate in cm sec^{-1} and p the pressure in atmospheres absolute. This corresponds at 1 atm to a rate of about 15 times greater than that extrapolated for ammonium perchlorate. Pressures higher than 7.7 atm resulted either in complete failure to ignite or in a deflagration down the sides of the strands leaving a central unburnt core.

Temperature profiles of the deflagration wave were made using 0.0005 inch Pt/10% Rh-Pt thermocouples. These indicated little heat release in the condensed phase. The flame temperature was measured for HP containing 2% thiourea and 2% sodium chloride by sodium line reversal. The experimental value of 2275 ±50°K was in close enough agreement with the theoretical temperature of 2224°K for it to be concluded that thermodynamic equilibrium is achieved in the flame.

4.5.3 Effect of catalysts

Shidlovskii et al.[59] found that addition of 5% of manganese dioxide, cobalt oxide (CoO) or cuprous chloride enabled HP to burn stably at atmospheric pressure in glass tubes of 1.05 cm inside diameter. The burning rates are given in Table 4. Addition of $Cu_2Cl_2.2H_2O$ did not give a mixture that will burn stably.

The burning rates for these catalysed mixtures are much faster than for the corresponding ammonium perchlorate mixtures.

The catalytic effects of copper chromite, potassium dichromate and magnesium oxide were shown by Levy et al [63]. It was observed that for stable combustion a minimum quantity of about 5% catalyst was required for the first two, whereas only 2% was required for magnesium oxide. Calcium oxide gave a burning rate that was somewhat lower than that given for a HP-fuel mixture. This may have been due to moisture absorption because of the hygroscopic nature of calcium oxide.

4.5.4 General

It was concluded[63] that the mechanism of HP combustion was a vaporization process similar to that of ammonium perchlorate. Two aspects of the combustion, the erratic nature of the burning of pure HP and the turbulent behaviour of the molten zone, indicate that a condensed phase reaction probably plays an important but not dominant role. The effect of catalysts was considered to involve the catalysis of condensed phase reactions.

Various propellents based on hydrazine perchlorate have been patented[78,79] although it is doubtful if these can have much practical value in view of Levy's finding that the upper limit for stable combustion is 7.7 atm. A burning rate of 4 inch sec^{-1} has been quoted[79] for a substituted hydrazine perchlorate

$$\left[\begin{array}{c} CH_2CH_2N \\ | \\ H_2N.xHClO_4 \end{array}\right]_n$$

where $n = 4$ and $x \sim 0.8$. However mixed oxidizer propellents may have a useful application. A composition[78] containing 30 gm fuel (a 50:50 mixture of styrene and unsaturated polyester) with 50 gm HP and 40 gm potassium perchlorate had a burning rate of 2.31 inch sec^{-1} at 1000 psi, whilst for the same propellent containing only potassium perchlorate the burning rate was 1.27 inch sec^{-1}.

5 HYDRAZINE DIPERCHLORATE $N_2H_6(ClO_4)_2$

5.1 General

Hydrazine diperchlorate (HDP) was first prepared by Turrentine[80] in 1915 by reaction of barium perchlorate with hydrazine sulphate in solution. The barium sulphate was removed by filtration and the hydrazine diperchlorate

obtained by evaporation on a water bath. The product was the dihydrate.

The direct preparation from hydrazine and perchloric acid has been described by Levy et al.[81] and by Batty[62]. Use of 72% perchloric acid with 85% hydrazine hydrate results in formation of anhydrous HDP,

$$N_2H_4.H_2O + 2HClO_4 \longrightarrow N_2H_6(ClO_4)_2 + H_2O \quad . \tag{40}$$

Although HDP is less sensitive than HP[62], the dehydration of the dihydrate can be hazardous[82] if an elevated temperature is used although dehydration at 80°C appears to be generally satisfactory. It is probable that the dihydrate crystals are coated with perchloric acid and under certain conditions decomposition may start at about 80°C. Batty[62] reports that a gas resembling chlorine dioxide is evolved and suggests that the decomposition may be facilitated by any trace of catalyst.

The properties of HDP are summarised in Table 3. It is extremely hygroscopic, 0.065 mole of water being absorbed per mole of powdered HDP in 40 minutes at 50% relative humidity[81].

5.2 Thermochemistry

The heat of dissociation

$$N_2H_6(ClO_4)_2 \rightleftharpoons N_2H_5ClO_4 + HClO_4 \tag{41}$$

was determined by Grelecki and Cruice[64] as 37 kcal mole^{-1} for the temperature range 100-140°C. The heat of formation of HDP deduced from the corresponding values for HP and perchloric acid of -42.05 and -1.20 kcal mole^{-1} is

$$\Delta H_f \; N_2H_6(ClO_4)_{2\,(s)} = -80.25 \text{ kcal mole}^{-1} \quad .$$

A better determination of the heat of formation was obtained from the heat of solution in aqueous potassium hydroxide by Caruso et al.[83]

$$N_2H_6(ClO_4)_{2\,(c)} + (2NaOH + 6000\ H_2O)_{soln} \longrightarrow$$

$$\longrightarrow (N_2H_4 + 2NaClO_4 + 6000\ H_2O)_{soln} + 2H_2O \quad . \quad (42)$$

The heat of reaction for (42) was found to be -11.8 ±0.2 kcal mole^{-1}. This yields, with NBS values[20] for the necessary heats of formation,

$$\Delta H_f\ N_2H_6(ClO_4)_{2\,(s)} = -70.1 \pm 1.0 \text{ kcal mole}^{-1} \quad .$$

It may be noticed that an estimate based on the heats of formation of the $N_2H_6^{++}$ and ClO_4^- ions[20] and an estimated heat of solution of 5 kcal mole^{-1} resulted[81] in a value of -71.8 kcal mole^{-1}, with an estimated accuracy of ±2 kcal mole^{-1}.

A redetermination of the heat of formation of HDP would be valuable since Gilbert and Cobb[69] showed that the heat of solution of hydrazine dihydrochloride was about 900 cal mole^{-1} greater than that of the monohydrochloride. On a parallel basis the heat of solution of hydrazine diperchlorate might be expected to be ca. 10 kcal mole^{-1} resulting in a heat of formation of about 75-76 kcal mole^{-1}.

The apparent best value was -70.1 kcal mole^{-1} but confirmation by an alternative route was required. This redetermination was provided recently by Gilliland and Wagman[60] from measurement of the heat of reaction (43),

$$N_2H_4.2HCl + 2AgClO_4 \longrightarrow N_2H_4.2HClO_4 + 2AgCl \quad . \quad (43)$$

The resulting heat of formation,

$$\Delta H_f\ N_2H_6(ClO_4)_{2\,(c)} = -69.2 \pm 0.5 \text{ kcal mole}^{-1}$$

is the best value.

5.3 Thermal decomposition

The thermal decomposition in vacuo at 100-150°C was studied by Grelecki and Cruice[64,72] who observed an extended induction period during which a gradual

pressure rise was observed. At the end of the induction period the reaction accelerated sharply and complete decomposition resulted. Analysis of the gaseous products by mass spectrometry and of the condensed products by conventional techniques indicated that the overall stoichiometry was

$$12N_2H_6(ClO_4)_2 \rightarrow 4NH_4ClO_4 + 12HClO_4 + 22H_2O + 10N_2 + 5O_2 + 4Cl_2 \,. \qquad (44)$$

An activation energy of 23.5 kcal mole^{-1} was deduced from the temperature dependence of the induction period. Since the reaction was apparently self-accelerating, the effect of addition of possible reaction products was examined.

Addition of perchloric acid dihydrate (1%) doubled the reaction rate. Anhydrous perchloric acid had a much more pronounced effect in that the rate was too fast to be measured at 140°C. It was estimated that the rate was increased by at least 60 times on addition of 1% anhydrous perchloric acid. Small amounts of ammonia gas greatly increased the induction period (reported in Ref.57). It should be noted that it was difficult to prepare 100% HDP - the usual impurities were small amounts of HP and perchloric acid, which could have a pronounced effect on the reaction rate.

The initial step was considered to be

$$N_2H_6(ClO_4)_2 \rightarrow N_2H_5ClO_4 + HClO_4 \,, \qquad (41)$$

because anhydrous perchloric acid was isolated as the only gaseous product during the early stages of the reaction. Since the activation energies they obtained[64,72] for the thermal decomposition of HDP (23.5 kcal mole^{-1}) and of HP (23.8 kcal mole^{-1}) were similar to that obtained for the decomposition of perchloric acid (22.2 kcal mole^{-1}) by Zinov'ev and Tsentsiper[84], it was concluded that the rate controlling step was the decomposition of perchloric acid in each case. However, the perchloric acid decomposition was studied in the liquid phase and two activation energies were deduced - one of 32.5 kcal mole^{-1} from the induction period and one of 22.6 kcal mole^{-1} from the temperature dependence of the maximum rate of oxygen liberation[1]. The activation energy obtained for HP has not been substantiated by later studies[73,74] which yielded a value of 35 kcal mole^{-1}.

Consequently, the rate controlling step is doubtful. Certainly the decomposition of perchloric acid plays an important role, but the acceleration resulting from the addition of 1% anhydrous acid is too great for the perchloric acid decomposition to be rate controlling. It is more probable that there is a competing reaction for the perchloric acid and thus addition of the acid accelerates the reaction markedly by eliminating the competition.

The mechanism proposed by Grelecki and Cruice[64,72] accounts satisfactorily for the overall stoichiometry (44) and takes the form of reaction (41) followed by

$$HOClO_3 \rightarrow OH + ClO_3 , \qquad (45)$$

$$OH + N_2H_6(ClO_4)_2 \rightarrow H_2O + \tfrac{1}{2}N_2 + NH_4ClO_4 + HClO_4 , \qquad (46)$$

$$ClO_3 + 6N_2H_6(ClO_4)_2 \rightarrow 3H_2O + 3N_2 + 6NH_4ClO_4 + 6HClO_4 + \tfrac{1}{2}Cl_2 . \qquad (47)$$

The HP formed in (41) is postulated to be also attacked by the OH and ClO_3 radicals formed in (45).

The decomposition of HDP was also studied by Levy et al.[57,81] over the temperature range 174 to 293°C. The gaseous and solid products were analysed and found to correspond to the equation

$$N_2H_6(ClO_4)_2 \rightarrow 0.5NH_4ClO_4 + 1.2HClO_4 + 0.7H_2O + 0.74N_2 + 0.20\,O_2 + 0.29HCl + 0.06N_2O + 0.03H_2 . \qquad (48)$$

The amount of water and perchloric acid were not experimentally determined but were chosen to give the best atom balance.

Levy[85] found that the pressure-time curves rose gradually to a steady value and did not display the rapid increase reported by Grelecki and Cruice. However, because of the complexity of the pressure-time curves, they were not used to evaluate activation energies.

Study of HDP using a low temperature matrix isolation technique[75,76] showed that it was difficult to free the sample from water and perchloric acid. At room temperature these two gases were evolved, and at 100°C a gradually

increasing perchloric acid:water ratio was observed. The residue was then heated at 135°C for 40 hours and 140°C for 6 hours. The infrared spectrum of the resulting sublimate was that predicted for hydrazine monoperchlorate, thus providing confirmation of reaction (41). The rapid decomposition of HDP dihydrate to HP has been observed by Batty[62]. Attempts to recrystallise HDP dihydrate from solvents such as ether or tetrahydrofuran resulted in almost immediate transition to the monoperchlorate. This is probably due to the readiness with which anhydrous perchloric acid will form the monohydrate.

$$N_2H_6(ClO_4)_2 \cdot 2H_2O \longrightarrow N_2H_5ClO_4 \cdot \tfrac{1}{2}H_2O + HClO_4 \cdot H_2O + \tfrac{1}{2}H_2O \; . \qquad (49)$$

Consequently, anhydrous HDP may be expected to be more stable than the dihydrate though moisture will accelerate its decomposition.

The thermal decomposition with catalysts has only been briefly reported[85]. DTA experiments with HDP-copper chromite mixtures containing 5 and 10% copper chromite showed exotherms at 140 and 130°C respectively. Reaction was slow at 130-140°C, only a few per cent decomposition being observed in an hour. On the other hand, at 291°C an explosion occurred after about 45 seconds. This is in contrast to the steady reaction when no catalyst is present.

5.4 Combustion

5.4.1 Pure hydrazine diperchlorate

The main comprehensive study that has been published is by Levy[57,81]. The deflagration of pressed strands (density 2.11 gm cm^{-3}) was observed to be a non-luminous process which was characterized by a liquid layer, the thickness of which decreased with increasing pressure. There was considerable foaming and bubbling in the liquid but this was not observed above 30 atm and the liquid layer could not be seen with certainty above 100 atm. At pressures below 20-25 atm pulsation of the condensed phase was evident.

The lowest pressure at which strands burnt reproducibly was 6 atm although occasionally strands burnt at 1 atm. The burning rate of HDP at 1 atm extrapolated from data at higher pressures was 0.002 cm sec^{-1}. Small changes in HDP purity, of the order of 0.1%, caused the burning rate to vary by a factor of two. This is clearly due to the much higher burning rate of HP (0.1-0.2 cm sec^{-1}) because, for mixtures with insufficient perchlorate, the HDP contains HP.

Measurements of the flame temperature were made using fine chromel-alumel thermocouples. Platinum/platinum rhodium thermocouples, even when coated with NBS A-418 ceramic coating, did not readily give reproducible results. Flame temperature increased with pressure and at 103 atm was found to approach the theoretical temperature (~1600°K). The thermocouple trace at pressures above 18 atm as the combustion front approached showed no indication of any heat release in the condensed phase. However, at lower pressures the temperature records showed that some heat release occurred and thus that reaction in the solid phase was significant.

Experiments in which combustion was quenched by sudden pressure reduction showed that the fused layer on the surface of the HDP contained quantities of ammonium perchlorate. Thus the initial process involved in combustion would appear to be similar to that observed in decomposition, although under these quenching conditions, thermal decomposition may have continued until the sample had cooled.

Thus, at pressures below about 20 atm, combustion is a rapid thermal decomposition which is self-sustained by exothermic reactions in the liquid phase.

At high pressures, above about 100 atm, the flame temperature is close to the theoretical and it is considered that 'normal' combustion occurs with heat transmitted back to the solid from the gaseous reaction zone. In the intermediate pressure region a smooth transition is believed to take place between the two extremes.

It is suggested that in low pressure combustion the mechanism contains the processes shown in the previous section (reactions (41), (45), (46) and (47)) whereas at high pressure it is probable that the HP formed in reaction (41) will dissociate to hydrazine and perchloric acid and that these will be the important species in the gas phase. This is consistent with the equilibrium flame temperature being achieved with HDP as it was with HP. With ammonium perchlorate the experimental flame temperature is some 200-250°C below the theoretical. The similarity of the burning rates of HDP and ammonium perchlorate supports the idea that at pressures below 100 atm the decomposition is to AP followed by its combustion.

5.4.2 Hydrazine diperchlorate-fuel mixtures

The combustion of HDP spheres in a stream of fuel gas has been studied[57] using methane, propane and hydrogen. Deflagration rates were similar to those

for ammonium perchlorate and, as might be expected from the previous sub-section, the pulsating phenomenon was observed.

Fuels such as Delrin, thiourea and naphthalene which had been found to be compatible with HP (section 4.5.2) were incompatible with HDP[81]. However, T-burner experiments on HDP propellent containing a synthetic high-melting wax as fuel have been reported[54,86]. The wax was a mixture of ethylene diamine, stearic acid and sebacic acid with approximate formula $C_6H_{12}ON$. The burning rate of an 80% HDP-18% fuel-2% copper chromite propellent was 0.27 inch sec^{-1} at 250 psi, a value similar to that of an 80% ammonium perchlorate-18% fuel-2% copper chromite propellent which has the same theoretical temperature. The presence of the catalyst almost doubles the burning rates for both oxidizers.

5.4.3 Effect of catalysts

The effect of magnesium oxide, copper chromite and sodium nitroprusside on the rate of combustion of HDP has been studied[81]. The burning rates measured are shown in Table 5. All the catalysts increased the burning rate, the copper chromite being the most effective and magnesium oxide the least.

It was suggested that the greater effect of copper chromite on HDP than on HP or ammonium perchlorate might indicate a greater degree of condensed phase reaction, since it is assumed that catalysts, at least in part, accelerate these reactions.

6 HYDROXYLAMINE PERCHLORATE NH_3OHClO_4

This is also known as hydroxylammonium perchlorate.

6.1 General

Hydroxylamine perchlorate (HAP) was first prepared by Robson[87] by reaction of barium perchlorate and hydroxylamine hydrochloride in absolute alcohol

$$2NH_3OHCl + Ba(ClO_4)_2 \longrightarrow 2NH_3OHClO_4 + BaCl_2 \quad (50)$$

An alternative preparation[88] used hydroxylamine sulphate in place of the hydrochloride. In the latter case the solution was filtered and then evaporated on a water-bath until crystallization started when the solution was cooled. The product was 94.0-99.2% pure. However, the original method used by Robson has been reported to be best and samples of HAP that are 99.3-99.6% pure were

obtained by Grelecki and Cruice[89]. A novel method is the cathodic reduction of nitric acid in perchloric acid[90].

The properties[91,92] of HAP are summarised in Table 4. It is extremely hygroscopic, even more so than HDP. At 18% relative humidity, crystalline HAP absorbs nearly enough moisture to dissolve itself within 10 minutes. The infrared spectrum has been reported[93].

6.2 Thermochemistry

The heat of vaporization has been reported[92] as 32.3 and 33.5 kcal mole^{-1} using the Langmuir and Knudsen techniques respectively. This could be used to deduce a value for the heat of formation of HAP if a value for the heat of formation of gaseous hydroxylamine were available. As the vapour pressure measurements were at 95 to 160°C, the HAP would have been in the liquid state.

The JANAF thermochemical tables[94] report a heat of formation determined from measurements of the heat of solution of hydroxylamine in perchloric acid and of HAP in water. The heats of solution were -6.20 ±0.3 and +3.27 ±0.05 kcal mole^{-1} respectively. The heat of formation was then calculated using the value for ΔH_f $HClO_4$(aq) from Birky and Hepler (see Ref.1). Recalculation using the value previously obtained[1] for ΔH_f $HClO_4$(aq) yields

$$\Delta H_f \; NH_3OHClO_4 \; (s) \; = \; -66.15 \text{ kcal mole}^{-1} \; .$$

The accuracy is probably about ±1 kcal mole^{-1}.

6.3 Thermal decomposition

Decomposition was stated by Robson[87] to begin at 120°C. It was later reported[88] that HAP decomposed on heating with a flash but without explosion. DTA experiments on 99.2% pure samples showed two exotherms, one at 178-220°C and a second at 313-370°C, and an endotherm starting at 520°C. Gas evolution began at 180°C giving gaseous products that were neutral and consisted mainly of oxygen. The decomposition was presumed to proceed by

$$NH_3OHClO_4 \longrightarrow NH_4ClO_4 + \tfrac{1}{2}O_2 \; , \qquad (51)$$

since previous work[95] had shown that hydroxylamine sulphate decomposed to ammonium sulphate.

The endotherm in the DTA of HAP was ascribed to the sublimation of ammonium chloride. This is impossible if reaction is indeed by (51).

The vapour species evolved at 110-120°C from HAP were trapped in a cold matrix[75,76]. Infrared spectra showed the presence of perchloric acid and hydroxylamine, clearly indicating that vaporization was by a proton transfer process

$$NH_3OHClO_4 \longrightarrow NH_2OH + HClO_4 \cdot \qquad (52)$$

Other bands were assigned to water and nitrous oxide. It was suggested by comparison with previous work[96] on hydroxylamine hydrochloride decomposition, that HAP decomposition might proceed by

$$NH_3OHClO_4 \longrightarrow N_2O + H_2O + NH_4ClO_4 + N_2 \cdot \qquad (53)$$

(not balanced)

Ammonia was not trapped because enough perchloric acid would be present to form ammonium perchlorate.

The first comprehensive study of the thermal decomposition of HAP was made by Grelecki and Cruice[89]. They report that Vriesen[92] using mass spectrometric techniques observed no significant decomposition after heating at 150°C for one hour. At temperatures above 200°C the product gases were complex; the simple decomposition represented by (51) was not observed although ammonium perchlorate was found in DTA studies. DTA curves at a heating rate of 4.5 deg C min^{-1} showed an impurity peak at 65°C, a melting peak at 88°C and decomposition from 190 to 206°C.

Grelecki and Cruice examined the thermal decomposition to elucidate the mechanism. Pressure-time curves were obtained at 120 to 150°C and mass spectrometric analysis of the vapour not condensed at atmospheric pressure showed the gaseous products to be nitrous oxide and chlorine, although large quantities of hydrogen chloride were frequently detected. Analyses of samples that had been completely decomposed showed the overall stoichiometry to be close to

$$14NH_3OHClO_4 \longrightarrow 7N_2O + 2Cl_2 + 10HClO_4 + 23H_2O \cdot \qquad (54)$$

Decomposition at 180°C under steady evacuation resulted in a residue that contained appreciable quantities of ammonium perchlorate together with perchloric acid and undecomposed HAP.

Rate constants, k, deduced from p = kt where p, t are pressure and time gave an Arrhenius plot corresponding to an activation energy of 44.3 kcal mole^{-1}.

Supplementary experiments on the decomposition of hydroxylamine hydrochloride were used in deducing a possible mechanism for HAP. It is proposed that proton transfer (52) occurs followed by hydroxylamine decomposition

$$NH_3OHClO_4 \longrightarrow NH_2OH + HClO_4 \,, \qquad (52)$$

$$2NH_2OH \longrightarrow HO\text{-}\underset{\underset{HH}{\|}}{N}NH + H_2O \,. \qquad (55)$$

The perchloric acid is presumed to decompose virtually instantaneously to give strong oxidizing agents, written as [O], which react

$$\overset{\overset{HH}{\|}}{HONNH} + 2\,[O] \longrightarrow N_2O + 2H_2O \,. \qquad (56)$$

It is suggested that ammonium perchlorate is observed as a product only when the perchloric acid is removed, e.g. by constant pumping.

6.4 Combustion

The combustion of pure HAP has recently been studied by von Elbe[91,97,98] using samples either tamped in Pyrex tubes (density 1.10 gm cm^{-3}) or compacted into strands (density 2.05 gm cm^{-3}). The combustion was slightly luminous and appeared to have a thin foamy surface layer.

The lower pressure limit of flammability was found to be about 135 atm for HAP tamped in 8 mm diameter tubes. Considerable scatter was observed in the burning rate at pressures below 200 atm with variations in the linear burning rate at 150 atm from 2 to 4 cm sec^{-1}. The extreme hygroscopicity of HAP is probably a contributing factor. The pressure exponent at low pressures was thus inaccurate and lay between 0.7 and 2.6. At higher pressures the exponent is 0.52 and appeared to be reasonably reliable.

Variation in the diameter of the Pyrex tubes suggests that HAP will not sustain combustion below 100 atm even with large samples. This may be compared to the comparable limit for ammonium perchlorate[2] of 20 atm. There was no indication for HAP of a limiting quenching diameter below which combustion does not propagate, whereas ammonium perchlorate has a limiting diameter of about 2 mm. The burning rate of HAP increases steadily with increasing tube diameter from 3.8 up to 8.0 mm.

Product gas temperatures have been measured for HAP using fine chromel-alumel thermocouples and found to be 1305°K at 200 atm, somewhat less than the theoretical value of 1413°K.

Von Elbe et al.[98] compared the combustion of HAP and ammonium perchlorate and concluded that the differences could be due to a different degree of condensed phase heat release in the two cases. It was postulated that heat release at or in the condensed phase was required to maintain the combustion of HAP. They also concluded that HAP does not vaporize with dissociation into hydroxylamine and perchloric acid as in (52). However, this appears unlikely in view of the results obtained by Mack and Wilmot (section 6.3).

Propellents have been patented containing HAP[78,99] or metal hydroxylamine perchlorates[99] such as $LiClO_4 \cdot 2NH_2OH$ and $Mg(ClO_4)_2 \cdot 4NH_2OH$.

7 AMINE PERCHLORATES

A wide range of such perchlorates have been prepared[100-102]. Attention is limited here to perchlorates of which the thermal decomposition has been studied and which might be considered as oxidizers or monopropellents. Organic perchlorates have been reviewed by Burton and Praill[100].

In general, as the perchlorate becomes more covalent in nature there is an increasing tendency to instability and to explosive decomposition. The oxygen balance of the perchlorate is also an important factor in these respects. The hazardous nature of organic perchlorates arises from the presence in the same molecule of both fuel and the perchlorate group.

The more polar perchlorates, such as the amine perchlorates, are more stable and have been examined more extensively. This section describes simple amine perchlorates, guanidine perchlorates and pyridine perchlorate.

Various amine perchlorates[103], such as substituted hydrazine perchlorates[79], semicarbazide perchlorate[78] and aminoethylcellulose perchlorate[104], have been proposed for use in rocket propellents.

7.1 Simple alkyl amine perchlorates

The mono-, di-, tri- and quaternary-methylamine perchlorates are also known as the corresponding methylammonium perchlorates. The amine perchlorates are readily prepared either by direct reaction of the amine and perchloric acid or by reaction of the amine hydrochloride and a perchlorate salt. They are generally crystalline salts, which either vaporize or decompose on slow heating but ignite if suddenly subjected to a high temperature. The temperature at which a small sample will ignite/explode when dropped into a preheated test tube in a carbon dioxide atmosphere has been determined[105] for an extensive range of amine perchlorates. Values for some simple amine perchlorates are presented in Table 7. The diazonium perchlorates are reported[100] to be particularly hazardous when dry, the slightest shock being sufficient to result in explosion.

The methylamine perchlorates are impact sensitive. Values[106,107] are given in Table 8 in which their sensitivity is compared to that of RDX (cyclotrimethylene trinitramine) and ammonium perchlorate. Their general properties are summarised in Table 9 which also contains comparative data on ammonium perchlorate[2].

DTA curves have been obtained for the methylamine perchlorates by Stammler and Schmidt[106,107] at a heating rate of 20 deg C min^{-1}. Monomethylamine perchlorate was found to undergo various phase transitions (see Table 9) and to melt at 255°C. Slow decomposition occurred at temperatures above the melting point and deflagration resulted at about 320°C. Dimethylamine perchlorate melted at 180°C and again deflagration was observed at about 320°C. Trimethylamine perchlorate melted at 275°C. Slow decomposition also occurred at this temperature with deflagration at about 300°C. The tetramethylamine perchlorate exploded at about 430°C. Melting was not observed.

The effect of addition of 3.5% by weight of catalyst, such as ferrocene, was to reduce the deflagration temperature from 320°C to about 180°C for both the mono- and di-methylamine perchlorates[107]. Mixtures of these perchlorates with ammonium perchlorate which also contain 3.5% ferrocene cause a reduction in the deflagration temperature of ammonium perchlorate to 200°C (10% monomethyl salt) and to 180°C (22% monomethyl salt, 4.5% ferrocene).

The species vaporized from monomethylamine perchlorate at about 175°C have been studied[75,76] using the cold matrix isolation technique. Perchloric

acid and methylamine were positively identified, indicating vaporization by dissociation

$$CH_3NH_3ClO_4 \longrightarrow CH_3NH_2 + HClO_4 \; . \qquad (57)$$

No bands corresponding to the expected final decomposition products (hydrogen chloride, carbon dioxide and water) were found. However other bands were observed which were not identified, although some were considered suggestive of chlorine-oxygen or chlorine-oxygen-hydrogen species. They are similar to the bands observed under similar conditions from hydrazine perchlorate.

The combustion of propellents having part of the ammonium perchlorate replaced by monomethylamine perchlorate has been reported[107]. The burning rate of a propellent containing 71.5% ammonium perchlorate in a polybutadiene polymer with 4.5% n-butyl ferrocene as a catalyst was 1.45 in sec^{-1} at 2000 psi. Replacement of 15 and 22% of the ammonium perchlorate by monomethylamine perchlorate increased the burning rate to 2.40 and 2.95 in sec^{-1} respectively.

Ethylenediamine diperchlorate ($[CH_2NH_3ClO_4]_2$) has also been examined[106,107]. It exists as the hemihydrate and as the anhydrous salt. The hemihydrate DTA curve (at 20 deg C min^{-1}) indicates a reversible phase transition at 95°C and a dehydration at 120-130°C to give the anhydrous salt which then decomposes near 290°C.

7.2 Guanidine perchlorate $CH_5N_3HClO_4$

This has been more extensively studied because it has long appeared to have favourable properties for use in explosives. It is one of the most stable amine perchlorates[107], it is not hygroscopic nor is it hydrolysed in aqueous solution. Its explosive strength is reported to be similar to tetryl(N-nitro--N-methyl-2,4,6-trinitraniline) whilst its sensitivity to shock is comparable to that of picric acid[108].

It may be prepared by fusing dicyandiamide with ammonium perchlorate[108] at 150-160°C, or more readily in the laboratory by reation of guanidine chloride with either sodium perchlorate[109] or barium perchlorate followed by recrystallization twice from water

$$CH_5N_3HCl + NaClO_4 \longrightarrow CH_5N_3HClO_4 + NaCl \; . \qquad (58)$$

Some properties[109-112] are summarized in Table 10. Its shock sensitivity is reported as 60% explosions for a 2 kg weight falling 250 mm[102], and as 50% explosions for 124 kg cm[113].

7.2.1 Thermochemistry

The heat of formation has been determined from measurement[111] of the heat of solution of guanidine perchlorate (GP) in water, which gave the value of 10.416 ± 0.092 kcal mole^{-1} for a 1:1200 dilution. Measurements were also made of the heat of solution of barium perchlorate and of the heat of reaction

$$(CH_5N_3)_2H_2CO_3 + Ba(ClO_4)_2 \longrightarrow BaCO_3 + 2CH_5N_3{\cdot}HClO_4 \quad (59)$$

Heats of formation of guanidine carbonate[114], barium perchlorate[17] and barium carbonate[19] were then used to derive

$$\Delta H_f\ CH_5N_3{\cdot}HClO_4\ (s) = -74.10 \pm 0.55 \text{ kcal mole}^{-1}.$$

7.2.2 Thermal decomposition

This was first studied by Glasner and Makovky[109] who observed that a slight loss in weight occurred when GP was heated at or below 300°C for several hours at 1 atm pressure. At 300-400°C decomposition proceeded to completion, whereas above 400°C ignition occurred after an induction period. Product gas analyses[109] indicated that the decomposition at 340-390°C could be represented by

$$2CH_5N_3{\cdot}HClO_4 \longrightarrow 2HCl + 5H_2O + CO + CO_2 + 3N_2, \quad (60)$$

$$2CH_5N_3{\cdot}HClO_4 \longrightarrow 2HCl + 2NH_3 + 2CO_2 + 2N_2 + O_2 + 2H_2O. \quad (61)$$

The product analyses indicated that reaction (61) generally predominated with reaction (60) becoming more important as the temperature increased. Small amounts of chlorine, hydrogen and, above 400°C, nitrogen dioxide were also observed.

