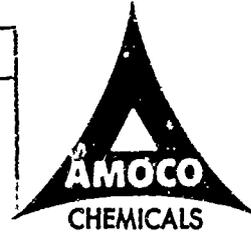


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FINAL REPORT

# PROPELLANTS DIVISION

TECHNICAL REPORT ON THE STUDY

OF

BORON PERCHLORATE AND RELATED SYSTEMS

FOR

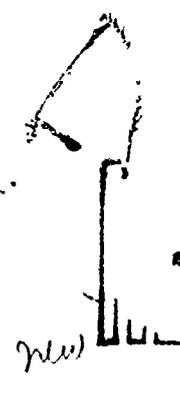
AIR FORCE OFFICE

OF

SCIENTIFIC RESEARCH

WASHINGTON, D. C.

CONTRACT AF 49(638)-1105


  
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OCTOBER 1, 1961 TO SEPTEMBER 30, 1964



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FINAL REPORT

TECHNICAL REPORT ON THE STUDY  
OF  
BORON PERCHLORATE AND RELATED SYSTEMS  
FOR  
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OF  
SCIENTIFIC RESEARCH  
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CONTRACT AF 49(638)-1105

OCTOBER 1, 1961 TO SEPTEMBER 30, 1964

AMOCO CHEMICALS CORPORATION  
PROPELLANTS DIVISION  
SEYMOUR, INDIANA

## FOREWORD

This study was initiated by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, Washington 25, D.C. The research was conducted by Amoco Chemicals Corporation, Propellants Division, Seymour, Indiana, under Contract No. AF 49(638)-1105. Principal investigators for Amoco Chemicals Corporation were Drs. R. A. Mosher, E. K. Ives and E. F. Morello. Major C. J. Donovan of the Propulsion Division was Contract Monitor for Air Force Office of Scientific Research. The research sponsored by this contract was started in October 1961 and completed in October 1964.

## ABSTRACT

The compounds  $\text{BCl}_2\text{ClO}_4$ ,  $\text{BCl}(\text{ClO}_4)_2$  and  $\text{B}(\text{ClO}_4)_3$  have been prepared by the reaction between  $\text{BCl}_3$  and anhydrous  $\text{HClO}_4$ . They are extremely sensitive to moisture undergoing rapid hydrolysis even at  $-78^\circ\text{C}$ . The compounds are also thermally unstable, where  $\text{BCl}_2\text{ClO}_4$  decomposes with evolution of chlorine,  $\text{BCl}(\text{ClO}_4)_2$  with evolution of chlorine and chlorine heptoxide and  $\text{B}(\text{ClO}_4)_3$  with evolution of chlorine heptoxide. All three compounds on decomposition give a residue which contains B, O, and  $\text{ClO}_4$ . The chloroperchlorates also undergo disproportionation reactions by loss of  $\text{BCl}_3$ , especially under vacuum treatment. Density, refractive index, molecular weight and surface tension have been determined for the boron chloroperchlorates. Molar refractivity and the parachor were calculated for the chloroperchlorates and both give values which agree closely with values for the postulated compounds. Heat of hydrolysis was determined calorimetrically for  $\text{BCl}_2\text{ClO}_4$  and from this, a value for the heat of formation was derived which agrees closely with a calculated value. The chloroperchlorates give solid adducts with  $(\text{CH}_3)_3\text{N}$ , the stability decreasing from  $\text{BCl}_2\text{ClO}_4$  to  $\text{BCl}(\text{ClO}_4)_2$ . The triperchlorate did not form an adduct with trimethylamine but did form a somewhat stable adduct with nitronium perchlorate. The reaction of some non-metal halides and anhydrous  $\text{HClO}_4$  were investigated briefly with the following results. One or two chlorine atoms in  $\text{PCl}_5$  can be replaced to give  $\text{PCl}_4\text{ClO}_4$  or  $\text{PCl}_3(\text{ClO}_4)_2$  both of which are white solids stable at room temperature. One or two chlorine atoms in  $\text{SiCl}_4$  can be replaced with  $\text{ClO}_4$  to give liquids stable at room temperature. An oxidation reaction occurs with  $\text{PCl}_3$ , and with  $\text{XeF}_4$  a decomposition reaction takes place probably preceded by dehydration of the perchloric acid. Exchange reactions between  $\text{BCl}_2\text{ClO}_4$  and  $\text{BF}_3$  gave only partial replacement of Cl by F, and replacement of both perchlorate and halogen occurs with chlorine trifluoride.

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## INTRODUCTION

In 1959 personnel associated with Amoco Chemicals Corporation became interested in the possibilities of polyvalent metal perchlorate systems for propellant applications as these systems were felt to offer unappreciated advantages. Company funded research demonstrated feasibility of such systems for delivering high impulse, and among the systems studied was one concerned with a new compound, boron perchlorate. In view of the fact that data on this compound was non-existent, except insofar as our research had provided, physical and chemical properties appeared particularly intriguing and it was felt important that adequate scientific study of this compound be conducted to elucidate the nature of the compound as the basis for future applied research. The Air Force Office of Scientific Research agreed to fund this program<sup>2</sup> and research was initiated under Contract No. AF49(638)-1105.

Boron perchlorate,  $B(ClO_4)_3$ , is of scientific interest because its structure and general chemistry reflect the non-polar nature of boron plus the polarity of the perchlorate group. The possible practical interest in propellants is obvious because of its high content of oxygen and the availability of boron for formation of boron nitride when used in nitrogenous systems. The latter was not the prime concern of this program, however. The program was designed to be of a scientific nature directed toward development of synthetic methods for preparation of boron perchlorate and its adducts followed by a systematic study of the chemical and physical properties of the system as well as determination of thermodynamic parameters. This work to be described was based on the study of these materials for the purpose of obtaining sufficient data of an unclassified nature to allow publication in the technical literature.

The general unstable nature of the boron perchlorate system and extension of the general synthesis reactions to some non-metal systems has provided quite diverse chemical reactions and new chemical compounds for study. The general areas of research conducted on this program to be described in this report are summarized below:

- (1) Synthesis and Structure Determination
- (2) Chemical and Physical Properties
- (3) Thermodynamic Properties
- (4) Decomposition Reactions
- (5) Methods of Stabilization
- (6) Study of Other Non-Metallic Perchlorates

## TECHNICAL DISCUSSION

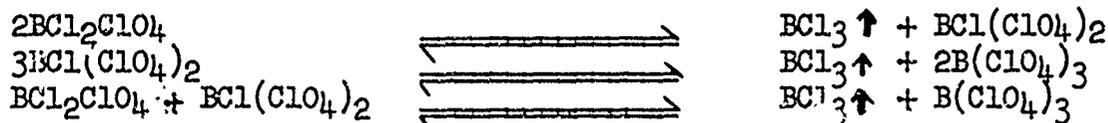
### A. Preparation and Properties of Compounds

The reaction of boron trichloride and anhydrous perchloric acid proceeds smoothly at  $-78^{\circ}\text{C}$ . with the evolution of HCl to give a quantitative yield of  $\text{BCl}_2\text{ClO}_4$ ,  $\text{BCl}(\text{ClO}_4)_2$  or  $\text{B}(\text{ClO}_4)_3$ . The compound or mixture of compounds formed is governed by the ratio of  $\text{BCl}_3$  to  $\text{HClO}_4$  used in the reaction. (Table I, reactions 12, 13, 24, 25). Best results are obtained by adding  $\text{HClO}_4$  to the  $\text{BCl}_3$ , thus avoiding the oxidizing effect of an excess of  $\text{HClO}_4$  in the reaction mixture. Prepared in this way, the compounds were usually pure white solids or liquids. The use of a solvent such as  $\text{CCl}_3\text{F}$  or perfluorobutene seemed to be advantageous in the case of the boron triperchlorate (Table I, reaction 25).