When reaction at 320-390°C was interrupted before complete decomposition had occurred, the solid residue consisted partly of ammonium perchlorate and partly of mixed melamine perchlorates. The mechanism proposed was that cyanamide,

ammonia and perchloric acid were initially formed and the cyanamide then underwent self-condensation to compounds such as melamine

$$CH_5N_3\ HClO_4 \longrightarrow CN.NH_2 + HClO_4 + NH_3\ , \tag{62}$$

$$3CN.NH_2 \longrightarrow C_3H_6N_6\ , \tag{63}$$

which were then oxidized by the perchloric acid.

Kinetic measurements[115] of the rate of pressure increase with time at 345-380°C showed the rate of gas evolution to be linear over the major part (15-80%) of the decomposition. The temperature dependence of the rate constant obtained from this linear region gave an Arrhenius plot expressed by

$$k = 2.4 \times 10^{11}\ e^{-32,400/RT}\ .$$

The mechanism shown by equations (62) and (63) was supported because equimolar mixtures of

(i) ammonium perchlorate and dicyandiamide,

(ii) ammonium perchlorate and guanidine hydrochloride

gave pressure increase curves similar to those of GP. On the other hand, a mixture of potassium perchlorate and guanidine hydrochloride decomposed much more slowly. This reduced reactivity was considered to be evidence that free perchloric acid was the effective oxidizer and not the perchlorate ion. Further support came from the observation that in pure GP there was a comparatively slow reaction at the start of the decomposition. No such lag was observed in GP containing ammonium perchlorate, indicating that the lag was probably associated with formation of ammonium perchlorate.

Induction periods before ignition at 390-440°C were measured[116] for GP. These were somewhat less than the induction period for ammonium perchlorate at the same temperatures. The temperature dependence of the log (induction period) yielded an activation energy of 30.5 kcal mole^{-1}.

DTA curves for GP showed[110] two endotherms and one exotherm. A marked endotherm at 180-182°C was also observed as an exotherm in the cooling curves. Consequently it was suggested that GP undergoes a phase transition at this

temperature. The second endotherm corresponded to the melting point and was observed at 248 ±2°C. Slow decomposition occurred at 300°C with a marked exotherm at 392°C corresponding to extensive decomposition and occasional ignition. The phase transition has been confirmed by DTA curves for GP-$LiClO_4$ mixtures.

Low temperature matrix isolation techniques have been used[75,76] to trap the species vaporized from GP at 250°C. Unlike other perchlorates, no free guanidine was detected by infrared spectra but because large amounts of perchloric acid were identified it was considered that proton transfer took place. Ammonia (in about a 1:1 ratio with the perchloric acid), cyanamide and possibly hydrogen chloride were identified. Guanidine was detected in similar experiments at lower temperatures with guanidine halides.

It was concluded that the initial reaction was

$$CH_5N_3\,HClO_4 \longrightarrow CH_5N_3 + HClO_4\,, \qquad (64)$$

followed by immediate decomposition of the guanidine

$$CH_5N_3 \longrightarrow CN.NH_2 + NH_3\,, \qquad (65)$$

which is identical to reaction (62) proposed for the thermal decomposition.

7.2.3 Catalysed decomposition

The effect of catalysts on the thermal decomposition of GP was examined[116] using weights of catalyst approximately proportional to the molecular weight (2-5% by weight). Three distinct groups were observed:

(i) oxides (MgO and Al_2O_3) which have a small accelerating effect but did not change the general character of the pyrolysis,

(ii) oxides (TiO_2, Cr_2O_3 and CoO) which have a more pronounced catalytic effect and may result in explosion or ignition at a reduced temperature,

(iii) oxides (V_2O_5, Fe_2O_3, CuO) and platinum metal (foil) which cause explosion at 300° or above.

Ignition temperatures reported for mixtures with Ag_2O, Hg_2O or MoO_3 were 320, 345 and 345°C respectively.

It was proposed that the catalysts are concerned with the decomposition of ammonia, and to support this it was stated that the catalysts similarly affect the ignition temperature of ammonium perchlorate. It is much more probable that the catalyst is effective by accelerating the pyrolysis of the perchloric acid[117]. Indeed, Glasner and Makovky[116] clearly propose that reaction of perchloric acid with organic fuel is the cause of the ignition temperature of GP being below that of ammonium perchlorate. Small additions of dicyandiamide or methyl methacrylate were reported to reduce the ignition temperature of ammonium perchlorate to 390°C, the same temperature at which GP ignites.

7.2.4 Guanidine diperchlorate, $CH_7N_3(ClO_4)_2$

The solubility of GP in perchloric acid solutions containing from 0% to 100% acid passed through a minimum and then rose to 36.7% in the anhydrous acid[118]. The salt crystallized from anhydrous perchloric acid solution was shown by analysis to correspond to guanidine diperchlorate.

It was hydrolysed in water with the removal of a molecule of perchloric acid. DTA indicated an endotherm at 6 ±2°C corresponding to incongruent fusion.

7.3 Triaminoguanidine perchlorate, $CH_8N_6HClO_4$

This was prepared[119] by first neutralizing aminoguanidine bicarbonate with perchloric acid to yield aminoguanidine perchlorate, which was then heated in an aqueous hydrazine solution. The melting point of the resulting perchlorate was 132°C. It is hygroscopic and impact sensitive. It is detonated with very high brisance by a 2 kg weight falling 7 cm. Both it and diaminoguanidine perchlorate have been considered for use as explosives[120,121].

Its use as a propellent ingredient has been patented[122] for a 35/65 to 65/35 mixture with lithium perchlorate as the oxidizer for use with conventional binders. The oxidizer mixtures have melting points in the range from 82°C to room temperature, thus giving with the 65/35 mixture a eutectic that is liquid. The lithium perchlorate is an effective desensitizer; 50% ignitions with a 2 kg weight occur at 20 cm for the 35/65 mixture as compared to <5 cm for the triaminoguanidine perchlorate.

7.4 Nitroguanidine perchlorate, $CH_4N_4O_2HClO_4$

The preparation from nitroguanidine and perchloric acid (72%) has been described[123]. It was also formed by reaction of guanidine perchlorate with nitronium perchlorate[118]. The physical properties are given in Table 11. It is hydrolysed in water to nitroguanidine and perchloric acid.

The DTA at 3 deg C min^{-1} showed an endotherm at 75-80°C and an exotherm at 120°C. Dilatometric measurements indicated that a phase transition occurred at 79°C.

The thermal decomposition was studied[123] at 107-119°C under dry nitrogen at 50 torr. The reaction commenced in the solid phase which became liquid during the decomposition as a result of eutectic formation, and finally solidified. Chemical and X-ray analysis of the products indicated a 1:1 mixture of guanidine and ammonium perchlorate. This fact together with total weight loss of 33⅓% and qualitative analysis of the gaseous products indicated that decomposition corresponded to the reaction

$$2C\begin{cases} NH-NO_2 \\ NH-HClO_4 \\ NH_2 \end{cases} \longrightarrow CH_5N_3HClO_4 + NH_4ClO_4 + CO_2 + NO_2 + \tfrac{3}{2}N_2 \quad . \quad (66)$$

The initial rate of decomposition up to the maximum corresponded to an activation energy of 60 kcal $mole^{-1}$. The second stage of the decomposition showed first order kinetics with a pre-exponential factor of 3.06×10^{11} min^{-1} and an activation energy of 24.4 kcal $mole^{-1}$.

Nitroguanidine diperchlorate was formed by crystallization from a solution of nitroguanidine perchlorate in anhydrous perchloric acid[118]. It is hygroscopic. DTA indicated an endotherm at 70°C corresponding to incongruent fusion, and an exotherm at 93°C at which decomposition, which was occasionally explosive, occurred.

7.5 Pyridine perchlorate, $C_5H_5N\ HClO_4$

This has been used as an intermediate in the purification of pyridine during which pyridine perchlorate is prepared and dried. The dry perchlorate is treated with dry ammonia gas and the pyridine distilled off from the ammonium perchlorate

$$C_5H_5N\ HClO_4 + NH_3 \longrightarrow C_5H_5N + NH_4ClO_4 \quad . \qquad (67)$$

Explosions have occurred, hence the properties of pyridine perchlorate have been studied[124].

Pyridine perchlorate melts at 288°C. On further heating decomposition begins with the evolution of white fumes at 335-340°C and spontaneous ignition (or explosion, if confined) occurs at a slightly higher temperature.

The effect of various additives on the ignition temperature was examined. Decomposition of pyridine perchlorate with ammonia produced ammonium perchlorate, hence the effect of adding ammonium perchlorate was examined. This reduced the ignition temperature of pyridine perchlorate. The mixture burnt without forming soot whereas pyridine perchlorate alone burnt with a sooty flame. Mixtures containing ammonium and pyridine perchlorates in a molar ratio between 1:1 and 3:1 burnt especially rapidly. The reactions involved were expressed as

$$5C_5H_5N\ HClO_4 + 7NH_4ClO_4 \longrightarrow 25CO + 23H_2O + 6N_2 + 12HCl\ , \qquad (68)$$

$$5C_5H_5N\ HClO_4 + 17NH_4ClO_4 \longrightarrow 25CO_2 + 38H_2O + 11N_2 + 22HCl\ . \qquad (69)$$

When heated on an aluminium or nickel plate the pyridine perchlorate burnt smoothly. The burning velocity was increased on plates of iron, lead and especially of copper or zinc (or their alloys).

The ignition temperature of an equimolar mixture of pyridine and ammonium perchlorates was reduced to a value as low as 200°C by addition of palladium, cuprous oxide, cupric oxide, brass shavings, a 1:1:1 mixture of cupric oxide, copper and zinc sulphate, or cupric pyridine complex. Copper, platinum and mercury showed only a slight catalytic effect and powdered glass showed none.

The explosions have also been ascribed to a trace of chlorate[100]. It is probable that the explosions have resulted from the catalysed perchlorate decomposition, possibly facilitated by the catalysed decomposition of the perchloric acid in the presence of the organic molecule.

8 NON-METALLIC PERCHLORATES

The perchlorates discussed here are of boron and fluorine. They are unstable compounds, extremely reactive and explosive.

8.1 Boron perchlorate $B(ClO_4)_3$

This has recently been prepared[125,126] by reaction of boron trichloride and anhydrous perchloric acid. The reaction proceeded smoothly at -78°C with evolution of hydrogen chloride to give a quantitative yield of product. The nature of the product was determined by the molar ratio of the reactants:

$$BCl_3 + HClO_4 \longrightarrow BCl_2ClO_4 + HCl \,, \qquad (70)$$

$$BCl_3 + 2HClO_4 \longrightarrow BCl(ClO_4)_2 + 2HCl \,, \qquad (71)$$

$$BCl_3 + 3HClO_4 \longrightarrow B(ClO_4)_3 + 3HCl \,. \qquad (72)$$

Use of CCl_3F or perfluorobutene as a solvent aided the production of the pure boron triperchlorate.

Some properties are summarized in Table 12 for the three compounds formed. They are all temperature and moisture sensitive, undergoing thermal decomposition and hydrolysis reactions, but under anhydrous conditions they are stable at low temperatures. They also undergo exchange reactions yielding the triperchlorate and boron trichloride:

$$2BCl_2ClO_4 \rightleftharpoons BCl_3 + BCl(ClO_4)_2 \,, \qquad (73)$$

$$3BCl(ClO_4)_2 \rightleftharpoons BCl_3 + 2B(ClO_4)_3 \,. \qquad (74)$$

These exchange reactions make purification by vacuum distillation of the mono- and dichloroperchlorates difficult because loss of the volatile boron trichloride drives reactions (73) and (74) to the right. These reactions are extremely slow at -78°C but proceed at a moderate rate at -40 to -45°C.

8.1.1 Thermochemistry

The heat of hydrolysis of boron dichloroperchlorate in solution in carbon tetrachloride has been determined[125] as -73.7 kcal mole^{-1}.

8.1.2 Thermal decomposition

The decomposition of boron chlorodiperchlorate, $BCl(ClO_4)_2$, has been studied[125] at 0 to 10°C by determining the free chlorine evolved. An

induction period (30 minutes at -12 and 0°C) was observed, followed by a rapid initial evolution of chlorine and then a first order decomposition. The residue had a $B:ClO_4$ ratio of 1:1 and it was suggested that a cyclic boraxole perchlorate might have been present.

Boron dichloroperchlorate decomposed in a similar way but with a longer induction period (6 hours at 0°C, 2.5 hours at 10°C) followed both by a surge of chlorine and a rapid rise in temperature. Chlorine formation was too erratic for the reaction order to be specified. The main products were chlorine and the proposed cyclic compound along with a small amount of chlorine heptoxide. Chlorine dioxide was not a product. It was suggested that decomposition proceeded either by an internal oxidation-reduction or by an oxidation-reduction reaction between a ClO_4 or ClO_3 radical and the chloride ion.

Boron triperchlorate was found to decompose by a different mechanism. Decomposition at 0°C resulted in formation of both a liquid and a solid phase. Evacuation of the mixture left a white solid of variable composition, whereas the very pale yellow distillate was identified as chlorine heptoxide. Decomposition at 0°C in vacuo resulted in a steadily decreasing rate of evolution of chlorine heptoxide. No induction period was observed. The decomposition was proposed to follow the reaction:

$$2B(ClO_4)_3 \longrightarrow Cl_2O_7 + (ClO_4)_2\,BOB(ClO_4)_2 \,. \qquad (75)$$

Various attempts were made to form adducts with improved stabilities. Amine adducts were prepared with the di- and mono-chloroperchlorates which were stable at room temperature. A similar adduct could not be prepared with the triperchlorate although an adduct stable up to its melting point at 135°C was obtained with nitronium perchlorate. Analysis of the adduct indicated its composition to be $NO_2B(ClO_4)_4$. Preparation of this adduct has also been reported by Guibert et al.[46] by reaction of boron trichloride with nitronium perchlorate in a 1:4 ratio at -50°C.

The adduct was found[46] to be shock sensitive (50% ignitions for 47.5 kg cm) and to have a density of 2.26 g cm^{-3}. Its heat of formation was found to be -80 ±10 kcal $mole^{-1}$. Its colour changed from white to yellow at ambient temperature and measurable decomposition occurred in 3-4 weeks. Decomposition was rapid at 70-80° and resulted in formation of nitronium perchlorate.

An ammonium adduct was also prepared. Its properties and stability were similar to the nitronium complex.

Thus, although it had been suggested[125] that boron triperchlorate would be an interesting oxidizer for high energy propellent systems, as it contains both boron and perchlorate groups, such an application requires a suitable adduct or other method of stabilization.

8.2 Fluorine perchlorate $FClO_4$

This was first isolated by Rohrback and Cady[127] by reaction of fluorine with 60% perchloric acid. Fractional distillation yielded a colourless liquid which boiled at -15.9°C under 755 mm pressure. Improved yields were obtained by passing undiluted fluorine over 72% perchloric acid in a platinum boat at 21°C.

Fluorine perchlorate was found to explode readily even when cooled to its freezing point (-167.3°C). A small flame or a spark would result in an explosion that shattered the open ended test-tube containing the gas. Grease, rubber tubing and even contact with 2M potassium iodide solution have been reported to result in explosions.

By analogy with boron perchlorate, fluorine perchlorate may be expected to decompose to yield chlorine heptoxide and oxygen difluoride, both explosive compounds:

$$2FClO_4 \longrightarrow OF_2 + Cl_2O_7 \cdot \qquad (76)$$

The infrared and nuclear magnetic resonance spectra of fluorine perchlorate in 50% solution in Freon 11 have recently been reported[128].

9 METAL PERCHLORATES

The thermal decomposition and combustion of metal perchlorates have, in general, not been widely studied except for special cases, such as potassium perchlorate, which have practical importance. This review is restricted to these aspects. Preparative methods and other properties may be found in Schumacher[101] and other reviews[129,130].

Data on the thermal decomposition are first summarized according to the mechanism of decomposition and consideration is then given to the combustion of metal perchlorates, and in particular of potassium perchlorate.

9.1 Thermal decomposition

9.1.1 General

Early studies of the thermal decomposition of a range of perchlorates using a thermobalance[131] and differential thermal analysis[132] showed that perchlorates could decompose either to form the chloride and oxygen or to the oxide and mixtures of chlorine and oxygen

$$MClO_4 \longrightarrow MCl + 2O_2 , \qquad (77)$$

$$MClO_4 \longrightarrow \tfrac{1}{2}M_2O + \tfrac{1}{2}Cl_2 + 7/4\ O_2 . \qquad (78)$$

Hydrated salts will also decompose by either (77) or (78) but in the latter case both the hydroxide and perchloric acid may be present in the products. In general, decomposition to the chloride is observed for the alkali metal perchlorates and for the alkaline earth perchlorates except for magnesium and calcium, which also form the oxide. With aluminium, ferric and the rare earth perchlorates, the oxide yield is predominant. Markowitz[133] has shown that free energy calculations may be used to predict the mode of the decomposition.

9.1.2 Alkali metal perchlorates

These decompose by (77) to yield mainly the chloride and oxygen, but small traces of chlorine have been observed in the gaseous decomposition products of potassium[134,135] and lithium[136] perchlorates. It has been suggested[133] that this chlorine formation may result from an oxygenation reaction

$$2MCl + \tfrac{1}{2}O_2 \longrightarrow M_2O + Cl_2 . \qquad (79)$$

This is supported by the observation[134] that chlorine is formed in vacuo but not in the presence of an inert gas. The formation of chlorine may be suppressed[136] by addition of small quantities of highly basic oxides such as lithium oxide.

The activation energies which have been determined[137-147] are summarized in Table 13. In general there is good agreement that the activation energy is

of the order of 60 kcal mole^{-1} with the exception of the data from Cabané and Bénard[140]

The thermal decomposition of the alkali perchlorates is complicated by the fusion of the perchlorates during decomposition due to the formation of the alkali chloride. Lithium perchlorate is an exception because it has a well defined melting point (247°C) well below the temperature at which decomposition begins. The fusion point and the decomposition of the other perchlorates are greatly affected by the amount of chloride present. For instance, the induction period for potassium perchlorate can be reduced or eliminated by addition of potassium chloride[143].

9.1.3 Other metal perchlorates

The alkaline earth and other divalent metal perchlorates generally decompose to yield the chloride and oxygen, although calcium and especially magnesium also form the oxide and chlorine. The trivalent metal perchlorates generally yield the oxide. The activation energies that have been measured[138,148,149] are presented in Table 14 from which it is evident that the activation energy is about 60 kcal mole^{-1} for the perchlorates decomposing to the chloride and considerably less, about 30 kcal mole^{-1}, for those which yield the oxide.

9.1.4 Mechanism

It is evident that decomposition according to reaction (77) is associated with an activation energy of 60 kcal mole^{-1} whereas that by reaction (78) is associated with the smaller activation energy of 30 kcal mole^{-1}. Clearly the activation energy depends on the mechanism involved.

The mechanism for alkali perchlorates has been proposed[135] to involve basically the breaking of a Cl-O bond

$$KClO_4 \longrightarrow KClO_3 + O \ , \qquad (80)$$

which is then followed by decomposition of the chlorate

$$KClO_3 \longrightarrow KCl + 3/2\ O_2 \ , \qquad (81)$$

also accompanied by

$$KClO_3 \longrightarrow \tfrac{3}{4}KClO_4 + \tfrac{1}{4}KCl \ , \qquad (82)$$

which is indicated by tracer studies[135]. The experimental data are, however, complicated by the fusion that occurs during the decomposition, thus both solid and liquid phase decomposition of potassium perchlorate are occurring. The mechanism has been discussed by Simchen[150] who proposed first order nucleation throughout the crystal followed by propagation by oxygen atoms migrating through the crystal lattice or through the melts.

Other tracer work has been reported[151] in which reaction (82) is replaced by the reverse of reaction (80) as slight oxygen exchange was detected.

The rate-determining step (reaction (80)) is in good agreement with the observed activation energy as the bond dissociation energy of the ClO bond is calculated[20] to be 64.295 kcal $mole^{-1}$.

The mechanism for the other perchlorates with an activation energy of about 30 kcal $mole^{-1}$ is more difficult to explain. It has been suggested[152] from the similarity of the pre-exponential factors and activation energies for the thermal decomposition of hexammine nickel perchlorate and ammonium perchlorate that both involve the reaction of a perchlorate ion on the surface with an ammonia entity. This does not appear feasible in view of the extensive evidence[2] that ammonium perchlorate decomposes by proton transfer to perchloric acid and ammonia. It is certainly possible with hexammine nickel perchlorate and hydrated perchlorates that perchloric acid is formed and that this decomposes with an activation energy of some 30 kcal $mole^{-1}$ heterogeneously on the surface. It is concluded that the mechanism for these other metal perchlorates requires more detailed chemical study before firm conclusions can be reached.

9.2 Catalysed thermal decomposition

The acceleration[143] of the decomposition of alkali metal perchlorate by the presence of the alkali metal halide has been mentioned above. It has been suggested[143] that the halide acts by facilitating the decomposition of perchlorate to chlorate. However, the activation energy and pre-exponential factors obtained[143] were virtually identical for potassium perchlorate alone and in a mixture with chloride (or bromide).

Catalysis by metallic oxides has long been observed for potassium perchlorate and also for potassium chlorate. Thus, Otto and Fry[142] examined the effect of ferric oxide and obtained an activation energy of 46.1 kcal with a pre-exponential factor of $10^{10.8}$ for a mixture containing $KClO_4:Fe_2O_3$ in the ratio of 1:4. Somewhat higher values were observed for mixtures with less oxide.

In later work the catalytic effect of magnesium oxide was examined[147,153]. The activation energy was found[147] to be the same as in pure potassium perchlorate,

70.5 kcal mole^{-1}, but the pre-exponential factor for the solid phase reaction increased and became virtually the same as for the liquid phase reaction. The effects of irradiating and of doping the metal oxide indicated that the results were consistent with a positive hole theory having a rate controlling mechanism involving the transfer of electrons from the perchlorate ions to positive holes in the oxide.

Later studies by Freeman and Rudloff[154] showed that a wide range of metal oxides exerted a catalytic effect in mixtures containing 1 metal ion for 5 potassium ions. The results are summarized in Table 15. It was suggested that the results were in agreement with an electron transfer step and that the catalytic activity of the oxides increased with increase in the p or n semi-conducting character of the metal oxides.

It is interesting to note the general similarity between this order of catalytic activity and that observed for the thermal decomposition and ignition of ammonium perchlorate[117], where proton transfer is believed to be the dominant step.

The thermal decomposition of potassium perchlorate with organic compounds ranging from various forms of carbon to polymers has been studied by Patai et al.[155-165] both with and without catalysts. Decomposition with carbon proceeded without any induction period and gave carbon dioxide as the sole gaseous product

$$KClO_4 + 2C \longrightarrow 2CO_2 + KCl \quad (83)$$

Various rate expressions were used and an activation energy of 40 kcal mole^{-1} derived for a 4:1 mixture of C:$KClO_4$. The decomposition was catalysed by alkali and alkaline earth halides (LiCl, $BaCl_2$, KCl, NaCl) and inhibited by basic salts such as lithium carbonate.

The effect of heating potassium perchlorate with a range of substances is summarized in Table 16. A particularly comprehensive study was made[157] of the reaction with polydivinylbenzene (PDVB) by studying both the rate of decomposition and the ignition delay. The activation energy was found to be 40.5 and 41.7 kcal mole^{-1} for PDVB-$KClO_4$ ratios of 1:2.5 and 1:6 respectively. Almost identical activation energies were obtained[158] for PDVB with sodium perchlorate (41.7), potassium bromate (41.3), potassium iodate (38.2) and potassium chlorate[165] (40.0 kcal mole^{-1}).

Catalysis was generally observed to result from addition of acidic substances although these had no effect on the decomposition of the perchlorate alone at the same temperature. Basic substances showed strong inhibition although general rules were not always evident - thus lithium chloride catalysed, lithium hydroxide and carbonate inhibited, but lithium sulphate had little effect. It was proposed that the catalysts might aid the movement of negatively charged oxygen (O^- or O_2^-), whereas bases would inhibit such movement. This concept is virtually the same as that proposed by Markowitz[166].

The closely similar activation energy observed for a range of metal oxysalts was ascribed[158] tentatively to an interface process between free oxygen (possibly as O^- and O_2^- ions) and the polymer, and not to the thermodynamic stability of the oxidants. However, the rates do differ for different metal oxysalts and it was suggested that this was related to the rates of halogen-oxygen bond cleavage and diffusion of oxygen through the crystals.

The catalysis of alkali perchlorates by manganese dioxide was examined by Markowitz[166]. The order of thermal stability for both pure and catalysed mixtures was found to be Li < Na < K, Rb Cs. Likewise the order of Cl_2 evolution from these perchlorates both with and without catalyst was Li >> Na > K > Rb, Cs = 0. The suppression of chlorine transformation by addition of a basic oxide such as Li_2O_2 was observed. However, the addition of a basic oxide or an oxide-producing compound also accelerated the thermal decomposition (cf. MgO[147], K_2CO_3[167] and NaOH[141]). Thus the temperatures from thermogravimetry for 2% decomposition of $LiClO_4$ mixtures were determined as:

no additive	470°C
5.0% wt Li_2O_2	281
4.35% wt Li_2O	306
8.11% wt Na_2O_2	311
5.21% wt LiOH	410
7.89% wt Li_2CO_3	431 .

This order corresponds to the order of the ease of formation of O^{2-} ions from the various anions. Further, samples containing Li_2O were shown to contain traces of O_2^{2-} after decomposition. It is suggested that this is evidence that O atoms are present in decomposing perchlorates. The mechanism is considered to be

$$MClO_4 \longrightarrow MClO_3 + O \ , \tag{84}$$

which could be followed by

$$2Cl^- + O \longrightarrow Cl_2 + O^{2-} \ , \tag{85}$$

or a more general explanation involving a self-ionization equilibrium

$$ClO_4^- \rightleftharpoons ClO_3^+ + O^{2-} \ , \tag{86}$$

which could then be followed by

$$ClO_3^+ + ClO_4^- \longrightarrow Cl_2O_7 \longrightarrow Cl_2 + 7/2\ O_2 \ . \tag{87}$$

Thus O^{2-} ion acceptors or acids will shift equation (86) to the right thus increasing the rate and extent of (87) whereas basic additives will shift equation (86) to the left and reduce Cl_2 production.

There is also evidence that chlorine oxides may be present in the products[167] which would be in accord with reaction (87). It is stated[166] that catalysts for $MClO_4$ decomposition may be divided into two groups: oxide catalysts (Fe_2O_3, MnO_2, Bi_2O_3, CuO, SnO_2, etc.) which yield substantially Cl_2 free oxygen, and oxide catalysts (P_2O_5, B_2O_3, WO_3, MoO_3, V_2O_5, etc.) which cause much Cl_2 production[136]. The first group are clearly true catalysts whereas the second are polymeric acids capable of capturing O^{2-} and thus reacting to yield chlorine.

A systematic study using thermogravimetry and DTA has recently been reported[168] in which the effect on the thermal decomposition of lithium perchlorate trihydrate of a series of oxides, in which there is a regular rise in the atomic number of the metal, was examined. It was found that most of

the oxides, including the lathanide oxides, lowered the decomposition temperature of the anhydrous perchlorate but that the total weight loss was the same as for pure lithium perchlorate. The decomposition temperatures were not lowered by additions of Al_2O_3, TiO_2 and ZnO. Two marked exceptions were chromium (III) oxide and vanadium (V) oxide. The weight loss was much greater for V_2O_5 and no chloride was detected in the residue. The weight loss agreed with that corresponding to

$$2LiClO_4 \cdot 3H_2O \longrightarrow Li_2O + Cl_2 + 7/2\ O_2 + 6H_2O \quad . \tag{88}$$

With chromium (III) oxide, the extent of weight loss was again greater than for pure lithium perchlorate[169]. Lithium perchlorate:chromium oxide in a 2:1 ratio resulted in quantitative oxidation of Cr (III) to Cr (VI) and the residual chloride was 0.1%. The following overall reaction was proposed

$$2LiClO_4 \cdot 3H_2O + Cr_2O_3 \longrightarrow Li_2Cr_2O_7 + Cl_2 + 6H_2O + 2O_2 \tag{89}$$

and a mechanism suggested in which a chromium (VI) peroxy compound is an intermediate formed by

$$2LiClO_4 + Cr_2O_3 \longrightarrow 2LiCl + [2CrO_3 \cdot 5O] \quad , \tag{90}$$

and which reacts with the chloride

$$2LiCl + [2CrO_3 \cdot 5O] \longrightarrow Li_2O + 2CrO_3 + Cl_2 + 2O_2 \tag{91}$$

and the final dichromate results from

$$Li_2O + 2CrO_3 \longrightarrow Li_2Cr_2O_7 \quad . \tag{92}$$

The final product, lithium dichromate, had no catalytic effect on the decomposition.

It was observed that this oxidation of Cr (III) oxide occurred in reaction with potassium, sodium and neodymium perchlorates, but not with ammonium perchlorate.

The mechanism postulated[166] for the catalysed decomposition in the presence of a basic oxide is

$$LiClO_4 + Li_2O \longrightarrow LiClO_3 + Li_2O_2 \qquad (93)$$

followed by

$$Li_2O_2 \longrightarrow Li_2O + 1/2\ O_2 \qquad (94)$$

and

$$LiClO_3 \longrightarrow LiCl + 3/2\ O_2\ . \qquad (95)$$

9.3 Combustion

9.3.1 Model systems

The metal perchlorates differ in one most important respect from the non-metallic perchlorates in that they will not support their own combustion and this has been one of the attractions of metal perchlorates as oxidizers in propellents.