Silver perchlorate and boron trichloride, gave  $\text{BCl}_2\text{ClO}_4$  as the only isolatable product. The di- and triperchlorates could not be separated from the silver chloride precipitate without decomposition. The dichloroperchlorate was best prepared by treating  $\text{AgClO}_4$  at  $-78^{\circ}\text{C}$ . with an excess of  $\text{BCl}_3$  which also acted as a solvent. The excess of  $\text{BCl}_3$  was removed and the  $\text{BCl}_2\text{ClO}_4$  was rapidly distilled to avoid disproportionation reactions. The boiling point of the  $\text{BCl}_2\text{ClO}_4$  was minus  $30-31^{\circ}\text{C}$ . at 0.3mm. and minus  $38-39^{\circ}\text{C}$ . at 0.01mm. (Table I, reactions 14, 15, 16).

Investigation of the solid-gas phase reaction of boron trichloride with silver perchlorate has demonstrated that the diperchlorate and monoperchlorate of boron can be synthesized by this method and correspond in properties to the products synthesized by the perchloric acid method. In general, tube reactions give low yields of mixtures as control of reaction variables, such as boron trichloride flow and surface area of silver perchlorate, are difficult to control. Reaction at low temperatures ( $-22^{\circ}\text{C}$ .) has given the diperchlorate of boron while reaction at ambient temperatures gives mixtures of the di- and monochloroperchlorates of boron in addition to decomposition products of the boroxole type. Apparently, residence time on the silver perchlorate is sufficiently short so that decomposition does not go to completion before materials are collected at Dry Ice temperatures. These mixtures have been separated (Reaction No. 11) by vacuum distillation at very low pressures and analysis of weighed samples of the di- and monoperchlorate fractions substantiate these structures. The majority of the reacted material remains on the silver chloride and unreacted silver perchlorate in the reaction tube, probably as the triperchlorate or its decomposition products.

The chloroperchlorates of boron in addition to being sensitive to heat and moisture also show another type of instability. These compounds readily undergo exchange reactions similar in nature to those observed for the alkyl chloroborinates,  $\text{BCl}_2\text{OR}$  and  $\text{BCl}(\text{OR})_2$  formed by the reaction of alcohols or phenols with  $\text{BCl}_3$ .



This property makes purification of the chloroperchlorates by vacuum distillation difficult, since the loss of volatile  $\text{BCl}_3$  is a driving force for the reaction. Disproportionation is extremely slow at  $-78^\circ\text{C}$ ., but proceeds at a moderate rate at  $-40$  to  $-45^\circ\text{C}$ . Even at  $-16^\circ\text{C}$ . under atmospheric pressure, exchange takes place as shown by change in analysis of samples taken at different times.

A sample of  $\text{BCl}(\text{ClO}_4)_2$  held at  $-78^\circ\text{C}$ . under 0.005mm. of Hg for three hours showed no detectable disproportionation, but at  $-40$  to  $-45^\circ\text{C}$ . and 0.01mm. of Hg the material disproportionated and at the end of four hours the residue in the flask analyzed approximately for  $\text{B}(\text{ClO}_4)_3$ .

The compound  $\text{BCl}_2\text{ClO}_4$  has been distilled by employing a rapid vacuum distillation and did not show appreciable disproportionation. Only a small percentage of the compound could be distilled before disproportionation occurred in the residue, however.

#### B. Analysis of Compounds

Analyses were carried out on the hydrolysates of the perchlorates by titration methods. Total strong acid, hydrochloric and perchloric, was determined by titration with standard sodium hydroxide to a methyl red endpoint. Any chlorine present was destroyed by 0.1N thiosulfate solution. Boron was determined on the same aliquot by adding mannitol after the methyl red endpoint was reached and then titrating to a phenolphthalein endpoint. Chloride was determined on a separate aliquot by the Volhard method. Perchlorate was obtained by subtracting the amount of chloride from the total amount of strong acid. In some cases, perchlorate was also determined by reduction with excess stannous chloride in the presence of molybdate catalyst followed by titration with permanganate of the excess stannous chloride.<sup>3</sup>

#### C. Physical Properties

A tabulation of physical properties determined on the boron chloroperchlorates is given below:

| <u>Compound</u>              | <u><math>d_4^{-16}</math></u> | <u><math>n_D^{-16}</math></u> | <u>Surface Tension</u><br><u>Dynes/cm</u> | <u>Mol</u><br><u>Wt.</u> |
|------------------------------|-------------------------------|-------------------------------|---|--------------------------|
| $\text{BCl}_3$               | 1.410                         | 1.4132                        | 22.6                                      | -                        |
| $\text{HClO}_4$              | 1.839                         | 1.3976                        | 38.8                                      | -                        |
| $\text{BCl}_2\text{ClO}_4$   | 1.728                         | 1.4288                        | 30.1                                      | 180                      |
| $\text{BCl}(\text{ClO}_4)_2$ | 1.872                         | 1.4348                        | 34.4                                      | 242                      |

A discrepancy is noted between the density of  $\text{BCl}_3$  given in the literature ( $d_4 = 1.434$ ) and our value. Therefore, density determinations for  $\text{BCl}_3$  were made at  $0^\circ\text{C}$ . and  $-16^\circ\text{C}$ . in a calibrated pycnometer. The values obtained were  $d_4 = 1.375$  and  $d_4^{-16} = 1.415$ . The value at  $-16^\circ\text{C}$ . compares well

with the value obtained using the Fisher Davidson Gravitometer. It appears that the literature value of 1.434 which was traced to A. Ghira<sup>4</sup> is in error.

#### D. Structure of Compounds

##### 1. Analysis and Molecular Weight

Chemical analysis and cryoscopic molecular weight determinations indicate quite clearly that our proposed structures for the compounds are correct. Boron triperchlorate was not measured due to its insolubility in inert solvents.

##### 2. Molecular Refractivity

Values for the molecular refractivity of  $\text{HClO}_4$ ,  $\text{BCl}_3$ ,  $\text{BCl}_2\text{ClO}_4$  and  $\text{BCl}(\text{ClO}_4)_2$  at  $-16^\circ\text{C}$ . were calculated using the equation of Lorenz and Lorentz (Table I). The experimentally determined values of the molecular refractivity ( $M_D$ ) for boron trichloride and perchloric acid and the known values of the molecular refractivity of the elements (H, O, Cl) allow a value for boron (2.83) to be obtained. Applying the additive nature of the molecular refractivity to  $\text{BCl}_2\text{ClO}_4$ ,  $\text{BCl}(\text{ClO}_4)_2$  and  $\text{HClO}_4$ , values of  $M_D$  for the  $\text{ClO}_4$  group were obtained (Table I). Good agreement for the  $\text{ClO}_4$  group is noted for the three compounds, and these values together with other data help to substantiate the structure postulated for these compounds. Good agreement is also noted between calculated and experimental values of  $M_D$  for the boron chloroperchlorates. Radell et. al.<sup>5</sup> in their paper on alkyl perchlorates calculated  $M_D$  for n-hexyl and n-octyl perchlorate and corrected values of 12.76 and 12.08, respectively, using their data were obtained for the  $\text{ClO}_4$  group. This is in excellent agreement with our values,  $M_D(\text{ClO}_4) = 12.33$  (average). Results are summarized in Table I.

##### 3. Parachor

Values of the parachor were calculated for  $\text{BCl}_3$ ,  $\text{BCl}_2\text{ClO}_4$ ,  $\text{BCl}(\text{ClO}_4)_2$  and  $\text{HClO}_4$  using the standard equation and assuming the vapor density was small enough to be neglected. The results are summarized in Table II.

The values are in excellent agreement and the deviation is well within experimental error. Calculated parachor values are based on nonpolar bonding between boron and the perchlorate group.

##### 4. Infrared Spectra

The boron chloroperchlorates show infrared absorption bands corresponding to B-Cl, B-O, and Cl-O stretching frequencies (Table III). The spectra of  $\text{BCl}_2\text{ClO}_4$  and  $\text{BCl}(\text{ClO}_4)_2$  in  $\text{CCl}_4$  are similar except that in the latter compound one of the B-Cl bands at  $949\text{ cm}^{-1}$  is missing. When the gas phase spectrum of  $\text{BCl}(\text{ClO}_4)_2$  was tried only the spectrum of  $\text{BCl}_2\text{ClO}_4$  was obtained indicating that

TABLE I

## MOLECULAR REFRACTIVITY DATA

| <u>Compound</u>                     | Molecular Refractivity |                   |              |              |                              |
|-------------------------------------|------------------------|-------------------|--------------|--------------|------------------------------|
|                                     | $\frac{-16}{d_4}$      | $\frac{-16}{n_D}$ | <u>Calc.</u> | <u>Expt.</u> | <u>ClO<sub>4</sub> Group</u> |
| BCl <sub>3</sub>                    | 1.410                  | 1.4132            | -            | 20.74        | -                            |
| BCl <sub>2</sub> ClO <sub>4</sub>   | 1.728                  | 1.4288            | 26.84        | 27.02        | 12.25                        |
| BCl(ClO <sub>4</sub> ) <sub>2</sub> | 1.872                  | 1.4348            | 32.94        | 34.16        | 12.68                        |
| HClO <sub>4</sub>                   | 1.839                  | 1.3976            | -            | 13.17        | 12.07                        |

|                  |                          |
|------------------|--------------------------|
| Hydrogen         | - M <sub>D</sub> = 1.10  |
| Chlorine         | - M <sub>D</sub> = 5.97  |
| Boron            | - M <sub>D</sub> = 2.83  |
| BCl <sub>3</sub> | - M <sub>D</sub> = 20.97 |

TABLE II

## PARACHOR VALUES

| <u>Compound</u>                     | <u>Experimental</u> | <u>Calculated</u> |
|-------------------------------------|---------------------|-------------------|
| BCl <sub>3</sub>                    | 181.3               | 178.8             |
| HClO <sub>4</sub>                   | 136.4               | 135.5             |
| BCl <sub>2</sub> ClO <sub>4</sub>   | 245.6               | 248.5             |
| BCl(ClO <sub>4</sub> ) <sub>2</sub> | 317.4               | 318.5             |

$$B = 17.1$$

$$Cl = 54.3$$

TABLE III

## INFRARED ABSORPTION BANDS

|  | <u>Cl-O</u> | <u>B-Cl</u> | <u>Cl-O</u>  | <u>B-O</u> | <u>B-O</u> | <u>Cl-O</u> | <u>Cl-O and B-O</u> |
|--|-------------|-------------|--------------|------------|------------|-------------|---------------------|
| $\text{BCl}_3(\text{g})$                   |             | 960         | 1000         |            |            |             |                     |
| $\text{BCl}_3(\text{CCl}_4)$               |             | 945         | 983          |            |            |             |                     |
| $\text{BCl}_2\text{ClO}_4(\text{g})$       | 700         | 955         | 1005         | 1033       |            | 1190        | 1225                |
| $\text{BCl}(\text{ClO}_4)_2(\text{CCl}_4)$ | 693         |             | 1001         | 1024       | 1039       | 1169        | 1218 1277           |
| $\text{BCl}_2\text{ClO}_4(\text{CCl}_4)$   | 694         | 949         | 1003         | 1029       | 1042       | 1179        | 1218 1285           |
| $\text{B}(\text{OEt})_3(\text{l})$         |             |             |              | 1049       | 1104       |             |                     |
| $\text{HClO}_4(\text{g})$                  | 728         |             | 1046<br>1099 |            |            | 1118        | 1258 1308           |
| $\text{Cl}_2\text{O}_7(\text{g})$          |             |             | 1020         |            |            |             | 1306                |
| $\text{ClO}_3\text{F}^6$                   |             |             | 1075         |            |            | 1191        |                     |
| $\text{ClO}_3^7$                           |             |             | 1061         |            |            |             | 1315                |
| $\text{RCIO}_4^3$                          | 704<br>709  |             | 1035         |            |            |             | 1230 1260           |

disproportionation occurred under the experimental conditions. The spectrum of the diperchlorate could not be obtained as a gas due to its tendency to disproportionate.

#### E. Thermodynamic Properties

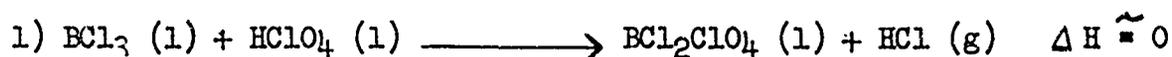
A calorimeter system for measuring heat of reaction has been fabricated and experiments to measure heat of hydrolysis for the dichloroperchlorate of boron have been completed. Since these compounds are thermally unstable and undergo vigorous hydrolysis, a technique for sealing samples in bulbs containing solvent was devised. The samples were dissolved in carbon tetrachloride during weigh-up so that the  $\text{BCl}_2\text{ClO}_4$  would be stable at  $25^\circ\text{C}$ . and also to moderate the hydrolysis reaction.

Using the above techniques, five final runs were made which gave very good results, and these are summarized below:

| <u>Run No.</u> | <u>Mole % <math>\text{BCl}_2\text{ClO}_4</math> in <math>\text{CCl}_4</math></u> | <u><math>\Delta H</math> (Obs.) Kcal.</u> |
|----------------|--|---|
| 1              | 53.0   | 73.6                                      |
| 2              | 32.2   | 72.9                                      |
| 3              | 88.9   | 73.6                                      |
| 4              | 29.5   | 72.4                                      |
| 5              | 45.8   | 72.8                                      |

By running samples in carbon tetrachloride solvent at various molar concentrations, it was possible to extrapolate experimental values to eliminate any solution effects of the carbon tetrachloride solvent and to obtain the true heat of hydrolysis of the dichloroperchlorate. Only a slight heat of solution in carbon tetrachloride was noted and a plot of the data to 100%  $\text{BCl}_2\text{ClO}_4$  did not differ radically from results in solvent. A  $\Delta H$  (obs.) of  $-73.7$  kcal./mole corresponds to the extrapolated value for the pure material. Skinner<sup>6</sup> gives a heat of hydrolysis for boron trichloride of  $-69.2$  kcal./mole which compares favorably with our experimental value.

An approximate heat of formation  $\Delta H_f$  of  $\text{BCl}_2\text{ClO}_4$  was calculated to be  $-92.0$  kcal./mole from known heats of formation from the following equation assuming the heat of reaction to be low.



This provided an approximate value of heat of hydrolysis ( $-71.8$  kcal./mole) which compares favorably with our experimental value of  $73.7$  kcal./mole for pure  $\text{BCl}_2\text{ClO}_4$ . Our experimental value for the heat of hydrolysis gives a value of the heat of formation  $\Delta H_f$  of  $-90.0$  kcal./mole for  $\text{BCl}_2\text{ClO}_4$  at  $25^\circ\text{C}$ . The difference in the calculated and experimental values of 2 kilocalories is actually in fair agreement and indicates the heat of reaction in Reaction (1) is indeed low. Skinner, using a similar apparatus for obtaining the heat of hydrolysis of boron trichloride, obtained a value of  $\Delta H_f$  of  $-103.0 \pm 1.0$  kcal./mole so there can be at least 1 kilocalorie variation possible.

Calorimeter runs were made with the diperchlorate of boron,  $\text{BCl}(\text{ClO}_4)_2$ , but samples gave values for  $\Delta H$  (obs.) of -61.8 and -54.7 kcal./mole which were low compared to the calculated theoretical value,  $\Delta H$  (calc.) = -74.2. Individual runs were also not in very good agreement. The variation results from product decomposition, as the calorimeter bulb solution developed a yellow coloration when brought to room temperature. The original  $\text{BCl}(\text{ClO}_4)_2$  was slightly yellow in color although it gave a satisfactory analysis. These calorimetric runs were repeated with repurified carbon tetrachloride and a new preparation of  $\text{BCl}(\text{ClO}_4)_2$  as the latter compound had previously appeared to be stable in carbon tetrachloride solution at room temperature. However, the values obtained for  $\Delta H$  (obs.) were -48.7 and -49.6 kcal./mole. This large deviation is a result of product decomposition and/or solvent interaction as evidenced by color formation in the samples when conditioned at 24°C. prior to hydrolysis.