Studies of the combustion of metal perchlorate systems has generally been limited to potassium perchlorate, some with lithium perchlorate and only occasionally with other perchlorates. The interest in potassium perchlorate arises from its non-deliquescent nature and in lithium perchlorate from its high solubility in organic solvents thus permitting homogeneous compositions to be prepared.

Potassium perchlorate combustion has not been described extensively in the Western literature although mention of potassium perchlorate propellents is made from time to time[170-172]. The vast amount of the published work comes from Russian sources and much of this is conveniently summarized in the book by Bakhman and Belyaev, available in translation[56].

In general, potassium perchlorate compositions have high burning rates, high flame temperatures and produce very dense smoke in a moist atmosphere. Ammonium perchlorate mixtures have lower burning rates and lower flame temperatures and produce less smoke[173]. One of the main differences from ammonium perchlorate propellents is the molten layer that forms on potassium

perchlorate propellents during burning as a result of the fusion of the potassium chloride produced. In addition, the flame structure must differ because there can be no monopropellent flame close to the oxidizer crystal but only a diffusion flame above the propellent surface.

The structures of the burning surfaces of fuels with ammonium, potassium and sodium perchlorate have recently been examined[174]. It was found that potassium and sodium perchlorates were similar in that they each formed a molten layer and had a higher surface temperature (600-700°C) than that for ammonium perchlorate mixtures (500°C). Comparison of the three oxidizers with fuels ranging from starch and naphthalene to graphite and tungsten indicate that combustion occurs more steadily over a wider pressure range with potassium perchlorate (and a slightly less wide range with sodium perchlorate) than with ammonium perchlorate.

In extensive studies of the combustion of potassium perchlorate propellents, the dependence of the burning rate on oxidizer and fuel particle sizes, pressure and the fuel-oxidizer ratio has been examined. Individual references are not quoted here and the reader is referred to Bakhman and Belyaev[56].

Compared to ammonium perchlorate, potassium perchlorate compositions generally show a greater pressure dependence - thus bitumen mixtures with an oxidizer/fuel ratio of 0.75 have pressure indices of 0.51-0.55 and of 0.78 respectively. Thus it might be expected that potassium perchlorate propellents would have a greater tendency to combustion instability. However, the contrary has been observed for polybutadiene acrylonitrile propellents[170,175].

The burning rate dependence on oxidizer/fuel ratio is much more pronounced in potassium perchlorate mixtures than in ammonium perchlorate mixtures. This probably reflects the importance of the condensed phase decomposition and reaction in the molten layer on the potassium perchlorate mixture because the transport velocity of the reacting species in such a melt is slower than in the gas.

The significance of this condensed phase reaction has been shown[176,177] by the flameless combustion observed when potassium perchlorate mixtures with naphthalene, starch or metal are heated in vacuo to about 600°C. This reaction was observed to be exothermic and the product gases could be burnt in air. It was concluded that under these conditions the mechanism of combustion of

potassium perchlorate mixtures was similar to that of double base propellents in that reaction occurred in the condensed phase evolving a combustible gas mixture which then burns above the surface of the combustion zone.

It is also interesting to note that spheres of potassium perchlorate, unlike those of ammonium perchlorate, would not burn[178] when ignited in a stream of propane. It was concluded that the potassium chloride produced on the surface caused the extinction.

9.3.2 Propellents

Whereas the thermal decomposition of metal perchlorates is known to be catalysed by metallic oxides, the action of such catalysts in the combustion of metal perchlorates is only scantily reported.

Small amounts of metal perchlorates have, however, been added[179] as burning rate catalysts to other propellents. Thus an ammonium nitrate propellent has its burning rate increased from 0.07 in sec^{-1} at 1000 psi to 0.15 in sec^{-1} at the same pressure by addition of 1% of manganese perchlorate[179].

Beryllium and titanium perchlorates have recently been described[180]. Titanium perchlorate reacts with formamide in a nitrogen atmosphere to give an immediate flame. It explodes with diethyl ether. Possible uses as ignition agents have been patented.

It is known[175] that burning rate modifiers used in ammonium perchlorate propellents, such as LiF, $SrCO_3$, copper chromite and ferric oxide, are not effective in potassium perchlorate propellents. This supports the suggestion that the catalysts are effective in the ammonium perchlorate monopropellent flame by catalysing either the perchloric acid decomposition or the ammonia oxidation.

The combustion of various systems of pyrotechnic interest such as $KClO_4$-Al [181] and $KClO_4$-Zn-hexachlorobenzene[182] has been examined. Thus aluminium fluoride was observed to cause ignition of the Al-$KClO_4$ mixture by forming a complex potassium-aluminium fluoride. The gaseous products of the aluminium fluoride-potassium perchlorate reaction were also expected to aid the ignition.

Study of the $KClO_4$-Zn system showed that carbon reduced the DTA ignition temperature for a stoichiometric $KClO_4$-Zn mixture from 520°C to 335°C and it was concluded that the carbon reacted with the potassium perchlorate

$$4C + KClO_4 \longrightarrow KCl + 4CO \quad . \qquad (96)$$

The use of surfactants as catalysts for lithium perchlorate propellents has also been described[183]. The one most effective sodium dinaphthylmethane disulphonate, also accelerated the thermal decomposition of lithium perchlorate as shown by DTA.

The use of stoichiometric mixtures of metals such as lithium, sodium, magnesium, calcium, beryllium and aluminium with the perchlorates of lithium, sodium, potassium, calcium and barium has been patented[184]. The addition of certain metals or metal oxides increased the burning rate (Table 17) and also extended the pressure range for stable combustion[184,185]. Other potassium perchlorate compositions containing polymer and metallic fuels have been described[186,187] and only a very slight variation of pressure-time curves with temperature reported[187].

Lithium perchlorate propellents have received some attention. Unlike the other alkali perchlorates, the solubility of lithium perchlorate in organic solvents is high[130,188] (Table 18). The alkaline earth perchlorates[189], such as magnesium perchlorate[190], also are reasonably soluble in organic solvents and are thus, along with lithium perchlorate, attractive for homogeneous propellent formulations. Thus, a lithium perchlorate-methanol mixture in a 62:38 weight ratio had a specific impulse at 1000 psi of 226 lb sec lb^{-1} and a non-smoky exhaust[188].

Other propellents have been patented which contain lithium, and occasionally magnesium, perchlorate in mixtures with alkylene oxides[191], alkylene polyamines[192], polyamides[193,194], polylactams[195], coal-tar[183,196], polyurethane[197] or boranes[198,199] as fuels.

Another property of lithium perchlorate which has been utilized in propellent compositions is its ability, also shown by magnesium perchlorate, to form coordination complexes with compounds such as hydroxylamine[99,200], hydrazine[201], polyamines[192] and even such compounds as triaminoguanidine perchlorate[122]. These coordination complexes contain 2 molecules of the nitrogen compound for each molecule of lithium perchlorate and 4 molecules per molecule of magnesium perchlorate. Eutectic mixtures are also readily formed between the perchlorates of lithium and hydrazine[192] or ammonia[202]. These eutectic or coordination compounds are generally solids with a melting

point of about 100°C or above. The eutectic with 65% by weight triaminoguanidine perchlorate and 35% lithium perchlorate is unusual in that it is liquid at room temperature[122], whereas the same system with 35% weight of triaminoguanidine perchlorate is a solid melting at 82°C.

These coordination compounds are usually used with conventional polymers to form propellents. An example of a liquid magnesium perchlorate system is one based on a nitromethane-ether mixture[203].

It may be concluded that whereas metal perchlorate systems have been quite extensively studied, the mechanism of their combustion and the action of ballistic modifiers is by no means as well understood as for ammonium perchlorate propellents. This more limited understanding reflects the much smaller practical importance of metal perchlorate compositions as rocket propellents, although they are of practical importance in igniters.

10 PERCHLORIC ACID, $HClO_4$

This section supplements the material reviewed previously[1], which is included as an appendix to this Report, with particular emphasis on the thermal decomposition and combustion. More general references are referred to, briefly, for completeness.

10.1 General

The evidence for and against the presence of substantial quantities of chlorine heptoxide in anhydrous perchloric acid as a result of the equilibrium

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \qquad (97)$$

was discussed previously[1]. It was concluded that the evidence for the importance of the equilibrium was not strong. Rosolovskii[204] has produced 'quantitative' evidence for the existence of the equilibrium from a study of the viscosity, vapour composition and the decomposition kinetics of the chlorine heptoxide-water system in the concentration region around 50 mole % chlorine heptoxide. From observations that linear dependences of these properties with concentration change their slope close to compositions corresponding to 100% perchloric acid, it is considered that, as the break does not occur precisely at 100% perchloric acid, the equilibrium must be involved. However,

the difficulties of accurate analysis in this concentration region are formidable and no details are given. The supporting evidence of chlorine heptoxide bands in the infrared spectra of anhydrous perchloric acid quoted from early work prior to 1953 is not unexpected in view of the relative ease with which the acid may be dehydrated.

It is concluded that whereas the equilibrium may occur to a slight extent, it is not considered to be important and the decomposition of perchloric acid is not considered to occur through decomposition of chlorine heptoxide.

The radiolysis of frozen aqueous solutions of perchloric acid has been further studied by Bugaenko using γ-radiation[205] and α-radiation[206]. Electron spin resonance was used to study the nature and approximate concentrations of the resulting intermediates, which were found to be H, OH, HO_2, ClO_2 and ClO_3. The effect of warming up the samples was studied and the mechanism discussed although this is still somewhat uncertain.

A revised value of the heat of formation in aqueous solution of -30.51 kcal $mole^{-1}$ has been discussed in section 2.2.

The structural parameters of anhydrous perchloric acid have been redetermined by gas-phase electron diffraction by Cruickshank et al.[207]. Values were obtained of 1.630 Å and 1.408 Å for the Cl-OH and Cl-O bond lengths respectively, in good agreement with the values obtained for the similar molecule, perchloryl fluoride.

The refractive indices of aqueous perchloric acid systems (0-72% by weight) have been redetermined[208]. Some physical properties (density, refractive index, surface tension, molecular refractivity and parachor) of anhydrous perchloric acid are reported[125] in a study of boron perchlorate. The vapour pressure of the components in the $HClO_4$-H_2O system and the composition of the azeotropic mixture at various temperatures have been determined[209]. The mass spectrum for perchloric acid has been reported[210].

Fume extraction systems for handling perchloric acid vapour have also been discussed and safety precautions recommended[129,211,212].

10.2 Thermal decomposition

The thermal decomposition of perchloric acid has been studied by Fisher[210] using a mass spectrometric method. Vapour from 72% acid was

pyrolysed at low pressures ($\sim 10^{-2}$ torr) in a reactor positioned so that sampled gases passed through a fine quartz leak into the ion source of the mass spectrometer. It was found that ClO and ClO_2 were the major products under these conditions, and ClO_3 was not observed. The mechanism proposed was decomposition of the acid to ClO_3 which had but a transitory existence and then decomposed to ClO radicals. The production of ClO_2 molecules could be by the extremely endothermic process

$$ClO_3 \longrightarrow ClO_2 + O \quad , \tag{98}$$

but more probably it occurs by heterogeneous decomposition of the perchloric acid on a surface

$$HClO_4 \longrightarrow ClO_2 + HO_2 \quad . \tag{99}$$

This mechanism is supported by a recent study of catalysed ammonium perchlorate pyrolysis[213] (described in detail in section 11) using time-of-flight mass spectrometry in which ClO_2 was observed to be a much more important product from the heterogeneous decomposition of perchloric acid.

The rapid decomposition of ClO_3 radicals to ClO

$$ClO_3 \longrightarrow ClO + O_2 \tag{100}$$

has received further support from mass spectrometric studies of the pyrolysis of chlorine heptoxide and chlorine hexoxide[214]. In neither case were ClO_3 radicals (or ClO_4 radicals) observed, although ClO and ClO_2 were the main products.

The pyrolysis of perchloric acid is also being examined in a conventional flow apparatus by Jacobs[215]. It is intended to study the heterogeneous decomposition of perchloric acid on various surfaces, which should greatly assist the understanding of the mechanism of catalysis of ammonium perchlorate decomposition.

10.3 Combustion

The study of perchloric acid flames has been greatly advanced since the previous review.

Composition profiles of low pressure methane-perchloric acid flames[216] were obtained using a batch sampling technique. The results indicated that methane-acid flames, compared to methane-oxygen flames, had an increased rate of carbon dioxide formation early in the flame. A reaction mechanism was proposed in which the main step was the consumption of methane by reaction with ClO radicals

$$HClO_4\ (+H) \longrightarrow ClO_3 + OH(+\ H_2O)\quad , \tag{101}$$

$$ClO_3 \longrightarrow ClO + O_2\quad , \tag{100}$$

$$CH_4 + ClO \longrightarrow CH_3 + HOCl\quad , \tag{102}$$

$$OH + HOCl \longrightarrow H_2O + ClO\quad , \tag{103}$$

$$CH_3 + ClO \longrightarrow CH_2O^* + HCl\quad , \tag{104}$$

$$CH_3 + O_2 \longrightarrow CH_2O + OH\quad , \tag{105}$$

$$CO + ClO \longrightarrow CO_2 + Cl\quad , \tag{106}$$

$$CO + OH \longrightarrow CO_2 + H\quad . \tag{107}$$

Other chlorine-oxygen radicals could be written instead of ClO with the addition of molecular oxygen to the right hand side of the equation. Reaction (106) was proposed to account for the earlier production of some of the carbon dioxide, and reaction (104) for the observed 'cool flame' band emission[217,218].

Very fuel-rich perchloric acid flames have been studied at atmospheric pressure using methane[219,220], ethylene[221] and ethane[222] as fuel. Sampling of the burnt gas showed that large quantities of fuel did not react but acted solely as a diluent. In general two molecules of fuel reacted directly with the perchloric acid decomposition products and further fuel molecules were consumed by pyrolysis and by side reactions. Carbon formation was not observed in methane-rich flames but was observed over a limited range in ethane-rich flames and a wider range in ethylene-rich flames. These results can be readily accounted for by the mechanism just cited.

Later work on mixed fuel-rich flames[223] showed that selective attack of the fuel occurred and the order of increasing resistance to attack was ethane < ethylene < methane. Approximate ratios of the rate constants for attack of the fuels were deduced and, from comparison with literature values for attack of the same hydrocarbons by H, O, Cl atoms or OH radicals, it was concluded that a chlorine-containing species was involved.

The two-flame structure of methane-perchloric acid flames with added oxygen at low pressures was previously discussed[1]. More recently, a similar two-flame formation has been observed at atmospheric pressure both with added oxygen[224] and in the absence of added oxygen in flames containing an appreciable amount of nitrogen or argon as diluent[225] (~12 moles per mole of acid). Sampling of the burnt gas zone has shown that for rich flames with added oxygen the second flame is essentially a methane-oxygen flame, whereas for diluted flames without added oxygen the second flame is the combustion of carbon monoxide along with small amounts of hydrocarbon which are not consumed in the first flame. As the mixture ratio is increased, the amount of methane in the burnt gas increases and the second flame changes from a carbon monoxide- to a methane-oxygen flame.

The formation of two flame zones in this manner on addition of oxygen is supporting evidence that the consumption of fuel in perchloric acid flames is by attack of a radical that is not present in methane-oxygen flames. It is not by H, O nor OH. This is further supported by studies of the flames of chlorine dioxide made by Combourieu et al [226-228]. These have many similarities to perchloric acid flames in that the flammability limits are extremely wide, the maximum burning velocity is given with a mixture on the fuel-rich side of the stoichiometric mixture, and a second flame is observed with added oxygen.

Kinetic studies of the reactions of ClO radicals and of chlorine oxides with hydrogen have recently been reported by Clyne[229] using chlorine dioxide and ClO radicals and by Phillips[230] using chlorine monoxide. Extension of these studies carried out at near ambient temperatures to higher temperatures would enable a useful assessment to be made of the probable reaction in flame systems.

Complete elucidation of the perchloric acid flames will require identification of the radicals using a collision-free molecular beam sampling system.

11 AMMONIUM PERCHLORATE, NH_4ClO_4

The previous review[2] covered papers published up to about September 1966. This section reviews the published literature for the subsequent 18 months, which is divided into sub-sections concerned with thermal decomposition, ignition and combustion. The opportunity has also been taken to include papers omitted from the earlier review.

Pittman[303] has reviewed much the same area as the previous review[2], but with particular emphasis on the effect of catalysts. More recently, Jacobs[304] has completed a review to be published in Chemical Reviews.

The previous value[2] for the heat of formation of ammonium perchlorate (AP) is now revised to -70.21 kcal $mole^{-1}$ as a result of the resolution of the discrepancy in the heats of decomposition of potassium perchlorate (see section 2.2).

11.1 Thermal decomposition

The extensive study of the thermal decomposition by Jacobs and Russell-Jones, previously available as a Ph.D. thesis, has now been published[231-234] and provides firm support for the proton transfer mechanism of thermal decomposition.

The elucidation of the chemical mechanism of ammonium perchlorate (AP) decomposition continues to receive attention. Thus, Petrella et al. have used a combination flash photolysis - flash pyrolysis system[235] to study the decomposition of AP [236]. After flashing, the gas phase temperature was determined to be about 2500°K from the rotational distribution of the CN radical spectrum. Absorption spectra of ClO_2 and OH were the principle bands observed 20 μs after the photoflash. The ClO_2 rapidly decreases with time and is hardly detectable after 100 μs. ClO was observed to increase with time up to about 100 μs and then to decay gradually whilst OH, NO and NH were observed to increase steadily over times of the order of 1 ms. Flash photolysis of ClO_2 showed dissociation to ClO + O in about 20 μs. A reaction scheme, quite plausible, was proposed to account for the observed intensity variations.

Mass spectrometric studies of the species which are volatilized when AP or propellent containing AP is heated (in vacuo) have become increasingly popular. Heath and Majer[237] heated the AP sample in a hypodermic tube sealed at one end and with the open end in the ionization box of the mass spectrometer (A.E.I. type MS 2). Volatilization began at 120°C and all the AP had sublimed at 200°C. No trace of the parent ion $NH_4ClO_4^+$ was found and it was concluded that the predominant process was proton transfer to give ammonia and perchloric acid.

A Knudsen-cell mass spectrometric technique was used by Goshgarian and Walton[238], who obtained reproducible results only after the AP had been heated at 200°C under vacuum for 48 hours. Consequently they could not study the low temperature thermal decomposition. Ion intensity values were obtained for the temperature range from 140 to 250°C and were used to derive activation energies from slopes of log IT/σ versus $1/T$ plots where I, T and σ are the peak height ion intensity, crucible temperature in degrees K, and the ionization cross section of the ion I, respectively. However, corrections were not made for contribution to ion intensities from parent ion fragmentation and as the decomposition products would be expected to vary with temperature, the derived activation energies are somewhat dubious. Further, no peak for perchloric acid was observed indicating that the experimental conditions allowed heterogeneous decomposition of the acid before it could be ionized.

Rapid pyrolyses of AP propellent using a Bendix time-of-flight mass spectrometer have been made by Coates[54]. The propellent was coated onto a platinum filament which was then heated by discharging a condenser through the wire, thus simulating the temperature rise in propellent combustion. The mass spectra obtained from an AP-polybutadiene-acrylonitrile propellent with and without catalyst (iron oxide or iron blue) clearly indicated not only hydrocarbon fragments from the binder pyrolysis but also ammonia, perchloric acid and chlorine-oxygen species. It was evident from the variation of the $ClO_2/HClO_4$ ratio, that with catalyst, chlorine dioxide was present to a much greater extent than in the absence of catalyst.

A Bendix time-of-flight mass spectrometer was used by Pellett and Saunders[239] in a more extensive study of AP decomposition. Chlorine, one of the major products, was used to characterise the rate of decomposition

in a number of constant temperature pyrolyses. Perchloric acid, from AP sublimation, was used, as was argon, as a means of normalizing the ion intensities of the decomposition products. The chlorine/perchloric acid ratio showed an acceleratory-deceleratory variation with time and, since oxygen and hydrogen chloride were proportional to chlorine over most of the pyrolysis, the direct decomposition

$$HClO_4 \longrightarrow HCl + 2O_2 \qquad (108)$$

had little significance under the conditions used. The perchloric acid evolution was essentially independent of the fractional decomposition and was a function of temperature only. A plot of relative ion intensities of perchloric acid and argon against 1/T yielded an activation energy of 21.5 kcal mole^{-1} for the sublimation.

Relatively small amounts of nitrogen and chlorine dioxide were found. Ions specifically sought and not found were NH_4^+, ClO_4^+, $NH_4ClO_4^+$, $HClO_4HClO_4^+$, $NOCl^+$, $N_2O_4^+$ and $Cl_2O_3^+$. Peaks attributed to $HClO_3^+$, $HClO_2^+$, $HClO^+$ and ClO^+ were approximately proportional to $HClO_4^+$ and were in agreement with Heath and Majer's[237] cracking pattern. The mole ratios $N_2O:Cl_2$, $HCl:Cl_2$ and $NO_2:Cl_2$ were unity over the temperature range studied. An atom balance required an $O_2:Cl_2$ ratio of 7:4 which compared well with the experimental ratio of 2.0. It was concluded that the stoichiometry could be expressed by

$$12NH_4ClO_4 \longrightarrow 4Cl_2 + 4N_2O + 4HCl + 4NO_2 + 7O_2 + 22H_2O \quad . \qquad (109)$$

The $Cl_2:HClO_4$ ratio was used for kinetic analysis using the Prout-Tompkins equations. The Arrhenius plot had two distinct slopes with activation energies of 10.4 and 55 kcal mole^{-1}. It was suggested that the break might be associated with a transition temperature at which competition between decomposition and sublimation alters the apparent kinetics of the decomposition.

This work has recently been extended[213] using a pulsed ruby laser as an intense heating source. The laser beam passes through the Bendix ion source to samples contained within the mass spectrometer. Since the AP crystal was transparent to the 6943 Å radiation emitted by the laser,

mixtures of AP with carbon black or metal oxides were studied. The substrate was preferentially heated and decomposition initially occurred at the hot substrate - AP interface thus causing the predominance of heterogeneous reactions. The effective temperatures were estimated to be 500 to 600°C.

Ammonia and perchloric acid were evolved in a small fraction of a millisecond following laser impact of AP - carbon black, - copper chromite, - ferric oxide or - manganese dioxide mixtures. All the major decomposition products, except for HOCl, appeared to be evolved at the same time. Perchloric acid and, to a lesser extent, ammonia had short lifetimes. Relative ion intensities indicated that there was always a large stoichiometric deficiency of perchloric acid as compared to ammonia. Chlorine dioxide was always a major gaseous product and was observed for a longer time than perchloric acid; it was also present in much larger quantities than chlorine.

Comparison of these results with those obtained in isothermal pyrolyses suggested that chlorine is a major product when adsorbed perchloric acid decomposes on an AP crystal surface, and chlorine dioxide a major product from heterogeneous decomposition on a catalyst.

Sampling of the decomposition products from AP pyrolyzed outside the mass spectrometer has also been carried out recently. Majer and Smith[240] allowed the vapour from subliming AP to pass through a second furnace maintained at a higher temperature than that of the subliming ammonium perchlorate. The reactions occurring in this second furnace were monitored by means of a pin-hole leak connected through a length of relatively narrow tubing to the ion source of the mass spectrometer.

The major products observed were H_2O, O_2, HCl, N_2O, NO_2, Cl_2 and NH_3. Traces of chloramine, chlorine dioxide and hypochlorous acid were also detected. No perchloric acid was observed, although a deposit of AP was observed downstream of the second furnace. Ammonia was first detected at 270°C but was present in measurable quantities only at 300°C. It is probable that reaction occurs within the sampling leak-mass spectrometer system.

The effect of added gases on the sublimed AP vapour was studied. Inert gases (N_2, CF_4 and CO_2) initially increased the partial pressure slightly of

NH_3, H_2O, HCl (N_2 only) and ClO_2 (N_2 and CO_2 only) but subsequently these decreased to zero. Ammonia addition decreased all products except for NH_2Cl which increased as the Cl_2 decreased. Oxygen addition had a similar effect to that produced by an inert gas.

Maycock et al.[241] decomposed AP at 10^{-3} torr in a constant volume system connected via a molecular leak to a Bendix time-of-flight mass spectrometer. Ammonia and perchloric acid were not observed and indeed it was hoped that they would recombine on cold surfaces. Pyrolysis of $^{14}NH_4ClO_4$ and $^{15}NH_4ClO_4$ at 230°C gave principally H_2O, N_2O, Cl_2 and O_2 along with significant amounts of HCl and N_2.

In later work[242], partially deuterated AP was also studied using both the earlier apparatus and a Knudsen cell sited in the mass spectrometer. The Knudsen cell experiments indicated H_2O (or NH_3), NO, N_2, O_2, Cl, HCl, N_2O and Cl_2 as products. Perchloric acid was again not detected. The results using the constant volume system agreed with those obtained previously[241]. Activation energies from the pressure-time curves obtained for oxygen and chlorine were the same, 28 kcal mole^{-1}. The ratio of O_2:N_2O:Cl_2 in the products was 3:2:2 indicating that the stoichiometry could be expressed by

$$4NH_4ClO_4 \longrightarrow 2N_2O + 2Cl_2 + 3O_2 + 8H_2O \qquad (110)$$

at temperatures of 200 to 230°C.

Maycock[243] has also studied the thermal decomposition of AP using a conventional constant volume apparatus. The effects of ageing at room temperature in vacuo, and at 110°C in air, of particle size, of decomposition products and of impurities such as $Cr_2O_7^{2-}$ and Ca^{++} were examined. Ageing especially at 100°C resulted in a marked decrease in the rate of gas release and this was attributed to annealing out of point defects. The rate was found to pass through a maximum as the particle size decreased from 4.4×10^{-3} inch to 8×10^{-4} inch. Product gases were also shown to reduce the rate of pressure rise with time. Doping with $Cr_2O_7^{2-}$ and CrO_4^{2-} accelerated the rate of pressure rise in agreement with the findings of other workers (see Ref.2). The same workers[244] have also examined the effect of the method of preparation and reported some further results on the ageing of AP samples. The method of preparation had a pronounced effect: samples

recrystallized from solution at room temperature had a much slower rate of pressure rise than samples recrystallized at +5°C. They proposed that perchloric acid monohydrate diffused into the AP crystal. This is unlikely. Further it should be chemically detectable as perchloric acid monohydrate is a strong acid. A more probable explanation is that, because Analar reagent material was used without further purification, the sample obtained by cooling to 5°C contained more impurity.

These experiments have been combined with other results on the electrical conductivity[245] to produce a mechanism[246] for the thermal decomposition of AP in terms of the point defects present. The electrical conductivity measurements plotted against the reciprocal of the temperature show several linear regions. The changes of slope occur at 92°C, 171°C, 255°C and 310°C. The break at 255°C is also observed from thermal decomposition measurements and is thus assigned to the crystal transition. The difference between this value and other values of 240-242°C is considered to be the result of different experimental arrangements. Since a plot of the electrical conductivity with time exhibits a minimum followed by a maximum, and the rate of decomposition, expressed as microns of mercury pressure rise in a given time, shows a similar but inverted shape, it was concluded that the charge carriers actually participate in the decomposition. However, conductivity measurements cannot differentiate between proton and electron transfer. Activation energies deduced from the time for the electrical conductivity to reach its minimum value are 30 kcal mole^{-1} at 200 to 250°C and 20 kcal mole^{-1} at 255 to 290°C.

Thermal decomposition measurements of pressure-time curves under both isothermal and adiabatic conditions indicated that there were three regions each with its own activation energy: 200-250°C, 30 kcal mole^{-1}; 270-340°C, 20 kcal mole^{-1}; and 380-440°C, 45.5 kcal mole^{-1}. A somewhat tenuous mechanism is proposed in which electron transfer occurs

$$NH_4^+ + ClO_4^- \longrightarrow NH_4 + ClO_4 \qquad (111)$$

which may be followed by

$$NH_4 \longrightarrow NH_3 + H \quad . \qquad (112)$$

At low temperatures (below 250°C) the ClO_4 is considered to decompose on the surface and oxidize the ammonia, whereas at higher temperatures the H atom

is presumed to combine with a ClO_4 free radical to form $HClO_4$, by what would be an extremely exothermic process. The resulting NH_3 and $HClO_4$ may then sublime or react. Additional evidence for an electron transfer process is drawn from the effect of divalent ions added to the crystal lattice. Thus SO_4^{2-} ions enhance the reaction rate at concentration levels between 10^{-4} and 1 mole %, and Ca^{++} ions inhibit the reaction rate over the same concentration range. These conclusions do not agree with the results obtained by Solymosi[258] who found that addition of zinc, magnesium or cadmium perchlorates had a marked catalytic effect.

The different activation energies observed from pressure measurements have been discussed by Jacobs and Russell-Jones[232], who have shown that a single unified mechanism of proton transfer with an activation energy of 30 kcal $mole^{-1}$ can account for the apparently different modes of thermal decomposition of AP[2]. The conductivity measurements of Maycock et al. may in fact indicate a charge transfer process involving protons as suggested previously by Wise (see discussion in Ref.2).

Other more conventional studies of AP decomposition have been reported. In several of these, quite elegant experiments are being made in attempts to elucidate further the mechanism and its dependence on a range of variables.

Differential thermal analysis (DTA) has been applied by Simchen[247] to study the effect on the exotherms of the heating rate, of AP particle size, and of addition of 'inert diluents' such as silicon carbide, silica, alumina or titanium dioxide. It was suggested that the first exotherm was related to AP dissociation to ammonia and perchloric acid which then reacted exothermally.

Systematic cycling in DTA was used in later experiments[248]. In this way products which may pyrolyse at higher temperatures can be detected. Thus with AP-potassium chloride and AP-barium carbonate mixtures, the corresponding metal perchlorates were formed[249]. Mixtures of AP with sodium chloride or calcium chloride gave intermediate compounds (two and one respectively) which in turn decompose to the metal perchlorates. These intermediates were not chemically identified.