A more inert solvent, fluorotrichloromethane, was employed in order to eliminate solvent interaction; but the samples reacted violently on hydrolysis shattering the Dewar calorimeter when an ampoule containing the sample was broken under water. Presumably, the  $\text{CCl}_3\text{F}$  solvent was too volatile to moderate the reaction. Suitable solvents for the diperchlorate, are limited and this experiment concluded calorimetric measurements with this material since a satisfactory solvent could not be found.

The heat of solution of carbon tetrachloride in water was determined and the resulting small temperature rise would not be significant in affecting the values for the heats of hydrolysis reported.

The triperchlorate was more of a problem due to its greater instability even at relatively low temperatures and a suitable solvent for reaction moderation has not been found. Conducting heats of hydrolysis measurements at low temperature is a tedious operation and was not felt to be worthwhile as the heat of hydrolysis values of the intermediate dichloro compound appear to be in reasonable agreement with theoretical values and should allow estimation of properties for the triperchlorate with reasonable accuracy.

In order to check the results obtained with our calorimeter, the heat of hydrolysis of  $\text{BCl}_3$  in  $\text{CCl}_4$  was determined. The results are summarized in the following table:

| <u>Run No.</u> | <u>Mole % <math>\text{BCl}_3</math> in <math>\text{CCl}_4</math></u> | <u><math>\Delta H</math> (Obs.) Kcal.</u> |
|----------------|--|---|
| 1              | 42.3   | 71.2                                      |
| 2              | 65.6   | 70.0                                      |
| 3              | 67.8   | 70.2                                      |
| 4              | 58.7   | 68.8                                      |
| 5              | 56.5   | 69.9                                      |

There was no detectable heat of solution effect and the average value for the heat of hydrolysis was  $\Delta H$ (obs.) = -70.0 kcal./mole. From the heat of hydrolysis of  $\text{BCl}_3$  a heat of formation was calculated and found

to be  $H_f = -102.3$  kcal./mole. Skinner<sup>7</sup> obtained a value of  $H_f = -103.0$  kcal./mole for  $BCl_3$  also by a hydrolysis method but without solvent. Agreement between the two methods is good.

#### F. Decomposition Reactions

Preparatory to conducting kinetic studies on the decomposition of the boron perchlorates, information was needed as to products of decomposition. A sample of  $BCl_2ClO_4$  was allowed to vaporize under vacuum into an infrared gas cell and decompose at room temperature. The only spectrum noted was that of gaseous  $BCl_2ClO_4$ . A yellow gas was evolved but was not  $ClO_2$  since it gave no spectrum. In another experiment a sample of  $BCl_2ClO_4$  was allowed to decompose at room temperature and the gas was collected. It proved to be chlorine from its boiling and freezing points. When  $BCl_2ClO_4$  decomposes thermally, it might be expected that  $ClO_2$  would be one of the products; but under the conditions used, only  $Cl_2$  was detected as a decomposition product.

Kinetic studies of the  $BCl(ClO_4)_2$  decomposition reaction have been completed by determining the free chlorine evolved during decomposition and a rather complex system is indicated. Decomposition of the diperchlorate of boron was allowed to proceed at  $0^\circ$  to  $10^\circ C$ . in separate experiments, and an induction period was observed. Rapid initial evolution of chlorine then occurred followed by a first order decomposition. The residue had an approximate 1:1 ratio of boron to perchlorate and was free of chlorine but has not been fully characterized. Based on a material balance, the oxygen to boron ratio was also 1/1 suggesting a cyclic boroxole perchlorate structure.

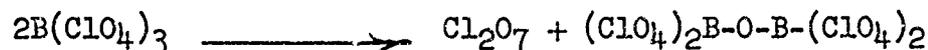
The decomposition of boron dichlorperchlorate was similar to that of the diperchlorate except for a longer induction period followed both by a surge of chlorine and a rapid rise in temperature. The formation of chlorine was too erratic to specify the kinetic order in this case, as temperature could not be controlled due to the exothermic nature of the decomposition. As with the previous compound, the main products of reaction were chlorine and supposedly the suggested boroxole compound, however a small amount of  $Cl_2O_7$  was also isolated as a product of the decomposition.

To provide a better understanding of the mechanism of chlorine formation during the decomposition of the mono- and diperchlorates, a large excess (over a 1/1 molar basis) of boron trichloride was allowed to condense into  $Cl_2O_7$  to ascertain whether a similar oxidation-reduction reaction would occur. Some reaction did occur at both  $-78^\circ C$ . and  $0^\circ C$ ., but no chlorine was generated.

It was thought that perhaps  $Cl_2O_7$  and the chloride ion would give an oxidation-reduction reaction to form molecular chlorine, but this was not the case. The actual products have not been thoroughly investigated except for simple chemical analyses which indicate a direct replacement of chloride has occurred rather than any oxidation-reduction reaction. Apparently internal oxidation-reduction is more facile or the mechanism of decomposition of the chloroperchlorates involves a radical such as  $.ClO_4$  or  $.ClO_3$  which can enter into an oxidation-reduction reaction with the chloride ion.

The decomposition mechanism of boron triperchlorate was also studied, but the reaction takes an alternate course. When the perchlorate was allowed to decompose at 0°C. or higher, a liquid and a solid phase were formed. When the mixture was evacuated, a white solid remained, analysis of which was dependent on reaction time and temperature. For example, boron to perchlorate ratios could be varied from 1:1 to 3:1. The solid reaction product is somewhat intractable and very little has been done to identify it. The very pale yellow distillate is a liquid at -78°C. and has been identified as chlorine heptoxide by chemical analysis and by comparison of its infrared spectrum with the spectrum of chlorine heptoxide prepared from anhydrous perchloric acid and phosphorus pentoxide. The spectrum of chlorine heptoxide prepared by this method has been run in this laboratory and also appears in the literature.<sup>8</sup>

A similar decomposition experiment was conducted under vacuum conditions at 0°C. and less color formation was noted; presumably removal of Cl<sub>2</sub>O<sub>7</sub> as formed prevented side reactions from occurring. A steady decline in rate of generation of chlorine heptoxide was observed after a small initial surge; and after several hours, the rate of decomposition drops off rapidly to form a relatively stable intermediate. This residue is a white solid which melts about 25-26°C. The compound contains a boron to perchlorate ratio of 1/2 and could well have originated from the simple decomposition scheme shown in the following equation.



An infrared spectrum of this material also indicates that this suggested product is not unreasonable. This intermediate decomposition product was unstable at higher temperatures and was observed to decompose further at room temperature. The products were again the somewhat volatile chlorine heptoxide (plus small amounts of some lower oxides of chlorine) and a brittle polymeric-like material that had a boron to perchlorate ratio of 3:1. The latter compound was stable for several days at ambient temperatures but was still sensitive to moisture.

The stability of the three boron perchlorate compounds is indicated by the induction periods which were noted in the kinetic studies of the decomposition. The induction periods are tabulated below:

| <u>Compound</u>                     | <u>Induction Period</u>           |
|-------------------------------------|-----------------------------------|
| BCl <sub>2</sub> ClO <sub>4</sub>   | 6 hrs. at 0°C., 2.5 hrs. at 10°C. |
| BCl(ClO <sub>4</sub> ) <sub>2</sub> | 30 min. at -12°C. and 0°C.        |
| B(ClO <sub>4</sub> ) <sub>3</sub>   | None at 0°C.                      |

#### G. Stabilization

Adduct formation has a bearing on stabilization of the boron perchlorates and investigations have been completed on this phase of the program. Trimethylamine was reacted with dichloroperchlorate in perfluorocyclobutane with the amine in excess and has resulted in formation of a white solid stable to ambient temperatures. The solid was water insoluble and was analyzed with the following results:

| <u>Analysis</u>       | <u>Found (%)</u> | <u>Calc. for <math>\text{BCl}_2\text{ClO}_4 \cdot \text{N}(\text{CH}_3)_3</math></u> |
|-----------------------|------------------|--|
| Boron                 | 5.31             | 4.51   |
| Chloride              | 5.33             | 29.55  |
| Perchlorate           | 40.98            | 44.45  |
| $\text{Me}_3\text{N}$ | -                | 24.58  |

If the percentages are converted to a molar basis and it is assumed that trimethylamine accounts for the difference of 48.38%, the following result: B = 1.19;  $\text{ClO}_4$  = 1.00; Cl = 0.35 and  $\text{Me}_3\text{N}$  = 1.99. It appears that using an excess of trimethylamine for adduct formation results in loss of chlorine to a large extent and to incorporation of two moles of trimethylamine. Under the conditions used, trimethylamine may merely be replacing the chlorine; however, the white solid does not melt at temperatures to 330°C. which would indicate adduct formation has occurred.