DTA was used by Rhees and Hammer[250] to study the effect of surface modification. This modification was achieved either by adding the required ions to an AP solution, or by surface coating with metal oxides, salts or various surfactants. The surface coating with oxides had the most marked effect on the DTA and of the materials used those of copper and magnesium had the greatest effect (Ti, Si, Al, Cr, Cu and Fe were precipitated as hydrated oxides, and Mg, Cr, Fe, Cu and Mn were mixed with AP as dry oxides). Even low concentrations had a marked effect especially on the first exotherm. The exotherm shape and position were observed to depend on the additive.

The decomposition of AP has been studied by Waesche and Wenograd[251] by differential scanning calorimetry to examine the effect both of pressure and of additives. The AP pyrolysis was studied over the temperature range 175 to 500°C, and pressures from 10 torr to 30 atm. Kinetic data were derived by assuming first order kinetics and equating the rate of heat evolution at a temperature T to the total heat of reaction Q

$$\frac{D_T}{(1 - \alpha_T) W_o} = k_T Q \qquad (113)$$

where D_T is the rate of heat evolution at temperature T and $(1 - \alpha_T) W_o$ is the weight of sample at T. An Arrhenium plot of k_T yielded an activation energy of 61.1 kcal mole^{-1} over the temperature range 400 to 450°C for purified crystals of AP. At 300 to 340°C the data showed much scatter but appeared to correspond to an activation energy of about 30 kcal mole^{-1}. Sample history, purity and particle size had no effect on the high temperature exotherm where 90% or more of the heat release occurred. Increase in pressure from 1 to 30 atm caused the second exotherm to occur at a lower temperature.

The effect of copper chromite and ferric oxide were also examined. As Jacobs had used the expression

$$1 - (1 - \alpha)^{\frac{1}{2}} = kt \qquad (114)$$

the expression (113) was replaced by one corresponding to a reaction order of $\frac{1}{2}$. An activation energy of 48 kcal mole^{-1} was obtained with a catalyst at 300 to 350°C in excellent agreement with that obtained by Jacobs.

Kinetic data with carbon black indicated similar behaviour to that with AP alone but with much higher pre-exponential factors. Propellent decomposition differed from that of AP because it occurred at a lower temperature. The heat release was greater, and the AP particle size had a significant effect.

Schmidt has continued[252] the study, previously reviewed[2], of the relationship between the burning rate of an AP composite propellent and the DTA behaviour. In his later work the decomposition of AP, AP containing potassium chlorate and AP - transition metal chelate mixtures was studied under both isothermal and non-isothermal conditions. The effects of various additives and experimental conditions are summarized in Table 19. The results support the proton transfer mechanism for AP decomposition, and it is considered that the catalyst acts by facilitating the perchloric acid decomposition, and not that of the perchlorate ion. This mechanism was supported by experiments in which potassium perchlorate catalyst mixtures were heated in an ammonia stream. No deflagration was observed even at temperatures above that at which AP normally deflagrated.

One type of catalyst (ferrocene, metal acetylacetonates, etc.) was observed to interact chemically with the ammonium ion to give a more reactive compound, not identified, which then lowered the AP deflagration temperature.

The effect of the gaseous products of the thermal decomposition of AP at 130 to 190°C was studied by Svetlov and Koroban[253]. It was found that AP decomposed to a point corresponding to a constant pressure at a particular temperature (1600 torr at 150°C); thus the extent of decomposition varied from 73 to 1% at 150°C depending on the ratio of the weight of AP to the volume of the reaction vessel. These results clearly showed that the decomposition products retarded the decomposition. Water was found to have a pronounced retarding effect, increasing the induction period and decreasing the pressure at which decomposition stops. Perchloric acid was found to be present in appreciable quantities in the products. A novel mechanism was proposed in which the perchloric acid decomposed to chlorine oxides which attacked the AP, e.g. by

$$NH_4ClO_4 + Cl_2O_6 \longrightarrow NH_4ClO_3 + Cl_2O_7 \qquad (115)$$

and the inhibition by water was ascribed to the reaction

$$Cl_2O_7 + 3H_2O \longrightarrow 2HClO_4.H_2O \quad . \qquad (116)$$

The effect of preliminary irradiation and of chlorate impurity on the rate of thermal decomposition of AP has been re-examined[254]. Irradiation by 200 KeV X-rays resulted in AP which decomposed much faster than AP containing an equal amount of chlorate. It is suggested that the additional acceleration of the decomposition results from the production of cationic and anionic defects by irradiation. An electron transfer mechanism is discussed.

Two recent papers[255,256] have described results of experiments on the detonability of AP.

11.2 Catalysed thermal decomposition

A few papers concerned with the catalyzed decomposition of AP were included in section 11.1 for convenience. Others solely concerned with the catalysis are now reviewed.

Continuing his extensive study of AP catalysis[2], Solymosi has made studies of the action of cadmium and magnesium oxide[257]. He concluded that both oxides react to form cadmium and magnesium perchlorate which, along with zinc perchlorate, have been shown[258] to be effective catalysts even when present in extremely small amounts (500:1 mole ratio for Cd and Mg perchlorates and 1000:1 for Zn perchlorate). Activation energies are summarized in Table 20. The catalysis was ascribed to the role of these salts in causing the AP to melt and to their high polarizing power.

The adiabatic method has been applied by Wise et al.[259] to a study of the kinetics of AP in the presence of catalysts. Activation energies are given in Table 20 but the data were less reproducible than those for pure AP because of difficulty in establishing isothermal starting conditions, of sample fracture during decomposition and of non-uniform distribution of catalyst through the sample. Study of an AP-carboxy--terminated polybutadiene propellent showed that the activation energy was 33 kcal mole^{-1}, almost the same as that previously obtained by Wise for

pure AP. It was also shown that pressure had no effect on the activation energy for AP decomposition which was also observed by Waesche and Wenograd[251]. It was concluded that the absence of a pressure effect indicated that the observed heat release is controlled by solid phase reactions.

The effect of catalysts on the product composition was studied at 200 to 300°C by Shmagin and Shidlovskii[260] who reported analyses for H_2O, O_2, HCl, Cl_2, N_2O, NO and N_2. Addition of metallic oxide (MnO_2, Co_2O_3, NiO, Fe_2O_3, Cu_2O and ZnO) was studied and generally found to result in a decreased yield of N_2O accompanied by an increase in NO except for the addition of ZnO. The chlorine/hydrogen chloride ratio was little affected by the addition of catalyst, except for zinc oxide which reacted chemically with AP when the amount of HCl was very small.

The effect of the particle size and surface area of nickel and copper oxide on the decomposition of AP at 230 to 300°C has been examined by Boldyrev et al[261]. The catalysts were found to be effective even when physically separated from the AP so that the sublimed AP passed through a layer of the additive.

The co-crystallization of AP with isomorphous compounds to give an increased catalytic effect has recently been patented[262]. AP containing co-crystallized salts such as chromates, permanganates and periodates is much more impact-sensitive than pure AP. Thus with pure AP, a 2 kg weight causes 50% explosions for a height of 100 cm, and AP with 2% potassium periodate requires a height of 27 cm only, less than that for RDX (33 cm). The accelerated thermal decomposition is shown by the results of TGA experiments summarized in Table 21.

11.3 Ignition

Further light has been thrown on the low calculated surface temperature (160°C) observed in the ignition of solid propellents using a shock tube. The effect of surface roughness was shown[263] to have a pronounced effect on the calculated surface temperature for ignition. Although these experiments were reported for double-base propellent the finding is certainly applicable to similar experiments with composite propellents based on AP.

It was noted that whereas ignition in the shock tube occurred in a few milliseconds with a calculated surface temperature of 130°C, a sample maintained at that temperature did not ignite in one hour. If acetone was used to wet the surface, a mirror-smooth surface could be obtained. This would not ignite even with gas temperatures in the shock tube some 200-300 deg C hotter than previously. When a scratch was made on the mirror-smooth surface, ignition occurred. Thus surface roughness has an important effect on ignition due to the presence of localised areas of higher heat transfer and should be considered in comparing samples.

Ignition of polymeric fuels similar to those used in solid propellents by perchloric acid vapour has been continued with a study of the effect of added catalyst[117]. It was shown that addition of catalysts such as copper chromate reduced the ignition delays markedly and that they did so only when the catalyst was in physical contact with the fuel. Short separations (5-10 mm) were not effective. It was also shown that heat release resulted when perchloric acid vapour was passed onto copper chromite, and that the chemical change that occurred in the catalyst corresponded closely to that observed by Rosser et al [264]. It was concluded that the catalyst acted by promoting the decomposition of perchloric acid and that ignition resulted from reaction of an unstable chlorine-oxygen species on the surface of the fuel.

Ryan et al.[265] have reported results of a study of the reactions in a polybutadiene acrylic acid (PBAA) AP propellent using the thin film technique to simulate ignition conditions. Addition of fine AP particles (< 5μ) to the PBAA film caused the temperature, at which regression starts, to be reduced from above 450°C to 390°C. At high heating rates, a rapid PBAA-AP reaction was observed at a lower temperature and it was concluded that the AP decomposition products were attacking the PBAA. Copper chromite was not observed to have much effect. It is possible that AP-catalyst contact was impeded by the polymer. The reaction and ignition of PBAA films in oxygen appear to [illegible] a non-luminous PBAA-oxygen reaction at the surface and a later gas phase reaction to produce a luminous flame. The importance of the AP-PBAA products reaction is in agreement with the observations that perchloric acid reacts readily with fuels at low temperatures[2,117].

High-convective heat flux studies have also been reported[265] in which the addition of 2% of ammonium dichromate, n-butyl ferrocene, cobalt oxide or copper chromite on propellent ignition were examined. The result of cobalt oxide was difficult to determine because surface roughness effects were significant. Copper chromite and ammonium dichromate were equally powerful catalysts, but n-butyl ferrocene was the most effective. It was suggested that the n-butyl ferrocene was so effective because it was added to the propellent mix in liquid form, hence ensuring excellent dispersion. A theoretical model for the ignition response of solid propellents was proposed, which predicts ignition behaviour with respect to pressure and surface heat flux in quantitative agreement with experimental measurements.

The effect of various additives on the ignition delay of AP has been described[266]. Preheating of AP to 360 or 400°C before measuring the ignition delay at 430°C showed that the ignition delay was reduced in proportion to the duration of the preheating. The nature of the ambient gas (N_2, air, NO or NH_3) had no effect on the ignition delay, but decrease in pressure increased the delay. Sample size (100-250 mg) had no effect on the activation energy (36 kcal $mole^{-1}$) observed for pure AP. A similar activation energy was obtained with additions of manganese dioxide or Co_3O_4-Co_2O_3. The quantity of catalyst required for maximum reduction in the ignition delay decreased as the AP particle size increased.

Recently, the role which condensed phase reactions may play in the ignition and combustion of AP propellents has received increased attention. Fishman[267], using embedded surface thermocouples, has examined the pre-ignition surface exotherms in AP propellents subjected to radiation from an arc image furnace. From the shape of the temperature-time trace it was concluded that exothermic reactions involving the condensed phase do occur in significant proportions during ignition in the pressure-dependent regime. Arc-image results from this regime do not lie on a log-time/log-flux line of slope -2.

Simulated propellents containing AP and powdered catalysts were studied by Wise et al.[268] by measuring the rate of heat release, burning rate and ignition delay. It was found that the calculated surface temperatures for arc image ignition at high heat flux were much higher than the surface temperatures for steady state combustion. Consequently ignition may not be interpreted solely as the time required to establish conditions prevailing during steady state burning. It was concluded that a condensed phase reaction does contribute

to ignition and combustion, and that this condensed phase reaction (either a homogeneous reaction in the solid or at the gas-solid interface) may be the necessary pre-requisite for ignition. It was considered that with increase in burning rate the contribution of the condensed phase reaction would decrease since the time available for reaction to occur would be less.

Shock tube studies of the ignition of a range of polymeric fuels have been reported by Shannon[269,270]. It is suggested that thermoplastic fuels ignite by a gas-phase process whereas elastomeric fuels may ignite by a heterogeneous process. However, it was accepted that the physical structure of the polymer surface was important. Studies of propellents in an arc image furnace indicated that the nature of the fuel had a major influence on the ignition delay below 0.75 atm abs and on the minimum pressure at which ignition occurred. The latter correlated well with the thermal stability of the fuel.

The study of flame spreading over the surface of igniting solid propellents and over thermoplastics typical of fuels used in propellents has been continued by McAlevy et al.[271,272]. Flame-spreading rates of fuels were measured in oxygen, and of ammonium perchlorate in methane. The rates with AP were observed to be much faster with loose crystals than with pressed samples. Simple observations were made with polystyrene and polymethylmethacrylate with 100% oxygen[271] and with oxygen mixtures containing various inert gases[272].

Mixtures of AP with polystyrene were tested in oxygen, and it was observed that the AP crystals ignited only after the polystyrene-oxygen flame had passed over them. It was concluded that the basic mechanism of flame spreading is essentially one of continuous gas-phase ignition. However, this cannot be regarded as proved for the ignition of actual solid propellent motors for which the ambient atmosphere is not 100% oxygen. It is probable that the perchloric acid liberated from the AP is important in practical systems.

11.4 Combustion

11.4.1 Experimental

Experimental techniques for the study of solid-propellent combustion have been reviewed recently by Friedman[273]. The emphasis was placed on the techniques rather than on the results because of the still limited amount of precise information about the combustion process.

Other effort is being directed towards elucidating the combustion mechanism. Thus, Hackman and Beachell[274] have examined the combustion of single AP crystals and of AP powders. The burning rate for single crystals was found to be 0.33 inch sec^{-1} at 1000 psi in good agreement with the value previously obtained by Hightower and Price[275]. Examination of the reacting surface showed that the product gases are transparent near the surface but within a distance of 500 to 1000 microns they become a dense white cloud due to product condensation. A globule was observed in one sequence with a glassy or molten surface. The effect of particle size, bulk density and of doping with rubidium or nitronium ions was investigated. The nitronium ion (0.01%) increased the impact sensitivity to a point where the doped AP was more sensitive than either pure AP or nitronium perchlorate. It increased the burning rate by about 50%. The results are discussed in terms of a characteristic burning surface area defined as the ratio of the actual surface area to the area of a single crystal. For 360 μ powder this was about 16.

Single crystal studies have been used by Beckstead and Hightower[276] in calculating the surface temperature of deflagrating AP crystals. The method is similar to that based on measurements of the phase-transition depth below the surface previously described by Selzer[277]. However, the use of single crystals offers several advantages and in the later paper[276] allowance was made for the variation of thermal properties with temperature. It was found that the solid surface temperature in the absence of fuel was virtually independent of burning rate in the range 525 to 600°C in reasonable agreement with previous results by other techniques.

Profiles of the emission intensity for OH, CH, NH and CN through the flame of an AP-polyisobutene propellent have been reported by Selzer[278] who has also observed that regression of burning propellent proceeds in a stepwise manner[279] with a frequency of 5 to 20 Hz. High speed photography was used to examine the flame appearance and shape associated with this phenomenon.

The detailed structure of the flame zone in AP propellents has been studied using fibre optics and high speed photography (up to 9000 frames per second) by Marxman et al [280]. It has been shown that both AP crystals and aluminium particles may ignite at or near the surface. Further, as the aluminium ignites at a temperature of about 1000°K, which is well below

the ignition temperature (2300°K) for aluminium in oxygen, this implies that the ignition results from attack by intermediate products from AP decomposition. This confirms that important heat release reactions occur near the surface, as found earlier by the same workers using DTA. The concept of surface heat release reactions has been incorporated in their model of the combustion process, which predicts that the gas phase flame temperature will increase as the burning rate increases.

Propellent analogues consisting of particulate beds have been used by McAlevy et al.[281,282] to study the combustion process. Three basic types of burner were used - gaseous fuel through a porous bed of AP particles, gaseous oxygen through porous thermoplastic granules, and an unbonded mixture of particles of AP and thermoplastic polymer. It was suggested that the nature of the fuel had an influence over and above that of its overall heat of combustion because, both with AP and with gaseous oxygen, polystyrene has a maximum burning rate at a different stoichiometric ratio from that shown by polymethylmethacrylate. The importance of the bonding technique in fabrication of AP porous plug burners was discussed in the light of results obtained by McAlevy and by others.

Further studies of simulated propellent systems using perchloric acid flames have been discussed in section 10. A similar fundamental study, but concerning the nature of the fuel pyrolysis products and their reaction with oxygen, has been described by Nagao and Hikita[283,284].

The importance of solid phase reactions in propellent combustion has been examined by Caveny and Pittman[285]. Experimental and analytical approaches were used to deduce the solid phase surface temperature and to evaluate the effect of AP solid phase decomposition rate on burning rate. AP was modified by irradiation with 9.8×10^6 rad of Co^{60} and also by thermal shock in liquid nitrogen, both methods resulting in greatly enhanced rates of thermal decomposition. If sub-surface reactions within the AP contribute significantly to the burning rate, it would be expected that propellents containing AP modified in this way would burn at a faster rate. This was found not to be so for a range of propellents ranging from 55 to 80% by weight AP content, 6 to 200 μ AP particle sizes and burning at 500 to 15000 psi pressure. The calculation of surface temperature followed the method used by Beckstead and Hightower[276] and yielded a somewhat lower surface temperature of 442 ±30°C. Sub-surface heat generation rates,

even at an upper limit, did not affect the calculated surface temperature. It was therefore concluded that AP sub-surface reactions do not control the burning rate at pressures above 500 psi. However, at low burning rates and lower pressures it was considered that sub-surface reactions would become increasingly important.

The burning rate of an AP-composite propellent has been shown[252] to be unaffected by the addition of potassium chlorate. However, burning rates were affected by metal chelates: [bis - (N - R - salicylaldehyde-amine) Cu (II)] compounds accelerated the burning rate uniformly between 300 and 1000 psi [252]. Similarly, metal acetylacetonates increased the burning rate, with a relative order of effectiveness below 1000 psi of Cu > Fe > Co ≈ Mn. It was considered that these additives act by catalysis of the perchloric acid decomposition both by (i) decomposition of the additive to molecular size oxide particles which have fresh surfaces, and (ii) exothermic reaction of perchloric acid with the organic fragments. It was further suggested that the most effective catalysts are transition metals having two stable oxidation states which involve a one electron change.

It was also shown that addition of 1% of basic amine (such as tributylamine or dimethyl-dodecylamine) to a propellent containing 75% AP greatly reduced its burning rate and pressure exponent giving plateau and mesa-type burning rate curves. It was proposed that a surface process was probably involved such as neutralization of the perchloric acid.

Recently, Jacobs and Powling[286] have combined results on (i) low-temperature isothermal sublimation (ii) the measurement of linear regression rates by hot-plate pyrolysis and (iii) the rates of combustion of AP at low pressures. The combustion was sustained by preheating the AP, or the use of a solid volatile fuel, or the passing of gaseous fuels through a porous bed of AP, or a counter-flow diffusion flame above the AP. It was found that all the data correlated well when the pressure-dependence of the sublimation rate was taken into account. Thus dissociative sublimation was shown to give a consistent interpretation for the data obtained from these three methods. An interesting experiment was reported in which the burning rate of AP-fuel mixtures, in which the AP had previously been heated until the low-temperature reaction was complete, was compared with control samples that had not been preheated. No difference in burning rate was observed thus indicating that any thermal decomposition occurring in the solid ahead of the combustion zone had no significant effect.

The characteristics of the burning surface of AP with a range of volatile e.g. (naphthalene) and non-volatile e.g. (graphite) fuels has been compared[174] with those of potassium and sodium perchlorate with the same fuels. For fusible fuels the projection of AP crystals above the surface was observed at pressures up to 30 atm; above 30 atm depressions were observed.

Thermally stable fuels accumulated on the surface during burning. It was concluded from observations on the three oxidizers that some reaction took place in the condensed phase or on the surface of the thermally stable fuels such as tungsten and graphite. Whereas this is almost certainly true for the latter fuels it cannot be regarded as proven for fuels of the type usually used in solid propellents.

The study of the increase in burning rates on the addition of catalysts has continued. Yamazaki and Tokui[287] have reported burning rates for propellent containing metallic foil (aluminium, silver and copper of various thicknesses) either in random or laminated form. Maximum burning rates were obtained for propellent laminated with foil oriented normal to the burning surface which burnt with V-shaped indentations with the metal foil at the point of the V. The burning rate enhancement was attributed primarily to the thermal conductivity of the foil.

The effect of various additives on the burning rate of AP in perspex tubes has been reported by Glaskova[288]. The effect of Cr^{6+} (as potassium dichromate) and Cr^{3+} (as chromic oxide) on both AP alone and a stoichiometric AP-coke mixture was examined. Potassium dichromate was shown to increase the burning rate to a greater extent than chromic oxide. Even higher burning rates were observed for a stoichiometric mixture of AP with metallic iron. Results were also obtained for combustion of AP with calcium stearate. By comparison with results obtained elsewhere, it was concluded that the similarity between the effect of catalysts on the burning rate and on the thermal decomposition of AP is not good. However, this comparison is not valid unless identical additives are used because the physical properties will otherwise differ.

Other recent papers have described the control of the low pressure deflagration limits[289] and the effect of spatial acceleration on the burning rate[290] of AP-composite propellents. Higher deflagration limits, and thus safer propellent compositions, were obtained by increasing the amount of binder, by using oxygenated binders, or by modification of the

aluminium and of the AP used. At the low pressure deflagration limit the combustion of fuel and oxidizer is probably premixed, so it is interesting that halogenated hydrocarbons had little effect, an observation in agreement with the lack of effect on the burning velocity produced by addition of halogenated hydrocarbons to perchloric acid flames. The tendency for the flame of a burning propellent to propagate into surface cracks has been examined for an AP-polyester resin propellent[291] as a function of crack width, AP particle size and pressure. It was found that there is a lower limit to crack width into which the flame will propagate.

11.4.2 Models of the combustion process

Summerfield[292] has reviewed burning rate data and has shown that his granular diffusion flame model is valid for AP composite propellents which are highly loaded with oxidizer of medium particle size (20-200 μ AP). The theory did not hold, nor was it predicted to hold, for very high pressures (above 2000 to 5000 psia) or for large particle sizes.

It was also found[292] that fuel-rich AP propellents containing small particle size AP do not burn normally at intermediate pressures and that plateaux and extinctions can occur. Thus with polybutadiene-acrylic acid- and polysulphide-AP propellent, plateau burning was observed in the range 300 to 800 psia for AP-particle sizes between 15 and 45 μ. Extinction occurred at 500 psia for particle sizes below 10 μ and the burning rate also passed through a maximum at 350 psia. Intermittent burning and pressure oscillations were observed between the burning rate maximum and the extinction point. This anomalous behaviour was ascribed to the burning surface being non-planar.

The 'phalanx flame model' has been developed by Fenn[293]. This represents the flame as burning at the interfacial region between streams of fuel and oxidant generated by volatilization of the solid components. Thus at high pressures most of the fuel and oxidizer burn in a diffusion flame, but a small and very important fraction burns in a premixed flame in the phalanx tip at the base of the diffusion flame close to the surface. The close proximity of the premixed flame to the surface implies that this region will be consumed first and thus that the surface will rapidly become non-planar. The phalanx model permits easy transition between the various combustion modes of AP-fuel mixtures, and also can qualitatively explain the plateau

and extinction burning discussed earlier. The expression derived by Fenn for the variation of burning rate with pressure is

$$r_b = \frac{p}{A + Br_b\, p^{(2-n)/2}}$$

where n is the order of reaction, r_b the burning rate at pressure p and A, B are constants. The similarity of this expression to that obtained by Summerfield for the granular diffusion flame model is pronounced.

Hermance has extended his previous model[294], in which surface heterogeneity and heat release effects were included, to one in which a heterogenerous reaction between the solid fuel and the oxidizer decomposition products is postulated[295]. The effect of diffusion mixing of the decomposition products released at the surface in the determination of flame height is also included in the extension of the model. Good agreement was observed between theoretical and experimental burning rate-pressure curves. The prediction of pressure exponents greater than unity at high pressures (300 atm and above) was also supported by experimental observations. Various other parameters were calculated and found to be in reasonable agreement with experimental values. It may be concluded that this model is quite representative of the AP-fuel combustion process, and that better experimental data will be required to permit critical examination of the predictions from the theory.

Other contributions to the model of combustion of AP have proposed that a cellular flame structure is involved[296] resulting in a more stoichiometrically balanced flame of ammonia and perchloric acid within the cell, and a flame extremely lean in fuel. However, it was not considered that this structure would apply to AP in a propellent. Arguments have also been put forward that the burning rate cannot be controlled by the processes occurring in any one stage[56,297].

12 CONCLUSIONS

The salient features of perchlorate decomposition and combustion are summarised in this section and common properties and behaviour are sought. Finally areas for future research are outlined.

12.1 Sublimation

The perchlorates may readily be divided into those that sublimate to yield perchloric acid with the corresponding base and those that do not.

Group A	Group B
Perchlorates that sublimate to perchloric acid and base	Perchlorates that do not sublimate to acid and base
$(HClO_4)$	$NOClO_4$
NH_4ClO_4	NO_2ClO_4
NH_3OHClO_4	$B(ClO_4)_3$
$N_2H_5ClO_4$	$FClO_4$
$N_2H_6(ClO_4)_2$	Metal perchlorates
$CH_3NH_3ClO_4$	
$CH_5N_3HClO_4$	
Other amine perchlorates	

It should be noted that hydrated metal perchlorates, such as those of aluminium and magnesium, yield perchloric acid on heating[298]. Further, the preparation of anhydrous metal perchlorates for other than the alkali metals is difficult[299]. Thus, it would in general appear that perchlorates containing hydrogen atoms will yield perchloric acid on heating, especially if the perchlorate is that of a non-metallic base. Nitronium perchlorate has been observed[299] to sublimate but this cannot yield perchloric acid and it is therefore assigned to Group B. The sublimation process may be

$$2NO_2ClO_4 \longrightarrow N_2O_5 + Cl_2O_7 \quad . \qquad (117)$$

12.2 Decomposition

It is expected that the behaviour of perchlorates in their decomposition will follow the division made in section 12.1. Thus, perchlorates in Group A, which on heating yield perchloric acid and the base, will decompose in a manner which depends on the less stable of the two components. On the other

hand, the perchlorates of Group B may decompose by rearrangement to yield chlorine heptoxide or by scission of a Cl-O bond. The latter route requires a high activation energy of some 60 to 70 kcal mole^{-1}.

The experimental activation energies are summarized for the two groups of perchlorates. It is most important to note that reaction kinetics deduced from pressure-rise observations may differ from those derived by weight-loss measurements because of gas phase reactions. Thus, apparent numerical inconsistencies may reflect different experimental methods. Moreover, these perchlorates have in general been studied much less intensively than has ammonium perchlorate, of which the modes of decomposition have only recently yielded a consistent interpretation.

Group A		Group B	
Perchlorate	Activation energy, kcal mole^{-1}	Perchlorate	Activation energy, kcal mole^{-1}
$HClO_4$ (g)	45.1	$NOClO_4$	-
(l)	22.6, 32.5	NO_2ClO_4	25 (<100°C), 15 (<100°C)
NH_4ClO_4	32	Alkali metal ClO_4	60-70
$N_2H_5ClO_4$	36.2	Other metal ClO_4	30-40
$N_2H_6(ClO_4)_2$	23.5		
$CH_5N_3HClO_4$	32.4		
NH_3OHClO_4	44.3		
$CH_4N_4O_2HClO_4$	24.4		

The activation energies for the vapour and for the liquid phase decomposition of chlorine heptoxide are the same[1], viz. 32 kcal mole^{-1}. The similarity with that for liquid perchloric acid decomposition has been proposed as evidence for perchloric acid decomposition through chlorine heptoxide as an intermediate

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \quad . \qquad (118)$$

On the arguments presented (section 10.1 and Ref.1) this is not favoured. Moreover, mass spectrometric studies of the decomposition of perchloric acid and chlorine heptoxide (section 10.2) have shown that their pyrolysis proceeds differently. That of perchloric acid begins at 550°C and that of chlorine heptoxide at 380°C.

Consideration of the activation energies for Group B suggests that decomposition proceeds either by Cl-O bond fission, as for the alkali metal perchlorates, or by chlorine heptoxide decomposition with an activation energy of about 30 kcal $mole^{-1}$. It is predicted that the activation energies of hydrated metal perchlorates may differ appreciably from those of the anhydrous perchlorates.

The activation energies for Group A perchlorates suggest that the common feature is the perchloric acid decomposition. The value for hydrazine diperchlorate is suspect because it decomposes on heating to perchloric acid and hydrazine monoperchlorate. This suggestion that perchloric acid decomposition is dominant would be confirmed if metal oxides have as pronounced a catalytic effect on the thermal decomposition of these perchlorates as they do on AP. Establishment of a parallel mode of decomposition will require determination of the kinetics using weight loss techniques, preferably in the same laboratory.

12.3 Combustion

The general division of perchlorates into Groups A and B on the basis of sublimation may be expected to continue into the sphere of combustion. Perchlorates sublimating to perchloric acid and the corresponding base are expected to exhibit monopropellent combustion. Further, in composite mixtures with fuel these perchlorates should have a premixed perchloric acid-base flame close to the oxidizer particles, followed downstream by a sedondary diffusion flame between the combustion products of the first flame and the vaporized fuel. However, the intensity of this second flame will depend on the fuel-oxidizer balance in the monopropellent flame. Thus a perchlorate such as guanidine perchlorate which is fuel-rich is not expected to show any secondary diffusion flame. Nor would it readily be a practical component for composite propellents because the addition of further fuel to provide a matrix for the oxidizer would only reduce the combustion temperature.

Flame temperatures have been calculated for Group A perchlorates as monopropellents and for both groups as components of stoichiometric mixtures with a high grade paraffin as fuel, which is assumed to have the formula $(CH_2)_n$ and a lower calorimetric value of 10400 cal gm^{-1}, or ΔH_f = -5.971 kcal $mole^{-1}$ at 298°K. The specific impulse for expansion from 1000 psi to 1 atm pressure has been computed for these mixtures.