Additional runs were carried out to prepare trimethylamine adducts of  $\text{BCl}_2\text{ClO}_4$  and  $\text{BCl}(\text{ClO}_4)_2$ . A solvent is necessary to moderate the reaction; otherwise, explosive decomposition occurs and no adduct is obtained. Perfluorobutene or trichlorofluoromethane are suitable solvents for this reaction. It was difficult to obtain satisfactory analysis of the adduct, but a structure of  $\text{Me}_3\text{N} \cdot \text{BCl}_2\text{ClO}_4$  is assumed for the compound. The amine adduct does not appear to react with water, and water washing of the adduct gave some improvement in analysis as shown in the following table.

| <u>Constituent</u>    | <u>Calculated (%)</u> | <u>Found (%)</u> |               |
|-----------------------|-----------------------|------------------|---------------|
|                       |                       | <u>Original</u>  | <u>Washed</u> |
| B                     | 4.51                  | 4.68             | 5.01          |
| Cl                    | 29.55                 | 21.41            | 27.70         |
| $\text{ClO}_4$        | 41.45                 | 58.65            | 40.20         |
| $\text{Me}_3\text{N}$ | <u>24.58</u>          | <u>22.44</u>     | <u>25.32</u>  |
|                       | 100.00                | 107.18           | 98.23         |

The adduct is a white solid stable at room temperature and not too soluble in water. It does not have a melting point but ignites in air with a flash when heated on a spatula to high temperatures.

The trimethylamine adduct of  $\text{BCl}(\text{ClO}_4)_2$  was prepared similarly and was a grey solid also stable at room temperature. It was analyzed but gave poor agreement with a theoretical 1:1 adduct. After washing with water and re-drying, analysis gave an anomalous boron value as shown below and additional work would be necessary for structure elucidation:

| <u>Constituent</u>    | <u>Calculated (%)</u> | <u>Found (%)</u> |                     |
|-----------------------|-----------------------|------------------|---------------------|
|                       |                       | <u>Original</u>  | <u>Washed</u>       |
| B                     | 3.55                  | 4.08             | 6.60                |
| Cl                    | 11.65                 | 9.80             | 13.01               |
| $\text{ClO}_4$        | 65.37                 | 58.05            | 76.06               |
| $\text{Me}_3\text{N}$ | <u>19.42</u>          | <u>20.40</u>     | <u>Not Analyzed</u> |
|                       | 99.99                 | 92.33            | 95.67               |

In view of the radical change in analysis with water treatment the amine adduct of chlorodiperchlorate appears more sensitive to hydrolysis. This is further substantiated by the fact that the adduct lost all of its chlorine when recrystallization from ethanol was attempted.

Attempts to prepare the  $\text{Me}_3\text{N}$  adduct of  $\text{B}(\text{ClO}_4)_3$  have been unsuccessful. The primary difficulties have been that the triperchlorate is insoluble at  $-78^\circ\text{C}$ . in inert solvents such as hexafluoroacetone, perfluorobutene and trichlorofluoromethane; and it reacts with more polar solvents. At  $-17^\circ\text{C}$ . it is insoluble in all the above inert solvents except carbon tetrachloride with which it reacts to liberate free chlorine.

One of the methods proposed for stabilization of the boron perchlorates involves formation of the fluoro analogues,  $\text{BF}_2\text{ClO}_4$  and  $\text{BF}(\text{ClO}_4)_2$ . Formation of free chlorine in the decomposition of the chloro intermediates indicates this substitution should be promising for stabilization, and work emphasized this line of attack. Direct reaction of boron trifluoride with anhydrous perchloric acid or silver perchlorate in solvents has not been successful in providing the desired compounds and two other synthetic methods were tested. The first involved passing boron trifluoride over silver perchlorate suspended in a tube heated to  $65^\circ\text{C}$ . Under anhydrous conditions no reaction occurred; and in the presence of trace amounts of water only reaction of the boron trifluoride and water was observed. An alternate method investigated an exchange reaction involving  $\text{BCl}_2\text{ClO}_4$  and boron trifluoride. This latter method met with limited success as partial replacement of chloride was obtained. The following analysis is typical (molar ratios):

Boron - 1.00  
Chloride - 0.76  
Perchlorate - 1.82  
Fluoride - 0.23

It is apparent that disproportionation of the monoperochlorate to the diperochlorate and  $\text{BCl}_3$  has occurred under vacuum treatment, but only partial replacement of chlorine by fluorine has occurred. Additional work on this replacement reaction would be necessary to determine whether it could be made to yield the compounds  $\text{BF}_2\text{ClO}_4$  or  $\text{BF}(\text{ClO}_3)_2$ . Attempts to replace Cl by F in  $\text{BCl}(\text{ClO}_4)_2$  through the use of  $\text{ClF}_3$  failed to give the fluoro-perchlorate. There was vigorous reaction between the two compounds at near liquid  $\text{N}_2$  temperatures without solvent or with  $\text{Cl}_2$  as solvent, but the exact course of the reaction has not been determined. It appears that only only is Cl replaced by F but also  $\text{ClO}_4$  groups were replaced.

Nitronium perchlorate formed a reasonably stable complex with  $\text{B}(\text{ClO}_4)_3$ . The material melted at approximately  $135^\circ\text{C}$ . with decomposition. The analysis gave molar ratios as follows:

Boron - 1.31  
Perchlorate - 5.45  
Nitro - 1.26

## H. Reaction of Other Halides with Perchloric Acid

### 1. Phosphorus Trichloride

Phosphorus trichloride and anhydrous perchloric acid in a 1:1 molar ratio reacted vigorously at  $-78^{\circ}\text{C}$ . to give a solid product stable at room temperature. Some chlorine was also evolved in the reaction. The reaction involved both oxidation of  $\text{P}^{+3}$  to  $\text{P}^{+5}$  as well as subsequent replacement of some of the chloride.

### 2. Phosphorus Pentachloride

The pentachloride did not react with anhydrous  $\text{HClO}_4$  at  $-78^{\circ}\text{C}$ . but proceeded at  $-30^{\circ}\text{C}$ . to give either a mono- or diperchlorate, depending upon the ratio of reactants. More chloride was not replaced even with an excess of  $\text{HClO}_4$ . The diperchlorate was soluble in chloroform at room temperature.

### 3. Silicon Tetrachloride

Silicon tetrachlorides will react with  $\text{HClO}_4$  to form either a mono- or diperchlorate. The reaction did not proceed further even at room temperature and with an excess of  $\text{HClO}_4$  present. The monoperchlorate was a colorless liquid stable at room temperature while the diperchlorate was a stable white solid melting about  $25^{\circ}\text{C}$ . Schmeisser<sup>7</sup> prepared  $(\text{Si}(\text{ClO}_4)_4)_4$  by the reaction of  $\text{AgClO}_4$  and  $\text{SiCl}_4$  in either solution and indicated the compound to be explosive although he did not isolate it in pure form.

### 4. Xenon Tetrafluoride

Xenon tetrafluoride and perchloric acid react between  $-110^{\circ}\text{C}$ . and liquid nitrogen temperatures without formation of xenon perchlorate. It may be that  $\text{XeF}_4$  dehydrates  $\text{HClO}_4$  to give  $\text{Cl}_2\text{O}_7$ , but this is not certain. Xenon disappears and the main isolatable product analyzes for equal parts of F and  $\text{ClO}_4$ . It is possible the  $\text{FClO}_4$  is formed since this compound is synthesized by the reaction of  $\text{F}_2$  and  $\text{HClO}_4$ .  $\text{XeF}_4$  is an extremely powerful fluorinating agent and could react in the same manner as  $\text{F}_2$ .

## EXPERIMENTAL RESULTS

### A. Anhydrous Perchloric Acid

The general procedure of G. Frederick Smith<sup>10</sup> was used with minor modifications. A one piece all glass apparatus with removable flasks was constructed for the preparation. Vacuum was applied through a side-arm equipped with an Ascarite tube which was isolated from the system by means of a fritted glass disc. KEL-F No. 90 grease was used on the top half of the ground glass joints without incident. Twenty ml. of 72% perchloric acid, Analytical Reagent Grade, was placed in a 200 ml. round bottom flask and 80 ml. of 20% fuming sulfuric acid, reagent A.C.S. was added slowly while cooling the flask with Dry-Ice (temperature less than 25-30°C.). The flask was connected to the apparatus, cooled to about -20°C. and a vacuum of about 0.02mm. was applied. The receiver (test tube shape) was kept at Dry-Ice temperature and the reaction flask was allowed to warm slowly (to avoid bumping). Distillation was continue for 6 to 7 hours ending with the reaction flask at about 45°C. by heating with a Glas-Col mantle. The anhydrous perchloric acid was stored in the dark at Dry Ice temperatures with an open Drierite tube attached to the vessel outlet (KEL-F 90 grease on ground glass joint). Anhydrous perchloric acid prepared in this way has been stored as above for up to two months without decomposition. KEL-F 90 grease if kept from direct contact with liquid acid is attacked only very slowly if at all by the acid vapor.

### B. Boron Trichloride

Matheson C. P. boron trichloride was used without further purification except distillation prior to use.

### C. Boron Dichloroperchlorate

An all glass appartus was used. It was specially blown and consisted of a 50 ml. flask with a vertical neck, equipped with a Drierite tube, and two side arms with stopcocks, one arm having a liquid nitrogen condenser sleeve. The sidearms were equipped with graduated tubes for measuring the  $\text{BCl}_3$  and  $\text{HClO}_4$  used in the reaction. Before use, the apparatus was assembled and evacuated for several hours and then filled with dry nitrogen. All ground glass joints were lubricated with KEL-F No. 90 grease. Both flask stopcocks were closed; anhydrous perchloric acid (18.0 mmole) was pipetted into one graduated tube and  $\text{BCl}_3$  in excess was condensed in the other graduated tube. Both were held at 0°C. to obtain volume measurements. The  $\text{BCl}_3$ , (19.9 mmole) (15% excess) was transferred by slow distillation to the reaction flask, which was held at -78°C. The stopcock on the  $\text{BCl}_3$  sidearm was closed, a liquid nitrogen bath was applied to the flask and to the condenser on the  $\text{HClO}_4$  sidearm, and a vacuum of 10 mm. of Hg was applied to the system. The  $\text{HClO}_4$  was now distilled slowly into the sidearm by gradually increasing the vacuum as necessary while holding the  $\text{HClO}_4$  at 0°C. to retain  $\text{HClO}_4 \cdot \text{H}_2\text{O}$  in the tube. When all the  $\text{HClO}_4$  had distilled, the stopcock was closed to the  $\text{HClO}_4$  sidearm. A Dry Ice bath was placed on the flask and the  $\text{BCl}_3$  was stirred by means of a magnetic stirrer and Teflon coated stirring bar in the flask. Application

of vacuum was discontinued and the system was filled with dry nitrogen to atmospheric pressure. The  $\text{HClO}_4$  in the condenser was allowed to warm slowly and drip into the  $\text{BCl}_3$  with stirring. The Drierite tube on the vertical neck of the flask allowed the  $\text{HCl}$  formed by the reaction to escape and the mixture was stirred for 15 minutes after addition of the  $\text{HClO}_4$ . It was then held at  $-20^\circ\text{C}$ . for 60 minutes or for 15 hours (overnight) at  $-78^\circ\text{C}$ . to insure complete reaction. Excess  $\text{BCl}_3$  and  $\text{HCl}$  were removed by applying a vacuum of 0.2 mm. of Hg. The vacuum was discontinued and the system was filled with dry nitrogen. The product, a colorless liquid at  $-78^\circ\text{C}$ ., solidifies to a glassy solid at lower temperatures. When stored at  $-78^\circ\text{C}$ . under anhydrous conditions, the compound appears to be stable for extended periods, while at  $-16^\circ\text{C}$ . it is stable for at least several hours.

Anal. Calcd. for  $\text{BCl}_2\text{ClO}_4$ : B, 5.97; Cl, 38.14;  $\text{ClO}_4$ , 54.89; mol. wt. 181  
Found: B, 5.91; Cl, 38.93;  $\text{ClO}_4$ , 55.15; mol. wt., 180.

#### D. Boron Chlorodiperchlorate

The general procedure used in preparing this compound was similar to that used for the boron dichloroperchlorate. Anhydrous perchloric acid (18.2 mmole) and  $\text{BCl}_3$  (9.4 mmole, 3% excess), were used. Before removing excess  $\text{HCl}$  and  $\text{BCl}_3$  by vacuum, the product was allowed to stand for 15 hours at  $-78^\circ\text{C}$ . Boron dichloroperchlorate is a white crystalline solid at  $-78^\circ\text{C}$ . which melts at  $-17$  to  $-15^\circ\text{C}$ . Once the compound has melted, recooling results in solidification either to a glassy or a crystalline solid depending on the purity of the compound. When stored at  $-78^\circ\text{C}$ . under anhydrous conditions, the diperchlorate appears to be stable for extended periods, while at  $-16^\circ\text{C}$ ., it is stable for at least several hours.

Anal. Calcd. for  $\text{BCl}(\text{ClO}_4)_2$ : B, 4.41; Cl, 14.46;  $\text{ClO}_4$ , 81.13; mol. wt. 245. Found: B, 4.32; Cl, 14.84;  $\text{ClO}_4$ , 80.85; mol. wt., 242.

#### E. Boron Triperchlorate

The general procedure used in preparing this compound was similar to that used for the boron dichloroperchlorate. Anhydrous perchloric acid (18.0 mmole) and  $\text{BCl}_3$  (6.0 mmole) were used. After distillation of  $\text{BCl}_3$  into the reaction flask, approximately 5 ml. of Matheson  $\text{CCl}_3\text{F}$  which had been dried and stored over magnesium perchlorate was distilled into the reaction flask. The  $\text{HClO}_4$  was now distilled into the liquid nitrogen cooled sleeve and was then added to the reaction flask as before with stirring. The product was held at  $-78^\circ\text{C}$ . for 4 hours and the solvent, excess  $\text{BCl}_3$  and  $\text{HCl}$  were removed under vacuum holding the reaction mixture at  $-30^\circ$  to  $-35^\circ\text{C}$ . The product was a white crystalline material which does not melt at temperatures up to  $-5^\circ\text{C}$ . and undergoes decomposition reactions before the melting point is reached. When stored at  $-78^\circ\text{C}$ . under anhydrous conditions the triperchlorate is stable for extended periods, while at  $-16^\circ\text{C}$ . it is stable for at least several hours. It is extremely sensitive to moisture and darkens rapidly at  $-16^\circ\text{C}$ . when exposed to traces of moisture.

Anal. Calc. for  $\text{B}(\text{ClO}_4)_3$ : B, 3.50;  $\text{ClO}_4$ , 96.50; Found: B, 3.48;  
 $\text{ClO}_4$ , 96.52.

#### F. Phosphorus Tetrachloroperchlorate

The general procedure for preparing this compound was similar to that used for boron dichloroperchlorate. Phosphorus pentachloride (4.17 mmole) was placed in the reaction flask and 5 ml. of  $\text{CCl}_3\text{F}$  previously dried over magnesium perchlorate was distilled into the reaction flask. Anhydrous  $\text{HClO}_4$  (4.50 mmole) was added to the flask with stirring keeping the  $\text{PCl}_5 \cdot \text{CCl}_3\text{F}$  slurry at  $-78^\circ\text{C}$ . No apparent reaction occurred until the reaction mixture was warmed to  $-30$  to  $-40^\circ\text{C}$ . at which point  $\text{HCl}$  was evolved. A white solid insoluble in  $\text{CCl}_3\text{F}$  was present. After one hour,  $\text{CCl}_3\text{F}$  and  $\text{HCl}$  were removed under vacuum. A white solid stable at room temperature remained.