Group A perchlorates

Perchlorate	Oxygen per cent	ΔH_f, kcal $mole^{-1}$	ΔH_f, cal gm^{-1}	Monopropellent combustion		Stoichiometric combustion*	
				Temp., °K 1 atm	Temp., °K 1000 psi	Temp., °K 1000 psi	S.I., lb sec lb^{-1}
$HClO_4(l)$	63.7	-9.36	-93.2	1014	1072	3530	269.9
NH_4ClO_4	54.5	-70.21	-597.5	1390	1417	2997	252.0
$N_2H_5ClO_4$	48.3	-42.15	-318.3	2253	2325	3126	263.6
$N_2H_6(ClO_4)_2$	54.9	-69.2	-297.0	1634	1667	3260	264.0
NH_3OHClO_4	59.9	-66.15	-495.7	1383	1409	3162	262.1
$CH_5N_3HClO_4$	40.1	-74.10	-464.5	2579	2799	Fuel rich	
$CH_8N_6HClO_4$	31.3	-23.8	-116.3	2581	2715	Fuel rich	
$NO_2Al(ClO_4)_4$	54.4	-110	-233.6	1194	1199	3590	256.7
$NH_4Al(ClO_4)_4$	57.8	-348	-456.2	1221	1280	3422	250.5

* The fuel is specified in the text

Group B perchlorates

Perchlorate	Oxygen per cent	ΔH_f, kcal mole^{-1}	ΔH_f, cal gm^{-1}	Stoichiometric combustion*	
				Temp., °K 1000 psi	S.I., lb sec lb^{-1}
$NOClO_4$	61.8	-36.8	-284.2	3317	253.3
NO_2ClO_4	66.0	+8.88	+61.0	3587	271.9
$KClO_4$	46.2	-103.22	-745.0	3024	206.5
$LiClO_4$	60.1	-90.83	-853.7	3096	235.8

* The fuel is specified in the text

Values for the specific impulse are not maximum values because the optimum value usually corresponds to a mixture slightly on the fuel-rich side of stoichiometric. Consequently, the values listed do not indicate the relative performance of perchlorates with closely similar values of specific impulse.

The linear burning rates for Group A perchlorates burning as monopropellents are shown in Fig.1 using data taken from various sources[2,57,296,300,301] for loosely tamped powders and for pressed strands (including single crystals). It is interesting to observe that hydrazine monoperchlorate has a much higher burning rate as a pressed strand, albeit over a limited pressure region, than has hydrazine diperchlorate, hydroxylamine perchlorate and ammonium perchlorate. These three have similar burning rates at pressures of about 100 atm.

Loosely tamped powders have an appreciably higher linear burning rate than pressed strands, especially for ammonium perchlorate. This higher burning rate has been ascribed to an increase in the surface area and in the number of packing voids.

The nature of the combustion surface, which is liquid for the hydrazine perchlorates at low pressures, does not markedly affect the burning rate. Moreover, burning rate catalysts, such as copper chromite which are effective for ammonium perchlorate, are also effective for hydrazine mono- and di-perchlorate. It is predicted that other Group A perchlorates will be catalysed by such compounds. Group B perchlorates will not be catalysed.

12.4 Sensitivities

The relative sensitivities of perchlorates are tabulated below for convenience. It is difficult to compare the literature data because of the significant effects of slight variations in sample purity and of the different experimental arrangements used.

Perchlorate	Bureau of mines 2 kg wt-50% fires		Rotter impact test 5 kg wt-50% fires		Unspecified test 5 lb wt	
	Height, cm	Ref.	Height, cm	Ref.	Height, in	Ref.
NH_4ClO_4	100	106,107	-		46	82
$N_2H_5ClO_4$	1.2	68	32	62	-	-
$N_2H_5ClO_4.\frac{1}{2}H_2O$	12.4	68	65	62	-	-
$N_2H_5ClO_4.H_2O$	27.5	68	-	-	-	-
$N_2H_6(ClO_4)_2$	-	-	82	62	21	82
$N_2H_6(ClO_4)_2.2H_2O$	-	-	190	62	-	-
$N_2H_5(ClO_4)_2$, acid wet	-	-	-	-	17	82
NH_3OHClO_4	15	87	-	-	-	-
$MeNH_3ClO_4$	20		-	-	-	-
$Me_2NH_2ClO_4$	22	106	-	-	-	-
Me_3NHClO_4	25	107	-	-	-	-
Me_4NClO_4	35		-	-	-	-
$CH_5N_3HClO_4$	62	113	-	-	-	-
Triaminoguanidine perchlorate	<5, 7	122,121	-	-	-	-

The relative order of sensitivity can be seen. Desensitization of some of these perchlorates may be achieved by using them in a mixture with lithium perchlorate[62,122].

The heavy metal perchlorates are, in general, sensitive, especially if traces of organic materials are present. The electronic absorption spectra and the explosive properties of metal perchlorates have been correlated[302].

12.5 Areas for future research

This review of perchlorates shows that significant correlations exist in their decomposition and combustion characteristics. These correlations require to be substantiated.

Thus, the thermal decomposition should be examined using weight loss measurements. Much of the present uncertainty about the relative merits of results from different laboratories could be eliminated by comparative measurements using a standard perchlorate such as ammonium perchlorate of specified purity. Standards are even more desirable for studying the effect of catalysts on perchlorate decomposition because the catalytic activity of a given material is greatly dependent on the source and even on the batch.

The decomposition of perchloric acid and of chlorine heptoxide in conventional kinetic systems should be re-examined and the effect of catalysts ascertained so as to determine whether the equilibrium

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \qquad (118)$$

plays a significant role in the decomposition of perchlorates.

Such studies on the thermal decomposition are expected to provide the first justification for the division of perchlorates into two groups. This division should then be confirmed by comparative studies of the ignition and combustion of the perchlorates. New techniques such as that of pulsed laser mass spectrometry should be extended to other perchlorates and propellents because they will give valuable information as to the actual species involved in the combustion and ignition processes. This information, together with an increased understanding of the relative importance to steady state combustion of homogeneous gas phase and heterogeneous surface reactions, will aid the development of models of the combustion process for perchlorate propellents.

An understanding of the mechanism of catalysts and other ballistic modifiers is necessary so that propellents may be formulated to give predictable burning rates.

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Table 1

PHYSICAL PROPERTIES OF NITROSYL PERCHLORATE

Property	Value	Reference
Formula	$NOClO_4$	
Molecular weight	129.4567	7*
Density at 18°C	2.169, 2.162 gm cm^{-3}	4, 8
Heat of formation at 25°C	-36.8 ±0.4 kcal $mole^{-1}$	see section 2B
Crystal structure	Rhombic	8
Crystallographic transition	Not below 100°C (onset of rapid decomposition)	9
Melting point	Decomposes without melting	10

*All molecular weights in this review are calculated using atomic weights based on $carbon_{12}$ = 12.00 as listed in Ref.7.

Table 2

PHYSICAL PROPERTIES OF NITRONIUM PERCHLORATE

Property	Value	Reference
Formula	NO_2ClO_4	
Molecular weight	145.4561	
Density at 25°C	2.2 gm cm^{-3} 2.25 gm cm^{-3}	37 38
Heat of formation at 25°C	8.88 ±0.25 kcal $mole^{-1}$	39
Crystal structure	Monoclinic	37, 40
Crystallographic transition	-	
Heat of solution at 25°C	-20.4 ±0.4 kcal $mole^{-1}$ for 1:10000 dilution	41
Vapour pressure	$<10^{-4}$ torr at ~25°C	
Melting point	Decomposes without melting	

Table 3

PHYSICAL PROPERTIES OF HYDRAZINE PERCHLORATES

Property	Hydrazine monoperchlorate		Hydrazine diperchlorate	
	Value	Ref.	Value	Ref.
Formula	$N_2H_5ClO_4$		$N_2H_6(ClO_4)_2$	
Molecular weight	132.504		232.962	
Density, gm cm^{-3}	d_{15}^{15} 1.939	58	2.21	57
	d_{4}^{15} 1.927	59		
Heat of formation, kcal $mole^{-1}$	-42.05	see section 4.2	-69.2 ± 0.5	60
Heat of solution, kcal $mole^{-1}$	9.77 (1:1000 dilution)	59		
Heat of fusion, kcal $mole^{-1}$	3.84, 1.68	61, 62		
Melting point, °C	142	62	190-192	57
Vapour pressure	$\log_{10} p(mm) = 10.2 - \frac{6400}{T}$	63		
Heat of dissociation, kcal $mole^{-1}$	58.4	63	37.0	64
Solubility in water, gm per 100 gm solution	23.6 at 0°C 68.9 at 40°C	58		
Crystal structure	Monoclinic	62		
Hydrate	$N_2H_5ClO_4 \cdot \frac{1}{2} H_2O$		$N_2H_6(ClO_4)_2 \cdot 2H_2O$	
	Dehydrates at 60.5°C	65	Monoclinic	62
	Heat of dehydration = 6.977 kcal $mole^{-1}$	65	Melting point 95°C	62
	$\log p_{mm} = -3047.6/T + 10.980$	65		
	Monoclinic	66		

Table 4

EFFECT OF CATALYSTS ON COMBUSTION OF HYDRAZINE PERCHLORATE AT 1 ATMOSPHERE

Author	Ref.	Catalyst	%	Density	Burning rate, cm sec^{-1}
Shidlovskii et al.	59	MnO_2	5	1.27	0.13
		CoO	5	1.29	0.85
		Cu_2Cl_2	5	1.27	1.5
		$Cu_2Cl_2.2H_2O$	5	Does not burn steadily	
Levy et al.	63	MgO	2	1.90	0.26
			5	1.91	0.31
			10	1.89	0.35
		Copper chromite	2.5	1.13	Does not deflagrate
			5	1.10	1.20
			5	1.93	0.72
		$K_2Cr_2O_7$	2.5	1.17	Does not deflagrate
			5	1.19	0.75
		CaO	2	1.31	0.12

Table 5

EFFECT OF CATALYSTS ON BURNING RATE OF HYDRAZINE DIPERCHLORATE

(From Levy[81])

Catalyst	Weight %	Pressure, atm	Burning rate, cm sec^{-1}
None	-	1	0.002 (extrapolated)
MgO	2.0	1	Incomplete combustion
	5.0	1	0.011
	2.0	8	Irreproducible
	2.0	11	0.16
Copper chromite	0.5	1	Incomplete combustion
	1.0	1	0.081
	2.0	1	0.12
	5.0	1	0.25
	10.0	1	0.24
	2.0	40	Too fast
	2.0	70	Too fast
Sodium nitroprusside	0.5	1	0.037
	1.0	1	0.052
	5.0	1	0.127

Table 6

PHYSICAL PROPERTIES OF HYDROXYLAMINE PERCHLORATE

Property	Value	References
Formula	NH_3OHClO_4	
Molecular weight	133.489	
Density	2.06 gm cm^{-3}	91
Heat of formation	-66.1 ± 1.0 kcal $mole^{-1}$	see section 6.2
Crystal structure	Monoclinic	91
Vapour pressure	10^{-5} torr at 95°C	91
Melting point, °C	85, 88	91, 92
Heat of vaporization	33 kcal $mole^{-1}$ (assuming no dissociation)	92

Table 7

IGNITION TEMPERATURES OF AMINE PERCHLORATES

(From Datta and Chatterjee[105])

Perchlorate	Ignition temperature, °C	Comments
Methylamine	338	
Propylamine	290	
Guanidine	367	Melts at 237°C
Semicarbazide	278	
Aniline	250	
Hydrazine mono-	238	
Hydrazine di-	215	

Table 8

IMPACT SENSITIVITIES OF METHYLAMINE PERCHLORATES

(From Stammler and Schmidt[106,107])

Compound	Height, cm
RDX*	33
NH_4ClO_4	100
$MeNH_3ClO_4$	20
$Me_2NH_2ClO_4$	22
Me_3NHClO_4	25
Me_4NClO_4	35
$[CH_2NH_3ClO_4]_2$	35

The height is that at which a 2 kg weight results in 50% explosions.

* Cyclotrimethylenetrinitramine.

Table 9

PHYSICAL PROPERTIES OF THE METHYLAMINE PERCHLORATES

Property	Ammonium perchlorate*	Monomethylamine	Dimethylamine	Trimethylamine	Tetramethylamine	Reference
Formula	NH_4ClO_4	$CH_3NH_3ClO_4$	$(CH_3)_2NH_2ClO_4$	$(CH_3)_3NHClO_4$	$(CH_4)_4NClO_4$	
Molecular weight	117.489	131.505	145.521	159.537	173.553	
Melting point	Decomposes at 440°C without melting	255°C melts and decomposes	180°C decomposes 300°C	275°C slowly decomposes	Detonates at about 430°C without melting	106, 107
Crystal form	Orthorhombic at 25°C Cubic above 240°C	Mono/triclinic at 25°C Tetragonal above 48°C Cubic above 178°C	Monoclinic (?) at 25°C Tetragonal above 38°C	? at 25°C ? above 116°C Tetragonal above 207°C	Tetragonal at 35°C ? above 340°C	106, 107
Transition temperature, °C	-190, 240	48, 178	38	116, 207	340	106, 107
Density, gm cm^{-3}	1.95 at 25°C 1.71 at 250°C	1.65 at 25°C 1.56 at 72°C 1.52 at 187°C	1.40 at 25°C 1.4 at 71°C	1.41 at 25°C 1.35 at 133°C 1.27 at 223°C	1.35 at 25°C	106, 107

*The data for ammonium perchlorate are taken from Table 1, Ref. 2.

Table 10

PHYSICAL PROPERTIES OF GUANIDINE PERCHLORATE

Property	Value	Reference
Formula	$CH_5N_3HClO_4$	
Molecular weight	159.519	
Density, g cm^{-3}	1.772 (calculated crystal structure) 1.743 (measured)	110
Melting point, °C	240, 248 ±2	109, 110
Crystal structure	Cubic above and below transition temperature	110
Transition temperature, °C	180-182	110
Heat of formation	-74.10 ±0.55 kcal $mole^{-1}$	111
Hygroscopicity	Not hygroscopic	112
Solubility, H_2O	31% by wt at 25°C	110
acetone	40.3% by wt at 25°C	
non-polar solvents	Insoluble	

Table 11

PHYSICAL PROPERTIES OF NITROGUANIDINE PERCHLORATE

Property	Value	Reference
Formula	$CH_4N_4O_2HClO_4$	
Molecular weight	204.516	
Density	1.93 ±0.05 g cm^{-3}	123
Transition temperature	79°C	123
Melting point	120°C, with decomposition	123
Hygroscopicity	Hygroscopic	123
Solubility, ether	0.23% at 0°C	123
acetone	50.8% at 0°C	
perchloric acid	48.1% at 25°C	

Table 12

PHYSICAL PROPERTIES OF BORON PERCHLORATES

(From Mosher et al.[125,126])

Property	Boron triperchlorate	Boron monochlorodiperchlorate	Boron dichloroperchlorate
Formula	$B(ClO_4)_3$	$BCl(ClO_4)_2$	BCl_2ClO_4
Molecular weight	309.172	245.174	181.177
Density at -16°C	-	1.872 g cm^{-3}	1.728 g cm^{-3}
Nature of material and melting point	White crystalline solid melts at -5°C	Crystalline solid melts at -15 to -17°C	Liquid at -78.5°C solidifies to glassy solid at lower temperature
Heat of hydrolysis	-	-49 kcal $mole^{-1}$ decomposition or reaction with solvent occurs	-73.7 kcal $mole^{-1}$

Table 13

THERMAL DECOMPOSITION OF ALKALI PERCHLORATES

Perchlorate	Temperature range, °C	Method*	Pre-exponential factor	Activation energy kcal mole^{-1}	Kinetic equation	Comments	Author	Ref
$LiClO_4$	392–415	TG	<40%:2.78 x 10^{13} sec^{-1}	52.2 ± 4.1	$\ln(1-\alpha)/\alpha = kt$	m.pt. 247°	Markowitz & Boryta	137
			>40%:1.55 x 10^{16} sec^{-1}	62.0 ± 4.1	$\ln \alpha = kt$			
			<0.5%	58.3	$t = Ae^{-E/RT}$			
	400–430	O_2P	-	62.0	Not stated	Cl_2 + ClO_2 in products	Solymosi & Braun	138
	350–450	O_2P	-	52 ±5	$LiClO_4 \rightarrow LiClO_3 + \frac{1}{2} O_2$	Effect of LiCl KCl and CuO studied	Asaba & Hikita	139
				40 ±5	$LiClO_3 \rightarrow LiCl + 3/2\ O_2$			
$NaClO_4$	330–420	Cl^-/ClO_4^-	-	20.0	Not stated		Cabane & Benard	140
	490–515	O_2P	-	62.6	Not stated			
	360–420	Cl formn.	2.52 x 10^{13}	52.7	First order	Decomposition in fused NaOH	Seward & Otto	141
		ClO_4^- formn.	2.52 x 10^{12}	47.3				
$KClO_4$	450–600	O_2P	1 x 10^{14}	61.0	$1-\log(1-\alpha) = kt$	No ClO_3^- in products	Otto & Fry	142
	537–600	O_2P	1.15 x 10^{16}	65.8	$\log(\alpha/1-\alpha) = kt$	No break in O_2 curve on fusion	Glasner & Weiderfeld	143
	530–550	O_2P - vacuo	-	69.3	-	Chlorate, Cl_2 in products Reproducibility poor	Phillips	144
	480–540	O_2P - vacuo	10^{14}, 10^{17}, 10^{19}	41.8, 51.4 61.2	$\log \frac{dn}{dt}$ vs $\frac{1}{T}$	Reproducibility poor	Glasner & Simchen	145
	530–620	O_2P - vacuo	$10^{8.42}$	37.0 60–75	For chain step For uni-molecular	Sensitive to impurities	Simchen & Glasner	146

Table 13 (Contd)

Perchlorate	Temperature range, °C	Method*	Pre-exponential factor	Activation energy kcal mole^{-1}	Kinetic equation	Comments	Author	Ref.
$KClO_4$ (Contd.)	556-582	O_2P	Solid 2.36×10^{13} sec^{-1} Liquid 1.31×10^{15} sec^{-1}	70.5 ±0.4 70.5 ±0.4	$\log(1-\alpha) = kt$ $\log(1-\alpha) = kt$	Chlorate in products	Harvey et al.	135 147
	375-480	Cl^-/ClO_4^-	-	30.0	Not stated	-	-	140
	490-515	O_2P	-	62.6	Not stated	-	-	138
$CsClO_4$	385-470	Cl^-/ClO_4^-	-	35.0	Not stated	-	-	140
	525-558	O_2P	-	57.1	Not stated	-	-	138
$RbClO_4$	457-570	O_2P	-	71.8	Not stated	-	-	138

* O_2P indicates rate of pressure increase of oxygen.

TG indicates thermogravimetric measurements.

Table 14

THERMAL DECOMPOSITION OF METAL PERCHLORATES OTHER THAN ALKALI METAL PERCHLORATES

Perchlorate	Temperature range, °C	Method*	Activation energy kcal mole^{-1}	Kinetic equation	Comments	Author	Ref.
$AgClO_4$	414-445	O_2P	62.7	$Log(\alpha/1 - \alpha) = kt$	$AgCl + O_2$ products. Activation energies of 49.5 and 52.4 also obtained	Solymosi	148
$Ba(ClO_4)_2$	440-480	O_2P	61.6		$BaCl_2 + O_2$ products.	Solymosi & Braun	138
$Mg(ClO_4)_2$	382-408		44.4		Cl_2 and ClO_2 in products, did not melt.		
$Cd(ClO_4)_2$	377-403		55.9		$CdCl_2 + O_2$ products. Addition of $CdCl_2$ accelerated reaction		
$Zn(ClO_4)_2$	285-310		39.9		Cl_2 and ClO_2 in products		
$Pb(ClO_4)_2$	330-355		55.0		$PbCl_2 + O_2$ products		
$Al(ClO_4)_3$	240-370	TG	19.8	$-ln(1 - \alpha) = (kt)^n$ Erofeyev equation	Products are oxides or oxychlorides, chlorine, oxygen	Bel'kova et al.	149
$Sc(ClO_4)_3$			20.9				
$Y(ClO_4)_3$			27.8				
$La(ClO_4)_3$			34.1				
$Ce(ClO_4)_3$			Two lines		Change in mechanism		
$Sm(ClO_4)_3$			28.8				
$Gd(ClO_4)_3$			26.5				
$Ho(ClO_4)_3$			26.0				
$Yb(ClO_4)_3$			25.3				
$Lu(ClO_4)_3$			25.1				

* O_2P rate of pressure increase of oxygen TG thermogravimetric measurements

Table 15

RELATIVE CATALYTIC ACTIVITY OF METAL OXIDES WITH POTASSIUM PERCHLORATE AS SHOWN BY DTA AND TGA

(From Freeman and Rudloff[154])

Catalyst	Temperature of initial decomposition, °C
None	600
ZnO	565
TiO_2	535
Al_2O_3	530
MgO	525
NiO	520
Ag_2O	520
MnO_2	460
Fe_2O_3	450
CuO	450
CoO	380
Cu_2O	380
Co_3O_4	375
Cr_2O_3	325

Table 16

OXIDATION OF FUELS BY POTASSIUM PERCHLORATE

Fuel	Temperature, °C	Catalysts	Inhibitors	Comments	Ref.
Carbon black	320-385			No induction period	155
Nuchar Sugar charcoal		Alkali and alkaline earth halides	Basic salts	CO_2 only gaseous product	156, 160
Carbon black	343	LiCl, $BaCl_2$, KCl, NaCl	KI, Li_2CO_3		161
Synthetic diamond	380	V_2O_5, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, Cu, Al	-	V_2O_5 best catalyst	164
Graphite	380	V_2O_5	-	Sandwich tablets also studied	164
Toluene, naphthalene, Anthracene	370-440 → 510	- -	- -	No reaction Explosion	159
Decalin, cyclohexane, cyclohexanol, cyclohexanone	350-380	-	-	Dehydrogenation	159
Polystyrene	300-550	-	-	No reaction	161
Styrene copolymer	360-400	LiCl	K_2CO_3 no effect		161
Bakelite	367	LiCl → ignition in 2-3 minutes	K_2CO_3 inhibited	15% reaction in 5 hours with no additive	161
Novolac	367	LiCl → ignition at 355°C K_2CO_3 → ignition at 367°C	-	30% reaction in 5 hours with no additive	161
Alicyclic compounds	-	-	-	Chromic oxide, BaO_2, PbO_2 had no effect	162
Polydivinylbenzene (PDVB)	400	O_2, air, CO_2	-	Air at various pressures	163

Table 16 (Contd.)

Fuel	Temperature, °C	Catalysts	Inhibitors	Comments	Ref.
PDVB	420-490	V_2O_5 and wide range of compounds	$LiCO_3$, Zn, Pb_3O_4, Al, Cu, Fe	From ignition delays Decomposition at 360° gave a similar division	157
PDVB	275-350	-	-	Sodium perchlorate as oxidizer	158

Table 17

CATALYSIS OF BURNING RATE OF STOICHIOMETRIC ALUMINIUM-POTASSIUM PERCHLORATE MIXTURES[184,185]

Additive	Weight, %	Burning rate, in sec^{-1} at 100 psi	Ref.
None		0.38	
Chromium dioxide	10	0.70	
Cobaltic oxide	10	0.80	
Ferric oxide	10	0.93	141
Manganese dioxide	10	0.89	
Nickel oxide	10	0.70	
Cobalt chromate	10	1.15	
Cobalt	10	0.87	
Copper	10	0.74	
Lead	13	0.90	142
Tin	6	0.94	
Ferrovanadium	10	0.63	

Table 18

SOLUBILITIES OF ALKALI METAL PERCHLORATES IN ORGANIC SOLVENTS[188]

Solvent	Solubility in gm per 100 gm solvent			
	$LiClO_4$	$KClO_4$	$NaClO_4$	NH_4ClO_4*
Methanol	182.3	0.11	51.4	6.85
Ethanol	151.8	0.01	14.7	1.91
n-Propanol	105.0	0.01	4.0	0.39
n-Butanol	79.3	0.005	1.9	0.017
Acetone	136.5**	0.16	51.7	2.26
Diethyl ether	113.7	Insoluble	Insoluble	Insoluble

* AP data from Ref.130

** Incorrectly listed in the patent as 156.3. The correct value is 136.5[130,192]

Table 19

EFFECT OF VARIOUS ADDITIVES ON THERMAL DECOMPOSITION OF AP

(Data from Schmidt[252])

Additive	Observed effect
NH_3 gas	Decomposition stopped at any temperature up to 400°C.
HCl gas	Accelerated the decomposition to 30% - no further effect. No effect on induction period.
Cl_2 gas	Accelerated the decomposition to 30%, which then continued to completion. No effect on induction period.
$KClO_3$	Accelerated decomposition to 30%, then decomposition at normal rate. Induction period reduced but not eliminated log τ vs 1/T gave 25.5 kcal $mole^{-1}$. No increase in burning rate at 300-2500 psi.
Ferrocene $Cu(AA)_2$*	Interact with AP at low temperature and major exotherm in DTA reduced from 475°C to 260-360°C + $KClO_4$ - no interaction below 340°C + NH_4Br - interaction below 200°C
Copper chromite	DTA results in deflagration at 320°C. Under ammonia, detonation occurs at the same temperature. Isothermal study at 265°C resulted in detonation.
Pressure	DTA shows exotherm at 310°C. As pressure increases, so does the rate of decomposition.
$(NH_4)_2SO_4$ $(NH_4)_2C_2O_4$	Temperature of first exotherm in DTA increases from ~310°C to ~400°C.

*$Cu(AA)_2$ is cupric acetylacetonate

Table 20

CATALYSED DECOMPOSITION OF AMMONIUM PERCHLORATE

Catalyst[a]	Mole ratio AP: catalyst	Activation energy (kcal mole^{-1}) by using equation[b]							Temperature range, °C	Ref
		1	2	3	4	5	6	7		
CdO_{500}	16:1	26.9	32.8	26.7	24.7	-	-	-	206-233	257
CdO	100:1	-	-	-	-	22.2	-	-	330-328	
	16:1	-	-	-	-	22.5	-	-	265-295	
MgO	16:1	30.3	-	-	-	(26.1)	28.5	-	206-231	
	100:1	-	-	-	-	26.8	-	-	270-324	
	50:1	-	-	-	-	31.8	-	-	280-324	
$Cd(ClO_4)_2$	10:1	29.3	-	33.0	-	(28.7)	-	-	210-231	258
$Mg(ClO_4)_2$	10:1	30.2	25.0	32.4	(26.6)	(31.9)	-	-	201-231	
$Zn(ClO_4)_2$	10:1	-	-	-	(37.8)	(24.5)	-	-	206-232	
	Wt % catalyst									
Copper chromite	2.9	AP particle size						40	250+	259
	4.8							46		
Ferric oxide	4.8	43-61 μ						36.6		
Copper chromite	4.8	88-124 μ						43		
Chromic oxide	4.8							68		
Carbon (Norit A)	2.5							52.5		
Ferric oxide	4.8							34.3		

[a] suffix indicates catalyst sintered at temperature shown

[b] 1 $\log [\alpha/1 - \alpha] = kt + C$: acceleratory

2 $\log [\alpha/1 - \alpha] = kt + C$: deceleratory

3 $\log p = kt + C$

4 $\log \omega = kt + C$: $(\log (1/(1 - \alpha) = kt + C)$

5 $\log \tau = E/RT + C$: τ is time to ignition (initiation)

6 $[- \log (1 - \alpha)]^{1/3} = kt$: Avrami-Erofeyev, $n = 3$

7 $\log (dT/dt) = -E/RT + C$: adiabatic kinetics

Table 21

DECOMPOSITION OF AMMONIUM PERCHLORATE WITH CO-CRYSTALLIZED OR MECHANICALLY MIXED CATALYSTS[262]

Sample	Catalyst type*	Temperature, °C	Heating time, min	Wt. loss, %
AP + 2% $CaCrO_4$	CC	233	4	88
AP + 2% $CaCrO_4$	MM	233	60	17.5
AP + 2% $TlClO_4$	CC	300	15	36
		300	40	50
		300	50	54.5
		300	60	58.5
AP pure	-	300	15	22
		300	40	35
		300	50	39
		300	60	42.5
AP + 2% $KMnO_4$	CC	176	20	99
	MM	208	60	8

* CC co-crystallized
MM mechanically mixed

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Appendix
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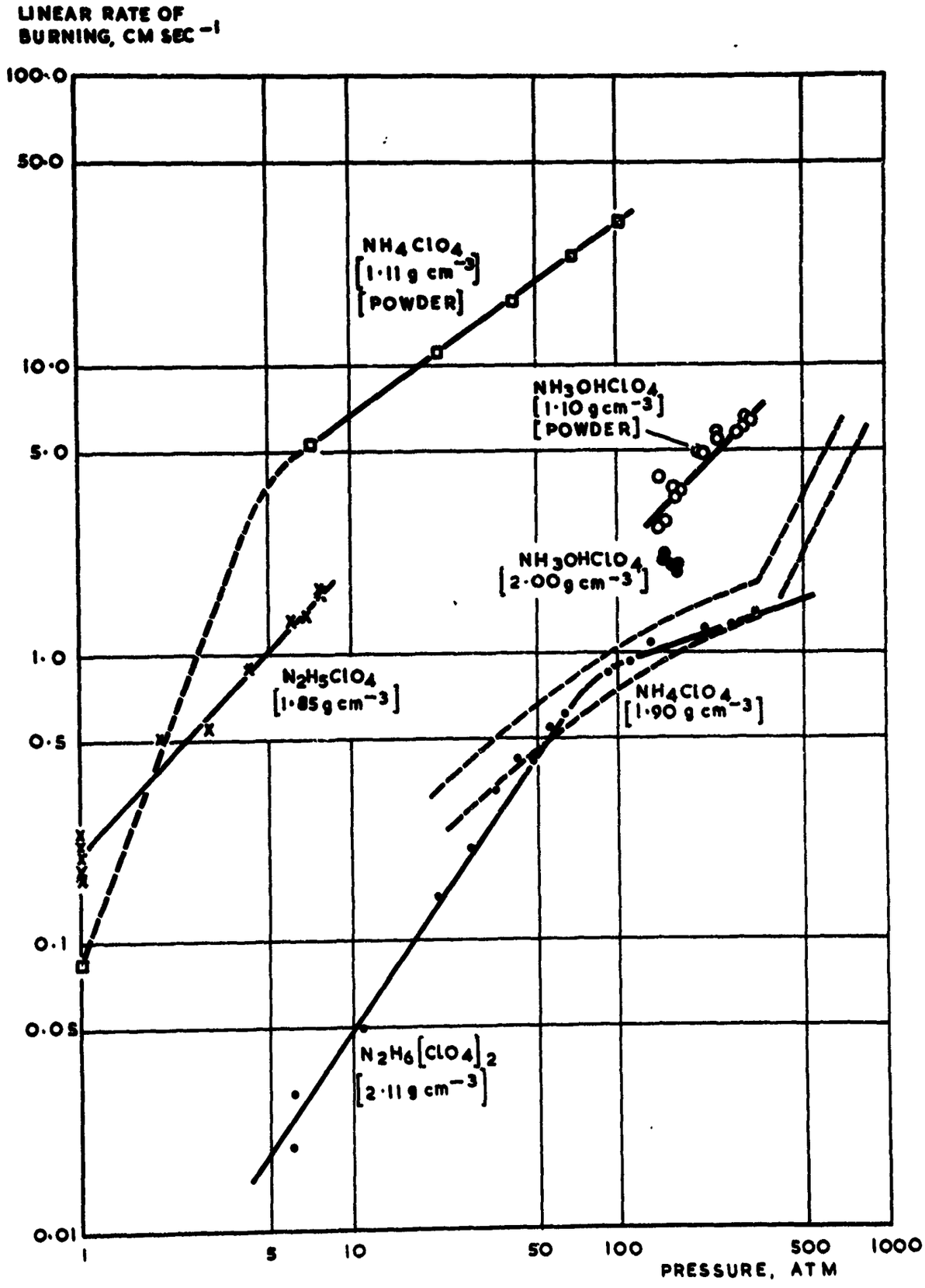

FIG. 1 LINEAR BURNING RATES OF PERCHLORATES AS MONOPROPELLENTS

Appendix

PERCHLORIC ACID: A REVIEW OF THE PHYSICAL AND INORGANIC CHEMISTRY

SUMMARY

Progress in the physical and inorganic chemistry of perchloric acid is reviewed with particular reference to the literature appearing in the last decade.

The nature of anhydrous perchloric acid is considered and it is concluded that the equilibrium

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O$$

does not occur to an appreciable extent. It is also concluded that pure perchloric acid is not explosive.

This review was previously issued as R.P.E. Technical Memorandum 352. It is included here for wider circulation and completeness.

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1 INTRODUCTION*

Perchloric acid is very widely used in industry and in the laboratory but it is only in the last decade that its chemistry has been at all closely examined.

In 1906 Van Wyk [203] suggested that the anhydrous acid did not exist alone but was always associated with chlorine heptoxide and perchloric acid monohydrate in an equilibrium represented by equation (1).

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \qquad (1)$$

This suggestion has still not been established and in this review the evidence for and against it will be discussed.

Perchloric acid, $HClO_4$, is one of the strongest acids and it contains more oxygen (63.7%) than any other common acid. However, its oxidizing power depends very markedly on both concentration and temperature. For example, the anhydrous acid at room temperature reacts very vigorously, and in many cases explosively, with all reducing agents, whereas the dihydrate (73.6% by weight of acid**) has little oxidizing power at room temperature but becomes a powerful oxidizer above 100°C. The perchlorate ion itself shows no oxidizing properties in solution.

II PREPARATION

A Anhydrous acid

Several methods have been described recently for the preparation of anhydrous perchloric acid. All involve the dehydration of the constant boiling point acid (72.4% by weight) or of more dilute acid by oleum, phosphorus pentoxide or magnesium perchlorate. The purity of the final product must be considered in each case since an excess of the dehydrating agent results in the formation of chlorine heptoxide [150].

The preparation of anhydrous acid by a simple laboratory method was described by Smith [172]. In this method 3, 4 or 5 volumes of 20% fuming sulphuric acid were slowly added to 1 volume of 72% perchloric acid cooled in

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* The literature survey was completed on 1 January 1965. This was published in 'Advances in Inorganic Chemistry and Radiochemistry', 8, 177-224 (1966), Academic Press, hence the references are listed in alphabetical order and are not numbered consecutively.

** Unless otherwise stated, all acid percentages in this review are by weight.

an ice bath. The anhydrous acid was obtained by distillation of the mixture at 1 mm Hg or less, at 20-25°C, and the distillate was collected in a receiver cooled by dry ice. Gradual increase of the temperature to 75°C results in a 75% yield of the anhydrous acid. No analysis of the product was reported other than by addition of the theoretical quantity of 72% acid which resulted in the crystallisation of the monohydrate. A test for the presence of sulphuric acid was negative.

The product from this method can contain quite large quantities of chlorine heptoxide as was shown by Levy [98] who obtained anhydrous acid containing up to 50% chlorine heptoxide. Analysis for the chlorine heptoxide was made by determining the number of moles of vapour, n_g, from the pressure, volume and temperature and the number of moles, n_a, of titrateable acid. It follows that as

$$n_g = n_{Cl_2O_7} + n_{HClO_4} \text{ and } n_a = 2n_{Cl_2O_7} + n_{HClO_4}$$

then

$$n_{Cl_2O_7} = n_a - n_g \qquad (2)$$

and

$$n_{HClO_4} = 2n_g - n_a. \qquad (3)$$

The presence of the chlorine heptoxide was confirmed by infrared spectrometry. Pure samples of the anhydrous acid were made by converting the product from the oleum - 72% acid distillation to the monohydrate by addition of the stoichiometric amount of 72% acid. The monohydrate was then distilled (no more than 5% of any one sample being used to ensure the absence of water) to give pure samples of anhydrous acid. Both analysis and the infrared spectra showed that chlorine heptoxide was absent.

Smith's process has been used on a microscopic scale by Sibbett et al [164, 165]. The ratio of oleum (20%) to perchloric acid (72%) was three to one, the temperature was not raised above room temperature and a pressure of 2×10^{-4} mm Hg was used. The anhydrous acid vapour was passed over a drying bed of magnesium perchlorate. Tests of the product for sulphate and chloride ions were negative. The only impurity was believed to be water, although no analysis was made for chlorine heptoxide. However, it is unlikely that

chlorine heptoxide was present in large quantities because the oleum/acid ratio was low and the infrared spectra did not have the characteristic peaks of chlorine heptoxide.

A continuous process for the preparation of the anhydrous acid has been described by Zinov'ev [220] who stressed the importance of careful control of the oleum/acid ratio in order to avoid contamination of the product by chlorine heptoxide. It was suggested that the correct ratio should be found by trial and error. No details were given of the analytical method.

More recently, Smith [173] has described a preparation using magnesium perchlorate (containing about 5% water) and the 72% acid in the ratio of 5 : 1. A yield of 85% was reported. Chlorine heptoxide was found to be a minor impurity which occurred in greater amount if the reaction mixture was not distilled immediately after its preparation. Its presence was shown by the fact that when the anhydrous acid was diluted to form the monohydrate the chlorine heptoxide did not react until 72 to 96 hours later. It was recommended that if the anhydrous acid was not to be used immediately, it should be converted to the monohydrate and then reconverted to the anhydrous acid by distillation when required.

Mascherpa [115] has described a preparation from 95% sulphuric acid and 65% perchloric acid in a ratio of 3 : 1 by distillation at 70 or 100 mm Hg using a falling film rectification column. A 75% yield of average concentration 99.98% was obtained but no details were given of the product analysis.

The preparation of a pure sample for thermochemical work was described by Trowbridge and Westrum [196] who used Smith's method for the preparation using oleum. Fractional fusion data indicated a maximum impurity of 2.5 mole % which was presumed to be the monohydrate. Conductometric titrations performed after the thermochemical experiments for acid and perchlorate content agreed, but only indicated 95% by weight confirming their visual observation that the sample had partly decomposed in the calorimeter. Attempts to identify the contaminant by infrared spectrometry were unsuccessful. Other preparations of anhydrous perchloric acid by dehydration under reduced pressure have been described by Taketa [190] and by Kakiuchi et al [87].

It must be concluded that anhydrous perchloric acid prepared by direct dehydration of the 72% acid will probably contain some chlorine heptoxide. The chlorine heptoxide content can be minimised by (i) use of a small ratio (3 : 1) of dehydrating agent to acid, (ii) by distillation at room temperature

and (iii) immediate distillation of the dehydrating agent-acid mixture. A pure sample of the anhydrous acid is best prepared by distillation of the monohydrate.

Solutions of anhydrous acid in halogenated hydrocarbons have recently been prepared [90] by addition of methylene or ethylene chloride to a mixture of 1 part by volume of 70% perchloric acid and 4 parts by volume of 25% fuming sulphuric acid. The monohydrate can be precipitated by passing moist air through the solution of the acid. Unsuccessful attempts have been made to prepare solutions of anhydrous perchloric acid in acetonitrile by reaction of barium perchlorate and sulphuric acid [47]. Although barium sulphate is very insoluble in acetonitrile, such solutions continued to deposit a precipitate after equilibrium for six months. The hazards of acetonitrile solutions of perchloric acid have been described [6].

Smith [172, 173] recommended that all ground glass joints exposed to anhydrous perchloric acid vapour should be lubricated with 72% perchloric acid. It was particularly stressed that silicone grease must not be used because it exploded with anhydrous perchloric acid. Hathaway [70] rejected the use of 72% perchloric acid because he found that joints sealed in this way would not hold a vacuum. He used a minimum quantity of silicone grease and found that explosions did not occur so long as liquid acid was not allowed to pass over a disconnected joint.

Moreover, leaks in apparatus lubricated by 72% perchloric acid have resulted in anhydrous acid coming into contact with the operator's gloves with consequent spontaneous ignition [108]. It was found that fluorocarbon grease carefully applied was quite safe [108] thus confirming Levy's observation [98] that Kel-F fluorocarbon grease was resistant to attack.

All-glass systems using break seals and completely free from grease have been described [98, 164, 192].

B <u>Hydrated acid</u>

60 and 72% perchloric acid are prepared on an industrial scale either by reacting sodium perchlorate with concentrated hydrochloric acid

$$NaClO_4 + HCl \longrightarrow NaCl + HClO_4 \qquad (4)$$

or by anodic oxidation of hydrochloric acid or a chlorate. Further details are given in the standard reference books, for example reference [158].

Recently details have been given [65] for the preparation of analytical grade perchloric acid from sodium perchlorate and hydrochloric acid. Magnesium perchlorate has been used as the dehydrating agent to produce 70-80% perchlorate acid [175]. Irradiation with light at 2537 Å has been used in a somewhat novel method of preparation [153]. The mixture irradiated consists of a gaseous mixture of water, chlorine and ozone at a pressure of about half an atmosphere. Hydrogen chloride can be substituted for the chlorine and most of the water and the ozone can be diluted with oxygen.

C Deuteroperchloric acid

Deuteroperchloric acid was first prepared as the constant boiling azeotrope [189]. Deuterium sulphate was prepared by solution of sulphur trioxide in 99.25% D_2O and then the sulphate removed by addition of barium perchlorate followed by centrifuging the precipitated barium sulphate. The deuteroperchloric acid (deuterium content 99±0.3%) was purified by vacuum distillation and the centre fraction of the constant boiling mixture was collected.

More concentrated deuteroperchloric acid was prepared by Giguère and Savoie [54] by distillation under reduced pressure at 65°C of a mixture of potassium perchlorate and deuterium sulphate (97%) in the ratio 1 : 5. The deuterium sulphate was prepared by condensation of sulphur trioxide onto a small amount of solid D_2O (99.7% deuterium) in a cold bath. The deuteroperchloric acid was distilled again to remove traces of deuterium sulphate. However, some contamination of the product by atmospheric moisture could not be avoided and from the relative intensity of the OH bands in the deuteroperchloric acid spectra the impurity was estimated to be about 15-20% $HClO_4$ in the $DClO_4$. The product was shown to be free from perchlorate ion because the spectra did not have any indication of the strong perchlorate ion band at 940 cm^{-1}. Some chlorine heptoxide was present as an impurity.

The anhydrous acid was prepared by Smith and Diehl [179] by distillation of a mixture of anhydrous sodium perchlorate with a two-fold excess of 98.2% deuterium sulphate at a pressure of 0.1 to 0.25 mm Hg and a temperature of below 105°C. The anhydrous acid was obtained in 70% yield.

III PERCHLORIC ACID HYDRATES

The classical study of the perchloric acid-water system was that carried out by Van Wyk in 1906 [203]. He constructed a melting point curve which indicated the existence of five hydrates of perchloric acid: those containing 1 H_2O, 2 H_2O, 2.5 H_2O, 3 H_2O (α and β forms) and 3.5 H_2O.

Brickwedde [23] in 1949 repeated Van Wyk's observations for the range 0 to 70% by weight and obtained a curve of the same general shape as that of Van Wyk. However, the temperatures measured by Van Wyk lie outside the experimental error of Brickwedde's work in many cases. Brickwedde was unable to confirm the existence of the hydrates.

Very recently Mascherpa [117] has studied the perchloric acid system in the region from 55 to 75% acid and has shown that the four hydrates containing 2 H_2O, 2.5 H_2O, 3 H_2O and 3.5 H_2O exist in this region.

A <u>Quarter hydrate</u>, $(HClO_4)_4 H_2O$

This was recently reported by Mascherpa [116] in a study of the region between 85.8 and 100% acid. From a study of the liquid-solid equilibrium he concluded that the quarter hydrate existed in two allotropic forms with a transition temperature of -100°C from the α to the β form and a decomposition point of the α form at -73.1°C.

B <u>Monohydrate</u>, $HClO_4.H_2O$

This is the best established perchloric acid hydrate. It is a colourless crystalline compound which melts at 49.905°C [180]. Its X-ray structure was shown by Volmer [208] to be similar to that of ammonium perchlorate, NH_4ClO_4. This was later confirmed definitely by proton magnetic resonance studies [85, 86, 87, 184], by Raman spectroscopy [126, 127, 193], by X-ray diffraction [97, 130] and by infrared spectroscopy [16, 126, 156]. Taylor and Vidale [193] showed that the solid existed in two crystalline forms with a transition point at about -30°C.

Rosolovskii and Zinov'ev obtained a transition at -23.4°C by differential thermal analysis [148] and at -24.9°C by dilatometry [225]. Mascherpa obtained -24.0°C by differential thermal analysis [147].

The crystal structure of both forms has been studied. The form stable at low temperature [130] belongs to the monoclinic space group $P2_1/n$ with parameters

$$a = 7.541 \pm 0.0006 \text{Å}$$
$$b = 9.373 + 0.011 \text{Å} \qquad \beta = 97°41 \pm 4'$$
$$c = 5.359 \pm 0.006 \text{Å},$$

whereas the high temperature from [97] belongs to the orthorhombic P_{nma} space group with parameters

$$a = 9.065 \pm 0.0008 \text{Å}$$
$$b = 5.569 \pm 0.004 \text{Å}$$
$$c = 7.339 \pm 0.004 \text{Å}.$$

C Dihydrate, $HClO_4.2H_2O$ and hydrates, $HClO_4.2.5\ H_2O$, $HClO_4.3H_2O$ & $HClO_4.3.5H_2O$

These were all first proposed by Van Wyk [203] and have recently been confirmed by Mascherpa [117]. However, Mascherpa was unable to detect the two forms, α and β, suggested by Van Wyk for the trihydrate.

Hydrate		Van Wyk m.pt., °C	Mascherpa m.pt., °C
$2H_2O$		-17.8	-20.65 ±0.1
$2.5\ H_2O$		-32.1	-33.1 ±0.1
$3\ H_2O$	(α)	-37	-40.2 ±0.1
	(β)	-43.2	
$3.5\ H_2O$		-44.3	-45.9 ±0.1

Evidence for the existence of these hydrates in solution has been obtained by Zinov'ev and Babaeva [222] as a result of their study of the specific gravity and viscosity of perchloric acid over a wide range of concentration.

Evidence for the dihydrate was obtained by Smith and Richards [185] in a proton magnetic resonance study. The results indicated that the hydrate was

$$H_3OClO_4.H_2O.$$

It may be concluded that the existence of the monohydrate is well established whereas that of the other hydrates is less fully substantiated.

IV STRUCTURE

A Anhydrous acid

1 Cryoscopic evidence

Van Wyk [203] suggested that the anhydrous acid could only exist in equilibrium with the anhydride (1)

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \qquad (1)$$

and this view has recently been supported by Zinov'ev and Rosolovskii [225]. Data were obtained by thermal analysis and visual melting point studies for the chlorine heptoxide-water system in the range from 25 to 100 mole %. The eutectic occurred at 53 mole % and -100 ±2°C whereas the melting point at 50 mole % was about -40°C. The components of the eutectic were believed to be the monohydrate, $HClO_4.H_2O$ and either chlorine heptoxide, Cl_2O_7, or a metastable compound such as $Cl_2O_7.2HClO_4$. No evidence for a congruent melting point was reported. Mascherpa [116] has re-examined the region from 84.8 to 100% acid and has found that this region is more complex than has previously been shown. It was found that there was a eutectic at -104°C between the quarter hydrate, $(HClO_4)_4 H_2O$, and another compound, perhaps the anhydrous acid. The melting point at 100% was about -100°C, well below that reported by the Russian workers.

Trowbridge and Westrum [196] have obtained a melting point of -101°C from a careful thermodynamic study of the anhydrous acid. They discussed the results obtained by Zinov'ev and Rosolovskii [225] and concluded that the proposed eutectic at 53 mole % was in error because such a eutectic would require the observed heat capacities to be non-linear over the range -100 to -51°C. In view of the difficulty in analysing high perchloric acid concentrations it was possible that the error was in the titrimetric method used, where a 0.5% error would result in a 3% error in the concentration range near 50 mole % chlorine heptoxide. It was also suggested that fine structure, in the form of a hypothetical congruent melting point, may not have been detected. The presence of a congruent melting point for perchloric acid would suggest its stability and lack of disproportionation in the solid.

2 Spectroscopic evidence

The infrared spectra of gaseous perchloric acid were obtained by Sibbett and Lobato [165] using a 10 cm cell on a Beckman IR-5 spectrophotometer. Absorption maxima were obtained at 3500, 1360 to 980 and 750 to 690 cm^{-1}. After three hours the maximum at 3500 cm^{-1}, which was ascribed to O-H bonding, disappeared and the other maxima, ascribed to O-Cl bonding, were modified. It was suggested that these changes were due to the reaction of perchloric acid with the lead sealing gasket between the sodium chloride windows and the cell body, and with the cell windows themselves.

A similar spectrum was obtained by Levy [98] who used a 10 cm cell on a Perkin Elmer 13 U infrared spectrometer. Perchloric acid vapour obtained

directly from the mixture of aqueous acid and fuming sulphuric acid had absorption maxima at 1300 cm^{-1} and 1025 cm^{-1}. After a quarter of the acid had been distilled off from the reaction mixture, the cell was refilled and found to have absorption maxima at 1265 to 1200 cm^{-1} and at 750 to 690 cm^{-1} which agreed well with those reported by Sibbett and Lobato. The first spectrum was identical to that of chlorine heptoxide.

Shchukarev et al [160, 161] using a 11.5 cm long cell and a pressure of 18 cm studied the infrared absorption spectra in the region 3700 to 2500 cm^{-1} and found an absorption peak at 3560 cm^{-1}. This band was also found in very dilute (0.001 M) solutions of perchloric acid in carbon tetrachloride thus showing that perchloric acid is monomeric in the vapour phase. Freshly prepared liquid anhydrous acid had a band at 3390 cm^{-1} and this shift was attributed to hydrogen bonding. An estimate for the energy of the hydrogen bonding of 3 kcal $mole^{-1}$ was made.

More recently, Giguère and Savoie [54] have made a detailed study of the infrared spectra of both anhydrous $HClO_4$ and $DClO_4$ in the vapour phase as well as in the liquid and solid phases. Their results are presented in Table 1. From the shift in the O-H bond for the gas to liquid phase change they estimated an energy of 3 kcal $mole^{-1}$ for the hydrogen bonding.

The Raman spectrum of solid perchloric acid has recently been measured by Dahl, Trowbridge and Taylor [40] who obtained results in good agreement with those from infrared studies. In particular they found no evidence of the very intense 921 cm^{-1} vibration of the monohydrate [193], nor of the 501 and 695 cm^{-1} vibrations of chlorine heptoxide [155]. This indicated that neither of these two species could be present in the solid in appreciable amount.

It can be seen from Table 1 that the sample used by Simon and Weist [168] for their Raman spectra studies must have contained chlorine heptoxide as it has a band at 284 cm^{-1}.

The spectroscopic evidence is thus clearly in favour of perchloric acid existing as such in the anhydrous state with no evidence for the existence of the equilibrium

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O. \qquad (1)$$

The interpretation of the spectroscopic evidence by Zinov'ev [221] in ascribing the 3560 cm^{-1} band to the hydronium ion, H_3O^+, is incorrect.

3 Other evidence

Electron diffraction studies of both anhydrous perchloric acid vapour and of chlorine heptoxide have been made by Akishin, Vilkov and Rosolovskii [3]. The results were in agreement with C_{3v} symmetry for perchloric acid in the vapour phase. Perchloric acid vapour was shown to be monomeric. The other evidence on the nature of anhydrous perchloric acid is chemical. Hathaway [70] has shown that anhydrous ferric and ferrous chlorides react with anhydrous perchloric acid to yield hydrated perchlorates. Anhydrous nitric acid behaved in a similar way with a wider range of salts. Since nitric acid dissociates to the extent of about ½% this can only be regarded as evidence that an equilibrium can occur but its extent in the absence of anhydrous ferric or ferrous salts may be very small. It was also shown that anhydrous nitrates reacted from hydrated perchlorates thus

$$MNO_3 + 3HClO_4 \rightleftharpoons MClO_4 + NO_2ClO_4 + H_3OClO_4. \qquad (5)$$

Because perchloric acid monohydrate is a product it is conceivable that this could lose water to the metal perchlorate resulting in formation of the hydrated perchlorate.

4 Conclusion

It is concluded that anhydrous perchloric acid certainly exists as such. The extent, if any, to which the equilibrium occurs is small. Further work is required to clarify this point and also the exact nature of the freezing point curve.

B Bond lengths, angles and strengths

Giguère and Savoie [54] deduced from empirical considerationss values of 1.70 Å and 1.45 Å for the bond lengths Cl-OH and Cl-O respectively. Better values of these bond lengths (1.64 ±0.02 Å and 1.42 ±0.01 Å respectively) were obtained by Akishin et al [3] who also calculated a value for the bond angle O-Cl-O of 100 ±2°. These may be compared with the corresponding values for chlorine heptoxide [3] of Cl-O = 1.42 ±0.01 Å, Cl-OCl = 1.72 ±0.34 Å and an O-Cl-O angle of 97 ±3°. Robinson [144] has collected data from the literature for the Cl-O stretching frequencies of seven oxychlorine compounds and ions. In a tetrahedral molecule of the type $XClO_3$ there should be one symmetric ClO_3 stretching frequency and two asymmetric stretching frequencies which are degenerate. In perchloric acid two asymmetric stretches have been observed and

this is attributed to a loss of tetrahedral symmetry in the molecule, whereas in fluorine perchlorate and perchloryl fluoride only one band has been observed [Table 2]. In a later paper Robinson [145] has compared calculated and experimental bond lengths [Table 3].

1 Perchlorate ion bond length

Lee and Carpenter [97] obtained a mean Cl-O bond length of 1.42 ±0.01 Å for H_3OClO_4 which was later revised by Truter [197] to 1.452 ±0.005 Å.

More recently, Nordman [130] obtained values for the Cl-O bond lengths in the low temperature modification of perchloric acid monohydrate of 1.445 ±0.006, 1.478 ±0.005, 1.465 ±0.007 and 1.468 ±0.006 Å in good agreement with the mean value of 1.46 Å suggested by Truter, Gruickshank and Jeffrey [198]. Values of the Cl-O bond length in perchlorates are presented in Table 4.

Infrared and Raman spectra of complex perchlorates have recently indicated that the co-ordinated perchlorate group may exhibit some covalent character [62, 71] and thus be of lower symmetry than tetrahedral.

2 Bond strengths

A value of the bond dissociation energy of the $HO-ClO_3$ bond was calculated by Levy [98, 99] from the heats of formation available for gaseous perchloric acid, gaseous hydroxyl and chlorine trioxide radicals. The value of 48.3 kcal $mole^{-1}$ was in good agreement with Levy's experimental value of 45.1 kcal $mole^{-1}$ for the activation energy of the rate-determining step in the thermal decomposition of perchloric acid vapour.

Heath and Majer [72] in a mass spectrometric study of the vapour of 72% perchloric acid obtained a value of the $HO-ClO_3$ bond strength from measurement of the appearance potential of the ClO_3^+ ion

$$A\,(ClO_3^+) = D\,(HO-ClO_3) + I\,(ClO_3)\,. \qquad (6)$$

The ionization potential of Dibeler [41] for I (ClO_3) was used to deduce a bond energy of 46 kcal $mole^{-1}$.

V THERMOCHEMICAL DATA

Thermochemical data for perchloric acid are somehwat sparse. It is only very recently that values have been obtained for the specific heat and

for the heats of evaporation and fusion of the anhydrous acid. The accuracy of much of the data on both the anhydrous and the diluted acid is uncertain.

A Specific heat

The available values are presented in Table 5. Only the value for the anhydrous acid is from a recent determination. No values are available for perchloric acid vapour.

B Heat of fusion

The heat of fusion of the anhydrous acid was determined by Trowbridge and Westrum [196] to be 1657 cal $mole^{-1}$ at the melting point, 171.13°K. A value for the heat of fusion of the monohydrate was deduced by Rosolovskii et al [147] from measurements of the heat of solution at 25 and 48°C for solid monohydrate and at 51°C for liquid monohydrate. This value of 2.46 ±0.08 kcal $mole^{-1}$ at 51°C was obtained by assuming the temperature coefficient of the heat of solution of solid monohydrate from 25 to 48°C to be valid from 48 to 51°C.

C Heat of vaporization

The experimental data available for the vapour pressure of anhydrous perchloric acid until recently were sparse. Tauber and Eastham [192] have measured the pressure for a temperature range from 0 to 20°C. Sibbett et al [164, 165] have made the only study of the vapour pressure over an extended range. Their early experiments indicated a boiling point at 760 mm of 97.2°C [165] but later this was corrected to 120.5°C [164]. These data give a value of the heat of vaporization of 8.13 kcal $mole^{-1}$. The values quoted elsewhere in the literature for the heat of vaporization (8.80 kcal $mole^{-1}$ by Zinov'ev [221] and 8.85 kcal $mole^{-1}$ by Trowbridge and Westrum [196]) are based on the very scattered data in the early literature and are unreliable. The entropy change can be used to obtain another value of 7.60 kcal $mole^{-1}$ using the entropy of the vapour [154] and liquid [196] states at 298°K.

The data available for the constant boiling point mixture are somewhat scattered. Measurements of the vapour pressure of perchloric acid (72.4%) over the range from 140 to 203°C and 100 to 760 mm Hg yielded a good straight line plot and gave a heat of vaporization of 14.76 kcal $mole^{-1}$ per mole of vapour produced [36]. A vapour density determination [39] showed that the 72% acid did not associate in the vapour phase.

D Heat of dilution

Heats of solution have been obtained under the differential experimental conditions indicated in Table 6 for the system $HClO_4, n_1 H_2O$ diluted to $HClO_4, (n_1 + n_2)H_2O$. A plot of the data suggests that those of Krivtsov et al, and of Vanderzee and Swanson, although not overlapping, appear to be consistent and are to be preferred to the other data. The heats of dilution of anhydrous, mono and dihydrated perchloric acid at 298°K are -21.15, -7.8 and -5.43 ±0.04 kcal $mole^{-1}$ respectively.

E Entropy

The vibrational frequencies measured by Giguère and Savoie [54] were used by these authors in conjunction with probable values of the structural parameters to calculate the entropy of anhydrous acid in the gas phase at 298°K. The derived value is 70.7 cal deg^{-1} $mole^{-1}$ [53] which is somewhat in error as the bond length for the Cl-OH bond was taken as 1.70 Å. This has been recalculated [154] to be 70.5 cal deg^{-1} $mole^{-1}$ (using a Cl-OH bond length of 1.64 Å [3]).

The entropy of anhydrous perchloric acid in the liquid phase at 298°K was determined by Trowbridge and Westrum [196] to be 45.02 cal deg^{-1} $mole^{-1}$. Using a rather large value of the heat of vaporization they calculated the entropy in the gas phase at 298°K to be 68.2 cal deg^{-1} $mole^{-1}$ and commented that the gas imperfection resulting from the intermolecular hydrogen bonding (estimated to be 3 kcal $mole^{-1}$ [54, 160, 161]) would tend to increase the entropy to a certain extent.

F Heat of formation

1 Perchloric acid at infinite dilution

Three methods have been used for the determination of the heat of formation of dilute perchloric acid: (a) measurement of the heat of solution of a perchlorate, (b) measurement of the heat of neutralization of the acid with a base and (c) measurement of the heat of solution of chlorine heptoxide. The first two methods require an accurate value for the heat of formation of a perchlorate. The heat of formation of a perchlorate is found by measuring the heat of decomposition to the chloride and oxygen, e.g. for potassium perchlorate

$$KClO_4 \longrightarrow KCl + 2O_2 \; ; \; \Delta H_1 \; . \qquad (7)$$

Using the known heat of formation of the chloride, the heat of formation of the perchlorate can be calculated.

Two values of ΔH_1 are currently available. That of -2.55 ±0.18 kcal mole^{-1} was obtained by Vorob'ev et al [210] whereas that of -0.96 ±0.08 kcal mole^{-1} was obtained by Johnson and Gilliland [83]. The discrepancy is considerable. Vorob'ev has discussed the two values [170] and has concluded that his is the more reliable for the following reasons:

(i) Two calorimetric methods were used yielding values of -2.5 and -2.6 kcal mole^{-1}.

(ii) ΔH_1 was measured for both sodium and potassium perchlorates. The results gave values for the heat of formation of aqueous perchloric acid of -29.82 and -29.73 kcal mole^{-1}.