Anal. Calcd. for  $\text{PCl}_4\text{ClO}_4$ : B, 11.38; Cl, 52.09;  $\text{ClO}_4$ , 36.53.  
Found: P, 11.25; Cl, 52.17;  $\text{ClO}_4$ , 36.58.

#### G. Phosphorus Trichlorodiperchlorate

The general procedure for preparing this compound was similar to that used for boron dichloroperchlorate. Phosphorus pentachloride (0.91 mmole) was introduced into the reaction flask. Anhydrous  $\text{HClO}_4$  (4.53 mmole) was used. This was enough  $\text{HClO}_4$  to replace all the chloride in  $\text{PCl}_5$ . The  $\text{HClO}_4$  was distilled and added to the  $\text{PCl}_5$  with stirring holding the flask at  $-22^\circ\text{C}$ . All of the solid dissolved in about 15 minutes and  $\text{HCl}$  was evolved.

The reaction mixture was held at  $-22^\circ\text{C}$ . for 3 hours and then vacuum was applied to remove unreacted  $\text{HClO}_4$  and  $\text{HCl}$ . The product was a white solid stable at room temperature which melted at  $34-34^\circ\text{C}$ . with decomposition.

Anal. Calcd. for  $\text{PCl}_3(\text{ClO}_4)_2$ : P, 9.21; Cl, 31.63;  $\text{ClO}_4$ , 59.16.  
Found: P, 8.37; Cl, 32.31;  $\text{ClO}_4$ , 59.31.

#### H. Silicon Dichlorodiperchlorate

The general procedure was similar to that used for preparing boron dichloroperchlorate. Silicon tetrochloride (1.5 mmole) was introduced into the reaction flask and 6.13 mmole of anhydrous perchloric acid was distilled into the  $\text{SiCl}_4$  holding the reaction flask at  $-78^\circ\text{C}$ . with stirring. The reaction mixture was warmed to room temperature and held there for 3 hours. It was then cooled to  $-12^\circ\text{C}$ . and excess reactants and  $\text{HCl}$  were removed under vacuum. The material  $\text{SiCl}_2(\text{ClO}_4)_2$  was a white liquid with a melting point close to room temperature and stable at this temperature.

Anal. Calcd. for  $\text{SiCl}_2(\text{ClO}_4)_2$ : Si, 9.43; Cl, 23.80;  $\text{ClO}_4$ , 66.77.  
Found: Si, 8.43; Cl, 23.59;  $\text{ClO}_4$ , 67.98.

The compound  $\text{SiClClO}$  can be prepared as above but using a molar ratio of  $\text{SiCl}_4$  to  $\text{HClO}_4$  of 1:2. It too is a white liquid stable at room temperature.

## I. Heats of Hydrolysis of $\text{BCl}_2\text{ClO}_4$ and $\text{BCl}_3$

The heat of hydrolysis was determined calorimetrically at  $25^\circ\text{C}$ . The calorimeter was a one pint unsilvered Dewar flask immersed in a water bath thermostated at  $25.00^\circ\text{C}$ . The neck of the Dewar was fitted with a Teflon plug through which passed a stirrer (120 r.p.m.), a wire wound resistance heater (encased in a glass tube), a 5000 ohm precision thermistor (Yellow Springs Instrument Co.) encased in a glass tube and an ampoule support on the bottom of the stirrer. Normal procedure was to attach the ampoule containing the  $\text{BCl}_2\text{ClO}_4 - \text{CCl}_4$  solution to the stirrer under approximately 400g of water in the Dewar. The temperature of the water in the Dewar was just under  $25^\circ\text{C}$ . at the start and equilibration to  $25^\circ\text{C}$ . was speeded up by using the electrical heater to bring the temperature very close to the equilibration point. Equilibration is extremely slow if the heater is not used to accelerate the process. Hydrolysis was initiated by stopping the stirrer, breaking the ampoule by lowering the stirrer, and immediately starting the stirrer again. Usually the reaction was over in 1-2 minutes when a temperature maximum was attained. The thermostated bath was held at  $25 \pm 0.003^\circ\text{C}$ . Temperature changes were measured in terms of changes in the resistance of the thermistor. The calorimeter system was calibrated electrically by the substitution method using a 12 volt storage cell as a source of current. Heat of hydrolysis for  $\text{BCl}_3$  was determined as above using  $\text{CCl}_4$  as a solvent to moderate the reaction. The  $\text{BCl}_3$  used was Matheson's C.P. grade with no purification other than distillation prior to use.

## J. Handling Procedures

Since the boron chloroperchlorates and boron triperchlorate are both temperature and moisture sensitive, special methods were necessary for handling these compounds. The problem was solved by modifying a frost free type home freezer (12 cubic foot) as a cold dry box. The freezer was held at  $-16^\circ\text{C}$ . and dry nitrogen gas was introduced to give a dry inert atmosphere. A double Plexiglas window and glove ports were installed in the freezer door and an analytical balance in the freezer was used for weighing analytical samples. A number of physical constants were also determined for the compounds by the use of the cold dry box, i.e., density, index of refraction and surface tension.

## K. Hydrolysis of Boron Perchlorates

These compounds react violently in the presence of water. Even when poured onto ice, the reaction occurs with a flash of light. For purposes of analysis, the hydrolysis was moderated by the addition of a solvent,  $\text{CCl}_3\text{F}$ , and stirring. The hydrolysis of weighed samples was carried out in a 25 ml. two neck flask equipped with a dropping funnel, liquid nitrogen knock back condenser and a Teflon stirring bar. The flask was held at  $-78^\circ\text{C}$ . and water was added slowly with stirring. Hydrolysis under these conditions was smooth and the hydrolysate was usually water white. The hydrolysate was filtered through a fritted glass filter to remove traces of KEL-F 90 grease and diluted to volume in a volumetric flask.

L. Physical Measurements

Density determinations were carried out at  $-16^{\circ}\text{C}$ . in the cold dry box using a calibrated Fisher Davidson Gravitometer. Refractive indices were determined at  $-16^{\circ}\text{C}$ . using a Bausch and Lomb Abbe 3L refractometer. There was a negligible change in refractometer reading between  $-16^{\circ}\text{C}$ . and  $25^{\circ}\text{C}$ . due to changes in refractometer optics. To facilitate reading the refractometer through a Plexiglas window at a distance, the viewing hole in the eyepiece was enlarged to about 1/2 inch. Surface tension was determined at  $-16^{\circ}\text{C}$ . in the cold dry box by measuring the difference in liquid level in a U-tube with two different size capillary tubes. Molecular weight was determined cryscopically in carbon tetrachloride by depression of the freezing point.