(iii) A check was made for the possible decomposition to the oxide [109]

$$KClO_4 \longrightarrow \tfrac{1}{2} K_2O + \tfrac{1}{2} Cl_2 + 7/4\ O_2. \qquad (8)$$

On the other hand, full experimental details are given by Johnson and Gilliland [83] but not by Vorob'ev et al [210] hence it is not possible to choose between these values. The National Bureau of Standards has recently made further experiments to check their value for the heat of decomposition of potassium perchlorate, using a slightly modified method, but no significant difference was found [212]. In this review the values obtained by Johnson and Gilliland, corrected for the latest values available for the heats of formation of potassium and sodium chlorides, will be used throughout. However, values based on the work of Vorob'ev will be quoted in parentheses with a V to indicate source.

(a) Heat of formation from heat of solution of perchlorates

This method is based on the fact that at infinite dilution the perchlorate is made up of ClO_4^- and M^+ ions. When ΔH_f for M^+ is known that for ClO_4^- can be calculated and this is identical to the heat of formation of perchloric acid at infinite dilution. Values for the heat of formation of perchloric acid at infinite dilution derived from the heats of solution of potassium, sodium and lithium perchlorates are presented in Table 7. A slightly different treatment by Vorob'ev [209] gave a value of -29.46 kcal mole^{-1}.

(b) Heat of formation from heats of neutralization

The heat of formation of perchloric acid can be calculated from the heat of neutralization of perchloric acid with a base MOH, where the heats are known

for the formation, solution and dilution of the hydroxide [151, 213] and the perchlorate. Thus, where

$$HClO_{4(n_1\ H_2O)} + MOH_{(n_2\ H_2O)} = MClO_{4(n_1+n_2)H_2O} + H_2O;\ \Delta H_2 \qquad (9)$$

$$M + \tfrac{1}{2}Cl_2 + 2O_2 = MClO_{4(c)} \qquad ;\ \Delta H_3 \qquad (10)$$

$$MClO_{4(c)} = MClO_{4(n_1 + n_2)\ H_2O} \qquad ;\ \Delta H_4 \qquad (11)$$

the heat of formation, ΔH_5, of perchloric acid in $n_1\ H_2O$ is given by

$$\Delta H_5 = \Delta H_3 + \Delta H_4 + \Delta H_{f_{(H_2O)}} - \Delta H_{f_{(MOH\ in\ n_2\ H_2O)}} - \Delta H_2 . \qquad (12)$$

The various values for ΔH_5 are shown in Table 8.

(o) Heat of formation from heat of solution of chlorine heptoxide

The heat of solution of chlorine heptoxide

$$Cl_2O_{7(l)} + H_2O_{(l)} + n\ H_2O = 2HClO_4,\ n\ H_2O \qquad (13)$$

is a direct approach to the heat of formation of dilute perchloric acid. The heat of solution, in 5500 and 1758 moles of water respectively, was found to be -50.0 kcal mole^{-1} by Goodeve and Marsh [60] and -50.4 kcal mole^{-1} by Rosolovskii et al [147]. The mean value of -50.2 kcal mole^{-1} leads to a heat of formation of perchloric acid of -31.71 ±1.65 kcal mole^{-1}.

A mean heat of formation of perchloric acid can be computed (the results from the comparatively inaccurate data on chlorine heptoxide being excluded) to be -31.03 kcal mole^{-1} (V: - 29.93 kcal mole^{-1}). A best value for the heat of formation of dilute perchloric acid would be -30.48 kcal mole^{-1}.

2 Anhydrous perchloric acid

Since the heat of dilution of anhydrous acid (Section V,D) is -21.15 kcal mole^{-1}, the heat of formation of the anhydrous acid is -9.33 kcal mole^{-1}.

3 Heat of formation of perchloric acid vapour

Values can either be obtained by calculation from the heat of formation of dilute perchloric acid or from experimental studies of the heat of dissociation of ammonium perchlorate.

Values for the heat of vaporization of ammonium perchlorate of 56.6 kcal mole^{-1} and 58 kcal mole^{-1} have been obtained by Powling and Smith [140] and by Inami, Rosser and Wise [81] respectively assuming dissociation occurs as shown in equation (14)

$$NH_4ClO_{4(c)} \longrightarrow NH_{3(g)} + HClO_{4(g)} \quad . \qquad (14)$$

Using the value of Gilliland and Johnson [55] of -70.67 kcal mole^{-1} for the heat of formation of ammonium perchlorate, the heat of formation of perchloric acid vapour is -3.07 and -1.67 kcal mole^{-1} respectively. However, both of these studies were at considerably elevated temperatures and no correction has been made to obtain the heat of dissociation at 298°K.

Calculation using the heats of dilution and vaporization of anhydrous perchloric acid result in a value of -1.20 kcal mole^{-1} for the heat of formation of the vapour at 298°K.

A similar calculation can be made to give the heat of formation of the constant boiling mixture in the vapour phase at 298°K. This yields a value of -127.11 kcal mole^{-1} [36].

G Heat of adsorption

The heat of adsorption of anhydrous perchloric acid vapour on a pyrex surface at 150 to 260°C under pressures of up to half an atmosphere has been deduced by Sibbett and Geller [164] to be 9.7 kcal mole^{-1}. However, an alternative value of 15.85 kcal mole^{-1} appears to be possible (see discussion in Section VIII, B).

VI PHYSICAL PROPERTIES

A General

No attempt is made here to exhaustively review all the recent papers on the physical properties of perchloric acid. A literature source table is provided to indicate the properties and the concentration ranges which have been studied (Table 9). For completeness, some old references have been

included where these contain the only data available. Data for various physical properties of the 70-75% acid have recently been presented in graphical form [68]. Some selected topics are briefly discussed below.

B Acidity

Perchloric acid is one of the strongest acids known. Its solution in fluorosulphonic acid is one of the few cases where it is believed not to ionize to form the perchlorate ion [217]. An ionization of the type

$$HClO_4 + 2HSO_3F \rightleftharpoons ClO_3^+ + 2SO_3F^- + H_3O^+ \qquad (15)$$

was proposed.

The H_0 scale of acidity has recently been re-determined and extended to cover the range from 0 to 70% acid at 25° [218]. The H_0 scale decreases more rapidly than in aqueous sulphuric acid because 79% perchloric acid has an indicator acidity equal to that of 98% sulphuric acid. It was conservatively estimated that an H_0 value of -16 would be reached for 100% perchloric acid. Perhcloric acid was a much more efficient protonating medium than sulphuric acid. The activity coefficient has been measured for 3 to 10 M perchloric acid [76]. It was found that the molarity activity coefficient for $H^+(H_2O)_4\ ClO_4^-$ passes through a maximum near 8 M acid. This is in agreement with the observation [80] that perchloric acid extracts into ether with four moles of water. Later measurements of the activity coefficient indicate the existence of two more species, $HClO_4(H_2O)_3$ and $HClO_4(H_2O)_7$ [77]. The dissociation constant for anhydrous perchloric acid could only be reported as > 4 since the data did not extend to high enough concentrations. This may be compared with the estimate of the thermodynamic dissociation constant of 38 by Hood et al [78] who concluded that perchloric acid is such a strong acid because the degree of dissociation is high even in highly concentrated solutions.

C Transport numbers

The transport numbers for the cation in perchloric acid were determined recently for the 0.1 to 5.1 M concentration range at 25°C [64]. The results agreed well with those obtained earlier [10, 34].

VII CHEMICAL PROPERTIES

Anhydrous perchloric acid is an extremely powerful oxidizing agent. With most combustible materials there is an immediate explosive reaction in

the cold. Gold and silver are oxidised in the cold; platinum is not attacked but its presence results in rapid decomposition of the acid [196]. Consequently, all handling of the acid should be carried out in glass apparatus.

Sections VII, A and B discuss the nature of mixed acid systems and the explosion hazard concerned with the use of anhydrous acid. The system $HClO_4$ - H_2O - H_2O_2 has recently been studied [195] but no compound containing hydrogen peroxide was detected.

Other chemical reactions are summarized by Schumacher [158], Mellor [118, 119], and by Burton and Praill [30].

A Mixed acid systems

1 Acetic acid - perchloric acid system

The ion association constants which have been determined for perchloric acid in acetic acid at 25°C by potentiometric [24] and conductimetric [186] methods differ by a factor of 15. Recently a value of 0.0644×10^{-6} has been obtained [112]. Conduction with perchloric acid has been shown [113] to occur by a proton-jump mechanism in common with other solvated protons.

In the very concentrated system, that of perchloric acid monohydrate-anhydrous acetic acid, it has been shown that the perchloric acid retains its water of hydration [223].

2 Sulphuric acid - perchloric acid system

Infrared absorption spectra of the perchloric-sulphuric and sulphuric-phosphoric acid systems have been studied [162] in the region from 3700 to 750 cm^{-1}. The spectra indicate that chemical reaction occurs in the H_3PO_4 - H_2SO_4 system but not in the $HClO_4$ - H_2SO_4, confirming the results of Usanovich [202] on the electrical conductivity and viscosity in the system H_2SO_4 - $HClO_4$.

However, simultaneously another group of Russian workers [163] studied the freezing point diagram of the ternary system Cl_2O_7 - SO_3 - H_2O and observed the formation of an intermolecular compound $H_2SO_4 . 2HClO_4$.

3 Nitrous acid - perchloric acid system

This system has been particularly studied in connection with the reactivity of nitrous acid in acidic media.

The proportion of nitrosonium ion present in solutions of sodium nitrate in concentrated perchloric acid was measured spectrophotometrically in 1956 [169] but no equilibrium constant was available until 1958 [200]. Dilute

solutions of nitrous acid in 50% perchloric acid were observed to decompose steadily with time. This was confirmed by later workers [14] who also studied the kinetics of the nitrite decomposition [13] and found that the rate was strongly dependent on the perchloric acid concentration. The maximum decomposition occurred at about 50% by weight where both nitrous acid and the nitrosonium ion exist in appreciable concentration. The reaction of sodium nitrite with perchloric acid has been briefly studied [63].

4 Nitric acid - perchloric acid system

This system has been thoroughly examined by Goddard et al [57] and by Hillen [82]. They showed clearly that the reaction

$$HNO_3 + 2HClO_4 = NO_2^+ClO_4^- + H_3O^+ClO_4^- \qquad (16)$$

occurred on mixing the anhydrous acids at -40°.

B Explosive nature

Anhydrous perchloric acid has long had a reputation that it is explosive. Recently it has become clear that it is not and that its earlier reputation arose from the preparation of impure samples containing chlorine heptoxide, which can explode violently on shock or sudden heating. Samples of the anhydrous acid on standing at room temperature rapidly become coloured with chlorine oxides which are explosive. It must also be emphasised that contact of the anhydrous acid with many materials - especially organic ones - will result in explosion. The non-explosive nature of carefully prepared anhydrous acid has been shown by Levy [98]. However, samples of anhydrous acid in closed bottles can produce pressure bursts as a result of the formation of solid monohydrate round the stopper which is thus effectively cemented in (see also Section VIII, A).

Diluted perchloric acid (72% or below) is stable at room temperature as was shown by Dietz [44] and by Elliott and Brown [45]. Its mixture with organic compounds can be very dangerous, especially so with acid anhydrides which have the effect of producing a solution of anhydrous perchloric acid [107]. The dangers of mixtures with acetic anhydride used in electropolishing are reviewed by Schumacher [158]. Mixtures with ethyl alcohol have a detonation velocity of 1500 m/sec [95] whilst other mixtures with organic compounds have been proposed as monopropellent fuels [11, 215] and also as a means of producing explosions on surfaces [48]. The paper by Elliott and Brown is a particularly useful survey of the explosive nature of various perchloric acid mixtures [45].

Ventilating systems for perchloric acid vapour must be carefully designed [43]. The sealant in such systems must NOT be a litharge-glycerin cement since this has resulted in fatalities [201]. Portable scrubbers [167] and digestion units [105] have been described.

VIII THERMAL DECOMPOSITION

A Introduction

Until recently little information was available on the thermal decomposition of perchloric acid in either the gas or liquid phase, although the unstable nature of the anhydrous acid was well known. Mellor [118] stated that the anhydrous acid exploded if an attempt was made to distil it at atmospheric pressure; at 72°C the acid darkened in colour and at 92°C white fumes mixed with chlorine dioxide were evolved and on further heating explosion occurred. It is now clear that anhydrous perchloric acid is not explosive when pure. The fact that earlier workers often found even freshly prepared samples to be explosive can be explained by the ease with which the anhydrous acid can be dehydrated to the anhydride chlorine heptoxide, which explodes violently on shock or sudden heating. This has been shown by Levy [98] who found that samples of perchloric acid vapour, from acid prepared in the usual way by dehydration of the dihydrate, could be exploded either by heating a spiral of wire in the vapour or by plunging the bulb containing the vapour into a hot bath. These samples or acid were shown to contain as much as fifty per cent of chlorine heptoxide. Pure samples of vapour, freed from the chlorine heptoxide, did not explode. It is thus clear that statements such as the one by Sibbett and Lobato [165], that the sample of acid passed over phosphorus pentoxide in order to remove all traces of water was unstable, can be explained by formation of the unstable chlorine heptoxide.

An outstanding feature of the perchloric acid system is the marked increase in stability with increasing dilution of the acid. The monohydrate is a crystalline solid (m.pt 49.9°C) [180] and is stable up to about 110°C [199], the 72.4% acid is a constant boiling mixture which is quite stable and decomposes only slightly when heated to its boiling point (203°C) whereas the anhydrous acid is unstable even at -78°C [220]. It is suggested that this stability is associated with the formation of the perchlorate ion, i.e. the aci-form, and the inheren instability of the anhydrous acid with the covalent form.

B Gas phase decomposition

The thermal decomposition of anhydrous perchloric acid vapour was studied at 200 to 220°C by Sibbett and Lobato [165]. They showed that reaction proceeded according to the overall equation

$$HClO_4 = \tfrac{1}{2} H_2O + \tfrac{1}{2} Cl_2 + {}^{7}/_{4}\, O_2 \qquad (17)$$

although a complete analysis was not obtained. The kinetics were found to be second order in the early stages of the reaction, changing to first order as the reaction proceeded. The reaction was shown to be heterogeneous at 200 to 220°C.

Levy [98, 99] confirmed that the overall reaction yields chlorine, oxygen and water for the temperature range from 200 to 439°C. Hydrogen chloride was not a product. The decomposition kinetics from 200 to 350°C were determined in a static system using anhydrous perchloric acid and from 350 to 439°C in a flow system using 70% perchloric acid. Experiments at 294°C indicated that water had a moderate inhibiting effect: 2.53 moles of water per mole of acid decreased the first order rate constant from 0.062 to 0.038 min^{-1}. This indicated that the presence of small amounts of water in the acid should not affect the kinetics significantly.

Below 310°C a heterogeneous reaction was involved whereas above this temperature the decomposition was homogeneous, and first order. An Arrhenius plot of the data for the homogeneous reaction yielded the expression

$$k = 5.8 \times 10^{13} \exp(-45{,}100/RT)\ sec^{-1}. \qquad (18)$$

The first order nature of the reaction and the magnitude of the activation energy suggest that the rate determining reaction is

$$HOClO_3 \longrightarrow HO\cdot + ClO_3 \qquad (19)$$

followed by the fast reactions

$$HO\cdot + HOClO_3 \longrightarrow H_2O + ClO_4 \qquad (20)$$

$$ClO_4\cdot \longrightarrow \tfrac{1}{2} Cl_2 + 2O_2 \qquad (21)$$

$$ClO_3\cdot \longrightarrow \tfrac{1}{2} Cl_2 + {}^{3}/_{2}\, O_2 . \qquad (22)$$

Although reactions (21) and (22) are written as single equations it is likely that the decompositions of the ClO_3 and ClO_4 radicals are complex and involve formation and decomposition of lower chlorine oxides.

Using the heats of formation of $HClO_{4(g)}$ (-1.20 kcal mole^{-1} (Section V, F)), $\cdot OH_{(g)}$ (9.37 kcal mole^{-1} [213]) and $ClO_3\cdot_{(g)}$ (37 kcal mole^{-1} [61]), a value can be calculated for the heat of reaction (19) at 298°K of 47.6 kcal mole^{-1}, which agrees well with the experimental activation energy of 45.1 kcal mole^{-1}.

The heterogeneous reaction which occurred below 310°C was found by Levy to have an activation energy of the order of 10 kcal mole^{-1}. More recently, Sibbett and co-workers [166] have studied this heterogeneous reaction between 150 and 260°C. They proposed the following mechanism

$$2\ HClO_4 \xrightarrow{k_2} Cl_2 + 7/2\ O_2 + H_2O \qquad (23)$$

$$HClO_4 + H_2O \longrightarrow HClO_4 \cdot H_2O \qquad (24)$$

$$HClO_4 \cdot H_2O \xrightarrow{k_1} \tfrac{1}{2}\ Cl_2 + 3/2\ H_2O + 7/4\ O_2 . \qquad (25)$$

Rate constants for the second order reaction, k_2, and the first order reaction, k_1, have been computed from the initial and final data which were obtained by following the rate of pressure change. A computer solution of the simultaneous differential equations which represent the reaction scheme demonstrated that the observed pressure may be computed when the two rate constants are evaluated. Activation energies were calculated to be 8.9 and 21.3 kcal mole^{-1} for the second and first order steps respectively. Both steps were shown to be surface catalysed with a linear dependence of the two rate constants on the surface to volume ratio at 200°C.

This research has been further described by Sibbett and Geller [164]. The reaction was second order initially and then became first order. The amount of chlorine evolved was found to be directly proportioned to the amount of decomposed acid at all times. Computer multiple-trial calculations showed that the reaction scheme which best fitted the data was

$$2HClO_4 \xrightarrow{k_1} H_2O + Cl_2 + 7/2\ O_2 \qquad (26)$$

$$HClO_4 + H_2O \longrightarrow HClO_4 \cdot H_2O \qquad (27)$$

$$HClO_4 \cdot H_2O \xrightarrow{k_2} 3/2\ H_2O + \tfrac{1}{2}\ Cl_2 + 7/4\ O_2 . \qquad (28)$$

On the assumption that these reactions occurred on the glass surface (the data showed that most of the reaction, if not all, was heterogeneous) it followed that

$$-\frac{d\,[HClO_4]}{dt} = 2k_1\,[HClO_4]^2 + \frac{k_2[HClO_4]\,[H_2O]}{1 + K_B\,[H_2O]} \qquad (29)$$

where K_B is the equilibrium constant for the adsorption of some inhibiting species, presumed to be water, on the reactor surface. From consideration of Langmuir-Hinshelwood adsorption theory, it followed that reaction (26) occurs by a mechanism in which perchloric acid is weakly adsorbed and surface coverage is slight. Then the initial bimolecular process can be described by

$$V_1 = 2k_1'\,K^2\,[HClO_4]^2 . \qquad (30)$$

The experimental rate constant, $k_1 = k_1'\,K^2$, where K is the equilibrium constant for the adsorption of perchloric acid on pyrex. This requires that the observed activation energy

$$E_{a_1} = E_T - 2\,\lambda_{HClO_4} \qquad (31)$$

where λ_{HClO_4} is the heat of adsorption of $HClO_4$ and E_T is "the true activation energy for the homogeneous gas phase decomposition of $HClO_4$."

Two alternative possibilities exist for the surface processes in reactions (27) and (28). Either both $HClO_4$ and the inhibiting reaction product (assumed to be H_2O) can (1) compete for the same sites or (2) be adsorbed on two different types of surface sites. For competitive adsorption it was shown that

$$E_{a_2} = E_T - \lambda_{H_2O} \qquad (32)$$

and for non-competitive adsorption

$$E_{a_2} = E_T - \lambda_{H_2O} - \lambda_{HClO_4} . \qquad (33)$$

Sibbett and Geller in an early manuscript used the value of 32.8 kcal mole^{-1} obtained by Zinov'ev and Babaeva [224] for the liquid phase decomposition as the value of E_T in equation (31). This with the experimental value of E_{a_1} = 13.4 kcal mole^{-1} yielded a value for the heat of adsorption of $HClO_4$ of 9.7 kcal mole^{-1}.

Substitution of this value along with λ_{H_2O} = 13.3 kcal mole^{-1} for pyrex glass and the experimental value for E_{a_2} of 20.5 kcal mole^{-1} in equations (32) and (33) leads to values for E_T of 33.8 and 43.4 kcal mole^{-1} respectively. Hence it was concluded that the competitive adsorption process was more probable.

However, if the value obtained by Levy [98, 99] of 45.2 kcal mole^{-1} is used for E_T it follows that λ_{HClO_4} = 15.85 kcal mole^{-1}. Substitution of this value in equations (32) and (33) yields values of E_T of 33.8 and 49.65 kcal mole^{-1} respectively. Consequently it might appear that the non-competitive adsorption process is more probable.

Perchloric acid vapour (72% acid) has been introduced by Heath and Majer [72] into an A.E.I. Type M.S.2 Mass spectrometer. They studied the heterogeneous decomposition of perchloric acid vapour on a hot platinum wire just outside the ionisation box of the mass spectrometer. The results showed that the dominant mode of decomposition was into hydrogen chloride and oxygen:

$$HClO_4 \longrightarrow HCl + 2O_2 \quad . \qquad (34)$$

The equilibrium constants for the Deacon equilibrium [36]

$$2HCl + \tfrac{1}{2}\,O_2 \rightleftharpoons Cl_2 + H_2O \qquad (35)$$

show that at the temperatures and pressures used by Heath and Majer (estimated to be 950° and 1170°K) a preponderance of hydrogen chloride would be expected. The equilibrium constants at 450 to 700°K (the temperature range used by Levy) show that production of chlorine should be dominant at these temperatures.

C <u>Chlorine heptoxide thermal decomposition</u>

The gas phase decomposition was studied by Figini et al [46] at pressures of 1.5 to 80 mm Hg and temperatures of 100 to 120°C. The decomposition was found to be homogeneous, uni-molecular and to have an energy of activation of 32.9 ±1.5 kcal mole^{-1}. The reaction was followed by the pressure rise because analysis of the products showed the overall decomposition to be

$$Cl_2O_7 \longrightarrow Cl_2 + 3\tfrac{1}{2}\,O_2 . \qquad (36)$$

The effect of added chlorine and oxygen was studied. They both activated the decomposition but were about 4.5 times less active than pure heptoxide.

Experiments with added fluorine showed that the first stage was decomposition into ClO_3 and ClO_4 radicals

$$Cl_2O_7 \longrightarrow ClO_3 + ClO_4. \qquad (37)$$

The liquid phase decomposition has very recently been studied by Babaeva [7] at temperatures from 60 to 80°C. The isotherms of liberation of oxygen were very nearly straight lines. An activation energy of 32.1 kcal $mole^{-1}$ was deduced for the zero order process. Additions of trichloroacetic acid or carbon tetrachloride had no effect on the decomposition. However, additions of perchloric acid (1%) considerably modified the decomposition; the oxygen liberation rate increased, the oxygen liberation curves became S-shaped and the whole decomposition was more rapid. At 60-80°, the Cl_2O_7 became pale yellow but did not darken in colour in the course of the experiment. However, at 50° the colour became more intense and this led to an acceleration of the reaction in the final stage. The oxygen liberation isotherm became S-shaped.

The liquid phase decomposition is compared and contrasted with that of liquid perchloric acid in the next section.

D Liquid phase decomposition

Zinov'ev [220] in 1958 stated that, although anhydrous perchloric acid decomposed slowly at room temperature and even at -78°C, it also had an induction period when heated and it was because of this induction period that anhydrous perchloric acid could be distilled. An electrochemical study by Hissen and Sukhotin [122] showed that 97% perchloric acid decomposed at room temperature to give oxygen, chlorine dioxide and chlorine trioxide. They also found that highly concentrated perchloric acid contained chlorine heptoxide whose concentration increased rapidly as the perchloric acid concentration approached 100%. In view of the discussion in Section II this observation confirms that chlorine heptoxide is an impurity in highly concentrated perchloric acid when the latter is not specially purified. The decomposition of the acid was reduced by addition of 1 to 2% chloral hydrate to the concentrated acid.

A series of papers on the thermal decomposition of liquid perchloric acid has been published by Zinov'ev and co-workers [8, 9, 199, 224, 227]. It was assumed that the overall decomposition could be represented by the equation

$$HClO_4 \longrightarrow \tfrac{1}{2} H_2O + \tfrac{1}{2} Cl_2 + {}^{7}/_{4}\, O_2 \qquad (17)$$

and the reaction was followed by measuring the volume of oxygen evolved. The actual reaction is considerably more complex since chlorine oxides have been detected as intermediate products. The decomposition in the liquid phase was found to take place in three stages: an induction period, an active period in which the reaction rate rose sharply to a maximum, and a final period in which the reaction rate fell to zero. The final product was a yellowish liquid crystallising at 47 to 48°C and containing 85.3 to 86.0% perchloric acid. This corresponds to the monohydrate.

The earlier papers studied the decomposition of the 83-100% acid over the temperature range 40-95°C with experiments at 110-245°C for the 83% acid. Plots of the logarithm of the maximum rate of oxygen evolution against the reciprocal of the absolute temperature yielded a value for the activation energy of the second stage of 22.2 kcal mole^{-1} [227]. A later value was 22.56 kcal mole^{-1} [199]. The induction period was found to decrease with increase in temperature and increase in acid concentration. A detailed study of the induction period by Zinov'ev and Babaeva [224] who also studied the effect of inhibitors (trichloroacetic acid and carbon tetrachloride) led to a value for the activation energy of the induction period of 32.6 kcal mole^{-1}. This was obtained by plotting the logarithm of the induction period against the reciprocal of the absolute temperature. An identical activation energy was obtained with perchloric acid-chlorine heptoxide mixtures. The induction period study was extended [9] to six acid concentrations from 84.8 to 100% and activation energies of 32.5 and 22.58 kcal mole^{-1} were obtained for the induction period and active period respectively. The mechanism by which the inhibitors act was not discussed [224] but it was apparent that the C-Cl bond is the effective agent because this is the common factor in the known inhibitors (chloral hydrate, trichloroacetic acid and carbon tetrachloride).

More recently kinetic curves have been obtained for the formation and consumption of chlorine, chlorine dioxide and chlorine trioxide during the decomposition of anhydrous perchloric acid [8]. The shape of the kinetic curves was complex and no detailed mechanism was suggested.

Tsentsiper [199] proposed that the decomposition was a chain process initiated by fission of the HO-ClO_3 bond. The sharp fall in the rate of decomposition with increase in dilution was ascribed to a decrease in the concentration of the pseudo (covalent) form $HOClO_3$ and an increase in the concentration of the more stable aci-form ClO_4^- as indicated by Raman spectra.

However, Zinov'ev and Babaeva [224] suggested that the decomposition rate was determined by the formation and subsequent decomposition of chlorine heptoxide:

$$2\ HClO_4 \rightleftharpoons Cl_2O_7 + H_2O. \qquad (38)$$

This reaction would be facilitated by the tendency of perchloric acid to hydrate:

$$HClO_4 + H_2O \longrightarrow HClO_4.H_2O. \qquad (39)$$

This mechanism was based on three observations: (i) the activation energy for the decomposition was independent of the initial composition throughout the range from 84.8% perchloric acid through 100% acid to acid containing 35.4% chlorine heptoxide, (ii) the activation energy calculated for the induction period closely equalled that observed for the gas phase decomposition of chlorine heptoxide, and (iii) Missan and Sukhotin had detected chlorine heptoxide in highly concentrated perchloric acid [122]. Zinov'ev and Babaeva therefore rejected the mechanism proposed by Tsentsiper.

However, recent work has thrown more light on this controversy. It is now clearly established that concentrated perchloric acid when not specially purified will contain chlorine heptoxide. The recent work by Babaeva [7] on chlorine heptoxide in the liquid state indicates that it does not decompose in the same way as the anhydrous acid since (i) inhibitors for perchloric acid have no effect on chlorine heptoxide and (ii) addition of 1% perchloric acid to chlorine heptoxide changes the whole character of the decomposition. The earlier finding of Zinov'ev and Babaeva [224] that additions of chlorine heptoxide to the acid do not affect the kinetics of decomposition save by reducing the induction period when considered along with Babaeva's recent work do not lend support to the idea of decomposition through the heptoxide.

In fact the observed phenomena can be better explained by the alternative theory of Tsentsiper [199] along with the assumption that the dissociation

$$3\ HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \qquad (1)$$

does not occur to any great extent. The effect of addition of chlorine heptoxide to the acid can then be explained as being solely due to the shift

of this equilibrium to the left. The finding of Rosolovskii et al [147] that the heat of reaction for the above equation as written from left to right is $\Delta H = -2.8$ kcal also supports Tsentsiper's theory because increase in temperature will tend to shift the equilibrium to the left. Further, decomposition of 83% acid does not differ significantly from that of acid more concentrated than the monohydrate (84.8%); it is difficult to believe that chlorine heptoxide is present in 83% acid. The sole evidence remaining to support the decomposition of anhydrous perchloric acid through chlorine heptoxide is that the numerical value of the activation energy deduced from the induction period (32.5 kcal $mole^{-1}$) is the same as that in the gas and liquid phase decomposition of chlorine heptoxide as deduced from the pressure rise of products (32.9 and 32.1 kcal $mole^{-1}$ respectively). It would perhaps be more logical to compare the activation energies of the acid decomposition for the induction period with that of ammonium perchlorate also for the induction period (~ 32 kcal $mole^{-1}$) [187] or of guanidine perchlorate also for the induction period (~ 30.5 kcal $mole^{-1}$) [56].

IX RADIATION CHEMISTRY

A Photochemical irradiation

The optical density of perchloric acid is less than 0.1 in the 2300-2800 Å region [131] and the perchlorate ion absorbs light very slightly between 2000 and 8000 Å [74]. This is in accord with the method for the preparation of perchloric acid in which a mixture of chlorine, ozone and water vapour were photolysed at 2537 Å [153]. The photolysis by sunlight of a mixture of cerous and ceric perchlorates with perchloric acid has been used to produce microquantities of hydrogen and oxygen [73]. The perchlorate acted as a catalyst and it was hoped that this process may eventually be of economic importance.

B Ionizing radiation

Solutions of perchloric acid were found to be decomposed into chlorate and molecular oxygen by X-rays [143]. In the presence of ferrous ions, an additional interaction occurred in which the ferrous salt was oxidised and chlorine was produced.

The amount of chlorate formed by 200 kV X-rays was directly proportional to the perchloric acid concentration [121]. Ceric salts had no effect on the chlorate formation whilst ferrous salts resulted in the formation of an equivalent amount of chloride. Whereas irradiation of ferrous sulphate in

solution in sulphuric acid liberated equivalent amounts of hydrogen and ferric salts, this was not the case in perchloric acid solutions where a less than equivalent amount of hydrogen was liberated [143]. The discrepancy between the yields of hydrogen and the ferric salt became marked as the acid concentration increased. It was thus shown that irradiation of perchloric acid solutions results in a "direct effect", i.e. the energy of the radiation excites the perchloric acid molecules. The irradiation of perchloric acid solutions at 77°K by gamma rays from a 1000 curie Cobalt 60 source was found to produce substantial amounts of atomic hydrogen [102, 219]. The atomic hydrogen was detected by the paramagnetic resonance spectrometer which also showed lines from other unpaired-electron species formed by the irradiation and trapped stably at 77°K. The atomic hydrogen disappeared on moderate warming of the acid by a second order rate and with an activation energy of several kcal $mole^{-1}$.

Recently, the yields of atomic hydrogen have been measured by the paramagnetic resonance method along with the volumes of hydrogen and oxygen liberated on warming the irradiated acid [101]. It was found that the yields were independent of whether the acid was in a glassy or crystalline state, unlike the case for phosphoric and sulphuric acids. The yields of atomic hydrogen, hydrogen and oxygen increased steadily with the acid concentration up to a concentration of about 0.15 mole fraction at which point (a) the atomic and molecular hydrogen yields showed a sudden decrease, (b) the molecular oxygen yield showed a sudden increase, and (c) an unidentified gaseous species was detected in quantity increasing with acid concentration from 0.14 molar fraction. This unknown species was thought to be chlorine or a chlorine compound since it coloured yellow the liquid phase produced on warming. The yields of atomic hydrogen were greatly in excess of those of the molecular hydrogen liberated. This difference was ascribed to reaction of the hydrogen atoms with other unidentified species. The saturation of a 0.125 mole fraction solution of perchloric acid by irradiation gave a hydrogen atom concentration of 2.0×10^{19} atoms per gram - a factor of ten greater than that from sulphuric acid. Nitric acid addition scavenged the hydrogen atoms but not to as great an extent as in sulphuric acid.

Tritiated samples of perchloric acid solutions (molar ratios of $HClO_4 : H_2O = 1 : 7$ and $HClO_4 : H_2O : D_2O = 1 : 3 : 4$) have been studied by electron paramagnetic resonance [94]. H and D atoms were readily produced along with other unidentified species which coloured the acid yellow. The

change in H and D atom concentrations on warming was followed and at about $-150^{o}C$ it was found that the H and D concentrations decreased rapidly whilst a new unidentified radical species appeared and rapidly increased in concentration. The yields of molecular hydrogen from tritiated perchloric acid were in good agreement with the early work on gamma irradiated acid [101]. However, the ratio of the yields of molecular and atomic hydrogen was twice as high in tritiated acid as in gamma irradiated acid at the same concentration. This may be accounted for by the different linear energy transfer of these types of radiation.

Irradiation of perchloric acid solutions at room temperature has been studied by Cottin [32] using radiation from three sources: γ-rays from 25 and 90 curie Cobalt 60 sources, X-rays of 10 KeV, and α-particles from polonium. The yields of ClO_3^- and Cl^- were proportional to the concentration of the irradiated acid (0 to 4M) and were independent of the presence of dissolved oxygen or the physical state. Other products were hydrogen, chlorine, oxygen and chlorine dioxide.

The experiments indicated that the chloride ion was probably formed simultaneously with the chlorate ion. Possible reactions were

$$ClO_4^- \rightsquigarrow ClO_3^- + O \tag{40}$$

and

$$ClO_4^- \rightsquigarrow Cl^- + O\ , \tag{41}$$

although it was difficult to visualize a mechanism for the latter process. The energy required to decompose a perchlorate ion was 24.7 eV.

Bugaenko [25, 26, 27, 28] studied the effect of X-rays (up to 70 keV) on 2.5 M perchloric acid at 20 $\pm 1^{o}C$. The acid solutions were either saturated with hydrogen, nitrogen or oxygen, or contained 0.008 M ferrous sulphate. No chlorine dioxide was formed but chloride and chlorate ions and hydrogen peroxide were formed. Their accumulation curves were linear in all cases. As the G value for perchlorate ion reduction was the same in all cases and was the same for 2.5 M sodium perchlorate, it was deduced that the perchlorate ion was reduced directly by the ionizing radiation. The following mechanism was suggested:

$$ClO_4^- \rightsquigarrow ClO_4^{-*} \tag{42}$$

or

$$ClO_4^- \rightsquigarrow ClO_4 + e\ . \tag{43}$$

The excited perchlorate ions probably transferred their energy to neighbouring molecules and probably also decomposed by

$$ClO_4^{-*} \longrightarrow ClO_3^- + O \,. \qquad (44)$$

The perchlorate radicals decomposed by

$$ClO_4 \longrightarrow ClO_2 + O_2 \qquad (45)$$

which then reacted with hydroxyl radicals to form chlorate ions:

$$ClO_2 + OH \longrightarrow ClO_3^- + H^+ \,. \qquad (46)$$

Chloride ions were produced by the scheme

$$ClO_3^- \xrightarrow{OH} ClO_2 \xrightarrow{H} ClO_2^- \xrightarrow{2H} ClO^- \xrightarrow{H_2O_2} Cl^- . \qquad (47)$$

In the presence of hydrogen the reaction

$$H_2 + OH \longrightarrow H + H_2O \qquad (48)$$

occurred resulting in an increased yield of chloride ions. Addition of ethyl alcohol and acetone resulted in a decrease in the yield of the reduction of the perchlorate ion. This was believed to be due to the reaction

$$ClO_4 + RH \longrightarrow ClO_4^- + H^+ + R \,. \qquad (49)$$

Very recently, Katakis and Allen [88] have studied the radiolysis of perchloric acid in the absence and presence of radical scavengers over a range of acid concentrations. Irradiation was by gamma rays from a cobalt 60 source at a dose rate of 3.2×10^{20} eV/l min and by 33 MeV He^{++} ions from a cyclotron. Radiolysis of 10^{-2}M perchloric acid indicated that the free radicals from the water radiolysis did not react with the perchlorate ion. In more concentrated solutions, the perchlorate ion decomposed by the direct action of the radiation, with a yield increasing directly with its concentration, whilst the yields of hydrogen and other water decompositon products decreased. Up to 2.5M perchloric acid the yields of chlorate $F(ClO_3^-)$, and chloride ion $G(Cl^-)$, agreed with those obtained by Cottin [32] but above 2.5M Cottin's yields were higher.

This may have been due to differences in thermal reactions which were not investigated but were believed to involve a reaction between chloride and chlorate ions giving products which rapidly oxidized the hydrogen peroxide. Addition of 10^{-2}M sodium chloride increased the chlorate yield and below 3M perchloric acid this became equal to the sum of G (Cl^-) and G (ClO_3^-) as measured in the absence of added chloride ion. This indicated that the chloride ion was mainly a secondary product in the radiolysis resulting from the attack of the chlorate ion by free radicals. The added chloride ion protected the chlorate from this attack. This was verified by irradiation of chlorate ion in the presence and absence of chloride ion. The reaction involved was proposed to be

$$OH + ClO_3^- + H^+ \longrightarrow H_2O + ClO_3 \qquad (50)$$

followed by decomposition or reduction of the chlorate radical to yield a chloride ion. The oxygen liberated along with the chlorate may emerge as oxygen, hydrogen peroxide, HO_2 or OH radicals or as O atoms.

Since the yields all vary linearly with the perchlorate ion concentration, the excited perchlorate ions did not react with other perchlorate ions but rather decomposed unimolecularly. Two possible reactions were

$$ClO_4^{-*} \longrightarrow ClO_4 + e \qquad (51)$$

and

$$ClO_4^{-*} \longrightarrow ClO_3^- + O\,. \qquad (44)$$

The results indicated that reaction (51) was very unlikely and the usual process was production of chlorate ions and oxygen atoms. Most of the oxygen atoms will probably be in the ground state since Taube [191] has shown that oxygen atoms in the ^1D state react readily with water to form hydrogen peroxide and can also reduce perchloric acid to chloric acid. This was confirmed because the hydrogen peroxide yield was decreased.

X PERCHLORIC ACID FLAMES

A Ammonium perchlorate decomposition

Flames in which perchloric acid is used as the oxidizer have been studied recently because of the widespread use of ammonium perchlorate as oxidizer in composite propellents for rocket propulsion. It is believed that, at least under certain conditions, the monopropellent combustion of the ammonium perchlorate particles is the controlling factor in the burning rate of the propellent [2, 12]. There has been much discussion in the past decade on possible

mechanisms of ammonium perchlorate decomposition. Those favoured are

(i) decomposition of the perchlorate ion [20]

(ii) electron transfer [19, 51]

$$NH_4^+ ClO_4^- \rightleftharpoons NH_4 + ClO_4 \qquad (52)$$

and (iii) proton transfer [50, 157]

$$NH_4^+ ClO_4^- \rightleftharpoons NH_3 + HClO_4. \qquad (53)$$

Mechanism (i) seems unlikely because the activation energy for such a process in the crystal lattice would be too high. The bond dissociation energies for Cl-O and O-ClO are 63 and 57 kcal mole^{-1} respectively [33] and the activation energy for the thermal decomposition of potassium perchlorate is 70 kcal mole^{-1} [69, 135]. The observed activation energy for ammonium perchlorate is about 30 kcal mole^{-1}, thus it is unlikely that Cl-O bond fission is important.

It has been suggested by Jacobs et al [52] that ammonium perchlorate is decomposed by an electron transfer mechanism below 300°C and by a proton transfer mechanism above 350°C but recently Russell-Jones [152], working with Jacobs, has concluded that the same process is involved under all conditions and this process was deduced to be effectively proton transfer although free protons are not involved. Russell-Jones obtained activation energies of 30.6 kcal mole^{-1} for sublimation. Previous discrepancies in the values obtained for the high-temperature reaction were ascribed to the fact that gas phase reactions were limiting at high temperatures.

Evidence for the formation of free ammonia and perchloric acid continues to accumulate. Bircumshaw and Newman [19] showed that added perchloric acid reduced the induction period and added ammonia increased it as would be expected if the formation of decomposition centres was associated with the production of free perchloric acid. The effect of the perchloric acid addition to ammonium perchlorate is minimised in an ammonia atmosphere at 200 to 240°C [20]. Later work [110] showed that when calcium oxide is placed above the perchlorate in a tube in which sublimation is occurring, the amount of sublimate is considerably reduced presumably because of adsorption of the perchloric acid by the calcium oxide. A recent study of ammonium perchlorate, in which the salt was heated to a given temperature and then put into cold water and analysed for possible acids, indicated that the first reaction step

is dissociation into ammonia and perchloric acid [132]. This was found to be first order with an activation energy of 21.5 kcal mole^{-1}.

Sublimation experiments on ammonium perchlorate at 300°C with analysis of the sublimate [31] have resulted in the suggested decomposition reaction

$$NH_4ClO_4 \longrightarrow {}^1/_6\,(NH_3 + HClO_4) + {}^5/_6\,(HNO_3 + HCl + H_2O). \qquad (54)$$

Mack, Tompa and Wilmot [103] used methods of Knudsen's free flow and matrix isolation in the study of the gaseous species in equilibrium with crystalline ammonium perchlorate. The gaseous species effusing from a cell at 200°C were successfully trapped at liquid helium temperatures in a nitrogen matrix. Infrared spectra of these species studied over the range 4000 to 650 cm^{-1} showed that the only major species in the vapour are ammonia and perchloric acid. Confirmatory evidence has come from Inami, Rosser and Wise [81] who have studied the dissociation pressure of ammonium perchlorate at 510 to 620°K by passing helium through a porous bed of the perchlorate and condensing the sublimate on a cold finger some two cm from the porous bed. The cold finger was held at 340 ±10°K to prevent condensation of water. The sublimate was analysed for NH_4^+, ClO_4^- and Cl^-, and was found to contain equimolar quantities of NH_4^+ and ClO_4^-. The results were interpreted in terms of an equilibrium dissociation

$$NH_4ClO_{4(s)} \rightleftharpoons NH_{3(g)} + HClO_{4(g)} \qquad (55)$$

which was effectively confirmed by addition of ammonia to the helium gas stream. The sublimate was then found to contain equimolar quantities of NH_4^+ and Cl^- and only traces of ClO_4^-. The heat of dissociation was calculated to be 58 ±2 kcal mole^{-1}.

Powling [138, 139, 140] has studied the surface temperature of burning ammonium perchlorate at a range of pressures from 1/40 atmosphere up to 4 atmospheres. Because at a given pressure the surface temperature was independent of the burning rate it was assumed that near equilibrium conditions exist between the solid and vapour. Consequently, a surface temperature - pressure plot should yield the heat of sublimation (or dissociation) of ammonium perchlorate. The value obtained, 57 kcal mole^{-1}, is in such close agreement with the calculated value, 58 kcal mole^{-1}, that this may be regarded as strong support for the dissociation reaction [55].

A mass spectrometric study [72] in which ammonium perchlorate was heated in a compartment adjoining the ion source of the mass spectrometer showed spectra corresponding only to ammonia and perchloric acid. No trace of a parent peak corresponding to ammonium perchlorate was found.

B Perchloric acid - ammonia reaction

The vapour phase reaction of ammonia with perchloric acid has been studied briefly. Friedman and Levy [49, 100] made a preliminary investigation at 367°C. Separate streams of ammonia and perchloric acid in nitrogen were mixed, passed through a reaction vessel at a known temperature, absorbed and analysed. The main problem was the mixing of the two reactants in a time short compared to the residence time in the reaction vessel (ca 2 seconds). It was found that a greater percentage decomposition of perchloric acid occurred in the presence of the ammonia than would have occurred with the perchloric acid alone. They deduced a rate constant of about 2×10^6 cm^3 $mole^{-1}$ sec^{-1} on the assumption that the ammonia-acid reaction is first order in each reactant. An approximate value of 59.9 kcal $mole^{-1}$ for the heat of vaporization of ammonium perchlorate was obtained from the observation that solid formation occurred in the mixing chamber at 362°C but not at 367°C.

Sibbett and Lobato [165] studied the reaction between undiluted ammonia and anhydrous perchloric acid at 25, 48.4 and 60°C. Reaction was initiated by rupturing a break seal between two pyrex vessels at zero time, and conditions were arranged so that a jet of ammonia always passed rapidly into the acid vapour to start the reaction. The reaction appeared to be instantaneous because the pressure measuring system showed a single pressure rise to a fixed level. Analysis of the products indicated simultaneous oxidation of the ammonia by the perchloric acid along with direct combination to yield ammonium perchlorate. Results [89] at 230°C indicated that the ammonia triggered the decomposition of the acid. Attempts were also made to stabilize a diffusion flame using an opposed jet reactor with ammonia and anhydrous perchloric acid. Reactor pressures of 1 to 60 torr, acid flow rates of 4.3×10^{-6} to 2.6×10^{-4} mole min^{-1}, mole ratios of $HClO_4/NH_3$ of 0.05 to 7.7, temperatures from ambient to 180°C and various nozzle orifices from 0.5 to 2.0 mm were used. In no case could a stable flame be obtained despite the use of a spark or hot wire [166] igniter system.

Very recently, burning rates of mixtures of polymeric fuels with 72% perchloric acid have been studied at the University of Louvain [29]. Similar

burning rate-mixture ratio curves were obtained to those found with ammonium perchlorate in place of the perchloric acid. Detonations occurred with very lean mixtures.

C Flames

The earliest reference to perchloric acid flames in the literature is in a brief note by Dietz in 1939 when it was reported that perchloric acid vapour(72%) ignited at 400-405°C in the absence of any fuel [44]. Hydrogen passed into hot acid vapour ignited spontaneously at the same temperature but in the presence of steel turnings this ignition temperature was reduced to 215°C. Recently the value of 400-405°C for the spontaneous ignition temperature of methane - 72% perchloric acid vapour has been confirmed [134].

In 1958 Powling [137] stabilized flat diffusion flames of perchloric acid (72%) with ammonia and propane. The perchloric acid appeared to decompose in a flame zone emitting a reddish glow before reacting with the fuel. A thermocuple trace across the flame indicated an exothermal bump on the acid side. Because no spectral difference could be detected between ammonia-perchloric acid flames and ammonia-oxygen-chlorine flames, it was concluded that the perchloric acid probably decomposed before it reacted with the fuel.

Very recently, Hall and co-workers [35, 37, 38, 39] have succeeded in stabilizing premixed flames of perchloric acid (72%) at both 760 mm and at about 20 mm pressure. The production of premixed flames with ammonia was made difficult by the formation of solid ammonium perchlorate but other fuels have been successfully used. The flames which have been studied are presented in Table 10. A diffusion flame of methane and 72% perchloric acid was also studied briefly.

Spectroscopic studies of premixed methane-perchloric acid flames showed not only the C_2, CH and OH bands usually observed in hydro-carbon-oxygen flames but also "cool flame" bands. These bands were also observed in perchloric acid flames with methyl alcohol but not with formaldehyde. Low pressure flame studies indicated that these "cool flame" bands were confined to the early part of the flame whereas the C_2 and CH bands appeared later.

Methane-perchloric acid-oxygen flames have a second flame zone on the downstream side of the first zone and separated by a gap having little or no luminosity. The second zone was extinguished by removing the oxygen. Spectra at low pressure showed that the first zone had the usual perchloric acid flame structure and the second zone had the bands expected for a methane-oxygen flame.

Burning velocity measurements showed that in general the acid flames were about three times faster than the corresponding oxygen flame at the same temperature. The burning velocity maximum occurred at about $\lambda = 1.5$ (where λ is the ratio of the fuel present to that required for stoichiometric combustion) for acid flames and at $\lambda = 1.15$ for oxygen flames. The effect of nitrogen dilution on the burning velocity of stoichiometric methane-perchloric acid flames was examined. The results could be correlated with an activation energy of 29 kcal mole^{-1} using the same assumptions and equation as were used by Van Tiggelen to obtain an activation energy of 38 kcal mole^{-1} for methane-oxygen flames. Flame temperature measured by the OH reversal method gave values in good agreement with theoretical flame temperatures.

The effect of addition of inhibitors was also studied. A stoichiometric methane-perchloric acid flame with 3 moles of nitrogen per mole of acid ($HClO_4$) had a burning velocity of 99 cm sec^{-1} (relative to the unburnt gas at 20°C); replacement of 5 moles of nitrogen by hydrogen chloride reduced the burning velocity to 84 cm sec^{-1} and the theoretical flame temperature was decreased by 30°. Addition of 1% by volume of trifluorobromomethane to the original mixture reduced the burning velocity to 89 cm sec^{-1}. This is to be contrasted with the 50% reduction in burning velocity observed by a similar addition of trifluorobromomethane to a methane-oxygen flame.

All these observations suggest that in perchloric acid flames the acid does not decompose into hydrogen chloride or chlorine and oxygen before reacting with the fuel but that some intermediate chlorine-oxygen compound or radical is involved which reacts much more rapidly with the fuel than does oxygen.

A decomposition flame of perchloric acid vapour alone has been stabilized at 1 atmosphere [83]. Analysis of the product gases from a decomposition flame showed a ratio of chlorine to hydrogen chloride of 0.7. This is appreciably greater than the equilibrium ratio of 0.057 expected for a theoretical flame temperature of 1076°K. Correction of the flame temperature for the observed chlorine distribution gives a value of 1160°K since the heat release is greater for chlorine formation:

$$HClO_4 \longrightarrow HCl + 2O_2 \qquad \Delta H = -21 \text{ kcal mole}^{-1} \qquad (56)$$

$$HClO_4 \longrightarrow \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O + \tfrac{7}{4}O_2 \quad \Delta H = -28 \text{ kcal mole}^{-1}. \qquad (57)$$

The observed flame temperature after correction for heat loss from the thermocouple was 1125°K in good agreement with the calculated temperature. The observed burning velocity was 19 cm sec^{-1} (referred to unburnt gas at 210°C).

This was in very good agreement with the value of 20.3 cm sec^{-1} calculated from the Zeldovitch, Frank-Kamenetsky and Semenov equation using parameters obtained by Levy in his study of the thermal decomposition at 250-450°C. It may be inferred that the overall activation energy is about 45 kcal $mole^{-1}$. Different rate-determining steps are probably involved in premixed fuel-acid flames since a hydrogen-perchloric acid flame with 10 moles of added nitrogen and having the same flame temperature as a decomposition flame had a burning velocity about three times as fast as the decomposition flame. Burning velocities could be correlated with an activation energy of 15 kcal $mole^{-1}$ using the Zeldovitch, Frank-Kamenetsky and Semenov equation for a second order reaction.

Recent work has been devoted to obtaining composition and temperature profiles of methane-perchloric acid flames by batch sampling and mass spectrometric analysis.

XI USES

Perchloric acid is used very widely in analytical laboratories and in industry as a solvent for many materials because it does not readily form complexes [91] and for the destruction of organic matter [5, 84]. Smith in particular has pioneered the use of perchloric acid in the wet oxidation of organic material either by the acid alone [171] or with sulphuric [42, 177] or periodic acid [178] and even by use of ammonium perchlorate with nitric and hydrochloric acids [176]. Monk has modified the method which he found to be somewhat unreliable (see also [174, 194]) by addition of nitric acid [123, 134]. Perchloric acid has also been used in the determination of ammonia and nitrogen [22, 125], silica and aluminium [75, 182] and sulphur [17] and has been used in the analysis of coal [188], cosmetics [79], drugs [136] and propellents [104].

Other applications have included extraction of iron compounds and ores by perchloric acid solutions [58, 159]. In particular cation exchange behaviour in perchloric acid has been studied and used for a wide range of cations [128]. Perchloric acid extraction has also been used as a histochemical technique [4]. The extraction of perchloric acid by basic organic solvents has also been studied (Reference [216] reviews earlier work in this field). Deuterium perchlorate has been used as a solvent for spectrophotometry [211].

Perchloric acid has also been applied to the fractionation of deuterium since this is concentrated in the water molecules at the expense of the hydrogen ions [59, 206, 214].

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TABLE 1

Raman and infrared spectra of anhydrous perchloric acid (cm^{-1})

$HClO_4$			$HClO_4$			$HClO_4$		Cl_2O_7		$H_3O^+ClO_4^-$	
Vapour phase			Solid phase			Liquid phase		Gas phase	Solid phase	Solid phase +20°C	Solid phase -10°C
		4750									
3500	3560	3560	3260	3336		3275	3350			3285	3320
		2450		3040						3100	2930
		1450		2329							
1360		1326	1315	1550	1312	1315		1309	1294	1577	
to		1303									
980		1288									
		1263	1283		to			1271	1272		
		1200	1245	1243		1245					
					1182					1175	
		1134	1200			1215	1210				
		1050	1033	1038	1032	1033	1031	1025	1034		
		1047								921	
750		725	740	738	738	743	740				
to		721	760								
690								696, 680	695		

TABLE 1 (Continued)

$HClO_4$			$HClO_4$			$HClO_4$		Cl_2O_7		$H_3O^+ClO_4^-$	
Vapour phase			Solid phase			Liquid phase		Gas phase	Solid phase	Solid phase +20°C	Solid phase −10°C
		632	603					600	612)	627	
									595)		
		579	585	585	585	582	577	571	565		
		560	566		572	571		559	554		
		526									
		519						521	510		
								506	501		
		430	428	436	425	440	424				
		413	371								
			346								
		318									
		307	478			480		472(?)	472	436	
							284	271	270		
Refs: [165]	[160, 161]	[54]	[54]	[40]	[120]	[54]	[168]	[155]	[155]	[193]	[160, 161]

TABLE 2

Cl-O Stretching frequencies

		Stretching frequencies (cm^{-1})	
		Symmetric	Asymmetric
Perchloric acid	$HOClO_3$	1050	1326, 1263 } 1296
Fluorine perchlorate	$FOClO_3$	1049	1298
Perchloryl fluoride	$FClO_3$	1061	1315
Chlorine dioxide	ClO_2	943	1110
Chlorite ion	ClO_2^-	860	952
Chlorate ion	ClO_3^-	930, 930	975, 1087
Perchlorate ion	ClO_4^-	935	1110
Chlorine heptoxide	Cl_2O_7	1034, 1057 } 1045	1260, 1270, 1295 } 1275

TABLE 3

Bond lengths for Cl-O compounds

Compound	Force constant $k \times 10^5$	Bond order	Bond length, Å	
			$r_{obs.}$	$r_{calc.}$
Cl_2O_7	9.32	1.62	1.424 ± 0.01	1.44
$HOClO_3$ (Cl-O)	9.55	1.64	1.42	1.43
(Cl-OH)	3.79	1.05	1.64	1.66
ClO_4	8.20	1.50	1.46 ± 0.01 1.452 ± 0.005	1.47
$FOClO_3$	9.58	1.65	-	1.43
$FClO_3$	9.82	1.67	-	1.43

TABLE 4

Cl-O bond lengths in the perchlorate ion

Compound	Bond length, Å	Source	Ref.
$LiClO_4$	1.44 ± 0.01	Frosen	[141]
$LiClO_4 \cdot 3H_2O$	1.46 ± 0.02		
$XClO_4$	1.43 ± 0.02		
$KClO_4$	1.46 ± 0.05	Mani	[106]
NH_4ClO_4	1.46 ± 0.03	Venkatesan	[207]
$AgClO_4 \cdot C_6H_6$	1.44 ± 0.01 1.51 ± 0.01	Smith	[183]
H_3OClO_4	1.42 ± 0.01	Lee, Carpenter	[97]
H_3OClO_4	1.452 ± 0.005	Truter	[197]
NO_2ClO_4	1.464 ± 0.007	Truter et al.	[198]
H_3OClO_4	1.445 ± 0.006 1.478 ± 0.005 1.465 ± 0.007 1.468 ± 0.006	Nordman	[130]

TABLE 5

Specific heats of perchloric acid

Moles H_2O/mole $HClO_4$	Specific heat, cal gm^{-1} deg C^{-1}	Source	Ref.
0.0	0.288	Trowbridge & Westrum	[196]
3.085	0.501	Berthelot	[15]
5.4	0.575		
9.59	0.6705		
46.35	0.893		
100	0.9466	Richards & Rowe	[142]
590	0.993	Berthelot	[15]

TABLE 6

Heat of solution data

$HClO_4$, n_1 H_2O diluted to $HClO_4$, $(n_1 + n_2)H_2O$

n_1	$n_1 + n_2$	Source	Ref.
0 - 200	600	Berthelot	[15]
2.31 - 55.5	110	Bidinosti & Biermann	[18]
0 - 4	800	Krivtsov et al.	[93]
5.0 - 500,000	∞	Vanderzee & Swanson	[204]

TABLE 7

Heat of formation at infinite dilution

from heat of solution of perchlorates

	Potassium perchlorate	Sodium perchlorate	Lithium perchlorate
Heat of solution, kcal mole^{-1}	+12.115 ± 0.05 [96] +12.31 ± 0.06 [21] +12.14 ± 0.01 [210]	+ 3.326 ± 0.011 [210] + 3.315 ± 0.007 [204]	- 6.25 ± 0.03 [111] - 6.295 ± 0.009 [210]
Mean value, kcal mole^{-1}	+12.14	+ 3.320	- 6.27
ΔH_f for perchloric acid at infinite dilution, kcal mole^{-1}	-31.28 (V-29.73)	-30.97 (V-30.08)	-30.77 (V-29.70)

TABLE 8

Heat of formation, ΔH_5, at dilution

$HClO_4$, n_1H_2O from heat of neutralization, ΔH_2

Base	ΔH_2 kcal mole^{-1}	Source	Reference	ΔH_5 kcal mole^{-1}	n_1
KOH	-13.35	Vorob'ev	[210]	-31.54	4500
NaOH	-13.380	Bidinosti	[18]	-30.94	55.5
NaOH	-13.34	Hale	[66, 67]	-30.99	∞
NaOH	-13.66	Vorob'ev	[210]	-30.94	465
NaOH	-13.336	Vanderzee	[204, 205]	-30.99	∞
LiOH	-13.54	Markowitz	[111]	-30.81	225

TABLE 9

Physical properties of perchloric acid: references

Property	Concentration range				
	0–72%	72%	72–100%	100%	100% and upwards (i.e. Cl_2O_7 rich)
Acidity, H^o scale	[218]		[218]		
Activity coefficient	[76, 146]				
Boiling point		[36]		[115, 164, 165]	
Conductivity, electrical	[23, 92]				
Density	[92, 190, 222]		[190, 222]	[114, 115]	[149]
Heat of fusion				[54, 196]	
Heat of solution	[204]		[93]		[147]
Heat of vaporization		[36]		[164, 165, 221]	
Ionization potential		[72]			
Melting point	[23, 117]			[116, 196]	[225]
Osmotic coefficient	[146]				
Parachor				[190]	
Refractive index	[181]				

TABLE 9 (Continued)

Property	Concentration range				
	0–72%	72%	72–100%	100%	100% and upwards (i.e. Cl_2O_7 rich)
Specific heat	[15]			[196]	
Spectra, electron diffraction				[3]	
infrared			[160, 161]	[54, 98, 165]	
mass	[72]				
Raman				[40]	
ultraviolet	[74]				
Surface tension	[129, 190]			[190]	
Sound, velocity of	[1, 133]			[133]	
Transport numbers	[10, 34, 64]				
Viscosity	[92, 222]		[222]	[226]	

TABLE 10

Premixed perchloric acid flames stabilised

Fuel	Low pressure	Atmospheric pressure
None	-	Su, T, Spectra
Hydrogen	-	Su, T, Spectra
Methane	Su, Spectra	Su, T, Spectra
Ethane	Spectra	Su, Spectra
Carbon monoxide	Su	Su, Spectra
Formaldehyde	Spectra	-
Methyl alcohol	-	Su, Spectra

Su indicates burning velocity measured

T indicates temperature measured

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Common features in the behaviour of the perchlorates are ascertained and comparative data tabulated. Areas for future study are indicated.

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