TABLE IV

## SUMMARY OF BORON PERCHLORATE SYNTHESIS REACTIONS

| Rx. No. | Temp. °C. | ClO <sub>4</sub> /BCl <sub>3</sub> Ratio | Reactant           | Solvent          | Sample No. | B    | Product Analysis (mmoles)* |       | Comments  |
|---------|-----------|--|--------------------|------------------|------------|------|----------------------------|-------|---|
|         |           |  |                    |                  |            |      | ClO <sub>4</sub>           | Cl    |   |
| 1       | -35       | 1:1                                      | HClO <sub>4</sub>  | None             | I          | 1.00 | 1.43                       | 1.24  | Weighed sample  |
|         |           |  |                    |                  | II         | 1.00 | 1.42                       | 1.19  | Weighed sample  |
| 2       | -78       | 1:1                                      | HClO <sub>4</sub>  | None             | I          | 1.00 | 0.98                       | 1.83  | Weighed sample  |
|         |           |  |                    |                  | II         | 1.00 | 1.00                       | 1.85  | Weighed sample  |
| 3       | -22       | 2:3                                      | AgClO <sub>4</sub> | None             |            | 1.00 | 2.04                       | 0.63  | Cold tube   |
| 4       | -22       | 1:4                                      | AgClO <sub>4</sub> | CCl <sub>4</sub> |            | 1.00 | 0.63                       | 2.10  | Incomplete reaction-low solubility in CCl <sub>4</sub> ; Molecular weight sample            |
| 5       | -22       | 1:3                                      | AgClO <sub>4</sub> | CCl <sub>4</sub> |            | 1.00 | 0.85                       | 1.60  | Molecular weight sample   |
| 6       | -22       | 3:2                                      | AgClO <sub>4</sub> | None             |            | 1.00 | 1.20                       | 1.50  | BCl <sub>2</sub> ClO <sub>4</sub> -B <sub>2</sub> l(ClO <sub>4</sub> ) <sub>2</sub> mixture |
| 7       | -22       | 3:1                                      | AgClO <sub>4</sub> | None             | I          | 1.00 | 1.03                       | 0.325 | Decomposition products  |
|         |           |  |                    |                  | II         | 1.00 | 0.988                      | 0.245 | Decomposition products  |
| 8       | -22       | 2:1                                      | AgClO <sub>4</sub> | None             |            | 1.00 | 2.00                       | 1.01  | U-Tube reaction   |
| 9       | -70       | 1:4                                      | AgClO <sub>4</sub> | None             | I          | 1.00 | 0.964                      | 0.50  | Product analysis at 70°F.   |
|         |           |  |                    |                  | II         | 1.00 | 1.07                       | 0.053 | Product analysis at 70°F.   |
| 10      | 770       | 3:4                                      | AgClO <sub>4</sub> | None             | I          | 1.00 | 1.70                       | 1.40  | Weighed sample  |
|         |           |  |                    |                  | II         | 1.00 | 1.54                       | 1.42  |   |
| 11      | 70        | 2:4                                      | AgClO <sub>4</sub> | None             | I          | 1.00 | 0.81                       | 0.77  | CCl <sub>4</sub> insoluble portion  |
|         |           |  |                    |                  | II         | 1.00 | 1.43                       | 0.79  | CCl <sub>4</sub> soluble portion  |
|         |           |  |                    |                  | III        | 1.00 | 1.04                       | 2.00  | Weighed sample  |
|         |           |  |                    |                  | III        | 1.00 | 0.97                       | 2.11  | Weighed sample  |

TABLE IV (CONTD.)

| Rx. No. | Temp. °C. | ClO <sub>4</sub> /BCl <sub>3</sub> Ratio | Reactant           | Solvent                 | Sample No. | B            | Product Analysis (mmoles)* |              | Comments  |
|---------|-----------|--|--------------------|-------------------------|------------|--------------|----------------------------|--------------|---|
|         |           |  |                    |                         |            |              | ClO <sub>4</sub>           | Cl           |   |
| 12      | -78       | 1:1                                      | HClO <sub>4</sub>  |                         | I          | 1.00         | 0.97                       | 1.89         | Weighed sample  |
|         |           |  | Vacuum Residue     |                         |            | 1.00         | 2.56                       |              |   |
| 13      | -78       | 1:1                                      | HClO <sub>4</sub>  |                         | I          | 1.00         | 1.97                       | 1.89         | Weighed sample<br>d <sub>4</sub> <sup>16</sup> C = 1.728<br>n <sub>D</sub> <sup>16</sup> = 1.4288 |
|         |           |  | Vacuum Residue     |                         |            | 1.00         | 2.26                       |              |   |
| 14      | -50       | Large excess<br>BCl <sub>3</sub>         | AgClO <sub>4</sub> | Excess BCl <sub>3</sub> | I          | 1.00         | 1.99                       | 0.99         |   |
| 15      | -50       | Large excess<br>BCl <sub>3</sub>         | AgClO <sub>4</sub> | Excess BCl <sub>3</sub> | I          | 1.00         | 2.00                       | 1.01         | Weighed sample  |
| 16      | -50       | Large excess<br>BCl <sub>3</sub>         | AgClO <sub>4</sub> | Excess BCl <sub>3</sub> | I<br>II    | 1.00<br>1.00 | 1.85<br>1.69               | 1.00<br>1.01 | n <sub>D</sub> <sup>16</sup> = 1.4294   |
| 17      | -78       | 2:1                                      | HClO <sub>4</sub>  |                         | I<br>II    | 1.00<br>1.00 | 1.88<br>1.89               | 0.97<br>0.94 | Weighed sample #1<br>Weighed sample #2  |
| 18      | -78       | 3:1                                      | HClO <sub>4</sub>  |                         | I<br>II    | 1.00<br>1.00 | 2.80<br>2.59               |              | Weighed sample #1<br>Weighed sample #2  |
| 19      | -78       | 2:1                                      | HClO <sub>4</sub>  |                         | I<br>II    | 1.00<br>1.00 | 1.00<br>2.46               | 1.70<br>0.04 | Distillate<br>Pot residue   |
| 20      | -78       | 2:1                                      | HClO <sub>4</sub>  |                         | I<br>II    | 1.00<br>1.00 | 1.06<br>2.10               | 1.89<br>0.24 | Distillate<br>Pot residue   |
| 21      | -78       | 2:1                                      | HClO <sub>4</sub>  |                         | I<br>II    | 1.00<br>1.00 | 2.14<br>2.24               | 0.87<br>0.81 | Weighed sample<br>Weighed sample  |

TABLE IV (CONT'D.)

| Rx. No. | Temp. °C. | ClO <sub>4</sub> /BCl <sub>3</sub> Ratio (moles) | Reactant                             | Solvent | Sample No. | B    | Product Analysis (mmoles)* |      | Comments   |
|---------|-----------|--|--------------------------------------|---------|------------|------|----------------------------|------|--|
|         |           |  |                                      |         |            |      | ClO <sub>4</sub>           | Cl   |  |
| 22      | -78       | 2:1 + 6% (moles)                                 | HClO <sub>4</sub>                    |         | I          | 1.00 | 2.01                       | 0.94 | Weighed sample   |
|         |           |  |                                      |         | II         | 1.00 | 2.13                       | 0.87 | Weighed sample   |
| 23      | -78       | 2:1 + 6% (moles)                                 | HClO <sub>4</sub>                    |         | I          | 1.00 | 1.97                       | 1.01 | Weighed sample   |
|         |           |  |                                      |         | II         | 1.00 | 2.05                       | 0.94 | Weighed sample   |
| 24      | -78       | 2:1 + 12%  | HClO <sub>4</sub>                    |         |            | 1.00 | 2.03                       | 1.00 | d <sub>D</sub> <sup>16</sup> = 1.870<br>n <sub>D</sub> <sup>16</sup> = 1.438 |
| 25      | -78       | 3:1  | HClO <sub>4</sub> CCl <sub>3</sub> F |         |            | 1.00 | 3.02                       | None | Weighed sample   |

\* Analysis adjusted to boron equivalent to unity

## CONCLUSIONS

The results of this program indicate that the two chloroperchlorates and the triperchlorate of boron can be prepared in high purity and considerable data has been gathered to characterize these compounds with respect to chemical and physical properties, as well as structure elucidation. The triperchlorate was more difficult to characterize due to its greater instability and limited solubility in inert solvents, but its structure was conclusively proven.

The triperchlorate would be an interesting oxidizer for high energy rocket propellant systems, but due to its thermal and moisture sensitivity would be difficult to use directly for this purpose. However, the material can easily be prepared in high purity; and if a suitable method of stabilization could be devised that would not lower its oxidation potential, then it could be valuable as a new oxidizer system. Stabilization by complex formation appears feasible for the chloroperchlorates intermediates, but experiments with the triperchlorate have had only limited success due to its high reactivity and limited solubility. Attempts to prepare the fluoro analogues as a method of stabilization were not successful but may offer promise. Only a limited number of experiments were conducted in this area.

Several other non-metallic halides were investigated as alternates for the boron system and did indeed give more stable perchlorates. However, in most cases only partial replacement occurred under moderate reaction conditions with halides of phosphorous ( $P^{+5}$ ) and silicon ( $Si^{+4}$ ) and more drastic conditions resulted in decomposition, limiting the attractiveness of these systems.

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