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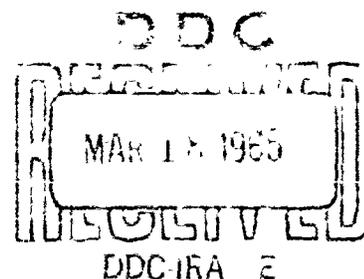
Propulsion Division
Office of Aerospace Research
Air Force Office of Scientific Research

RADIATION-INDUCED SOLID PROPELLANT DECOMPOSITION

Final Technical Report

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INTRODUCTION

Earlier work on this contract showed that the deflagration rates of many ammonium perchlorate composite solid propellants are altered by exposure to radiation. Two polysulfide-based propellants (Thiokols TP-L-3014 and TP-L-3014a) showed rate decreases, polyurethane (Thiokol TP-6-3129), polyacrylate (Hercules HES-6420) and polyacrylonitrile (Hercules HES-6648) based propellants showed increases while hydrocarbon (Thiokol TP-H-3062) and cellulose acetate (Hercules HES-5808) propellants showed no changes in deflagration rate.

Since these composite propellant formulations contain various additives in addition to the two basic components-binder and oxidizer- it was impossible to mechanistically ascribe the burning rate changes to propellant binder composition. For this reason, we initiated a more basic study of the effect of radiation on propellants. This has involved the determination of the effect of radiation on the deflagration rates of binder and oxidizer separately from each other and independent of additives or other substances. In addition, the chemical products of ammonium perchlorate radiolysis were studied in detail.

2.0 RADIOLYSIS OF AMMONIUM PERCHLORATE

2.1 Background and Previous Work

The radiolysis of solid salts of oxy-acids of chlorine, in general, and of perchlorates, specifically, have received little attention. Heal has reported the production of chloride, hypochlorite, chlorite and oxygen with G values of 1.9, 0.7, 2.6 and 2.9, respectively, in the X-radiolysis of potassium chlorate.^{1a} In a subsequent paper, Heal also inferred the probable presence of dichlorine hexoxide and chlorine dioxide with G values of 1.4 and 0.2, respectively.^{1b} Burchill on the other hand found oxygen, chlorite, chlorine dioxide, chloride, hypochlorite and chlorate with G values of 1.95, 1.34, 0.95, 0.23, 0.21 and 0.22, respectively, in the cobalt-60 radiolysis of sodium chlorate.² The same product spectrum was obtained for potassium and barium chlorates although yields were not reported.

Heal^{1c} reported the production of chloride, chlorate and oxygen, and the probable production of hypochlorite and chlorite in the X-radiolysis of potassium perchlorate with a G value for perchlorate decomposition of approximately 5.

By far the most extensive and elegant study in this field is that by Johnson and Prince on the cobalt-60 radiolysis of the alkali and alkaline earth metal perchlorates.³ The results of their work are shown in Table 1.

Although the radiation chemistry of almost all of the common metal perchlorates has been studied and elucidated, that of the common propellant oxidizer ammonium perchlorate has not. Only a few qualitative reports on the radiolysis of ammonium perchlorate are to be found in the literature. Thus, Freeman and co-workers have reported the presence of chloride, chlorate,

nitrite and nitrate in the cobalt-60 radiolysis of ammonium perchlorate.⁴ Prior to the present study at RAI, quantitative work on the radiolytic chemical yields of ammonium perchlorate had not been reported.

Table 1^{a,b}

G Values of Products of Radiolysis of Alkali and Alkaline Earth Perchlorates

Salt	G ClO ₃ ⁻	G ClO ₂ ⁻	G ClO ₂	G ClO ⁻	G Cl ⁻	G O ₂
Li	2.8	0.15	0.59	0.10	0.12	2.2
Na	3.6	0.17	0.11	0.09	0.42	3.0
K	3.0	0.18	0.12	0.09	0.45	2.7
Rb	4.1	0.20	0.12	0.14	0.75	3.8
Cs	5.3	0.22	0.10	0.17	1.1	5.3
Mg	4.3	0.14	0.07	0.03	0.15	2.6
Ca	3.4	0.00	0.51	0.08	0.12	2.0
Sr	3.9	0.19	0.14	0.11	0.19	2.6
Ba	1.8	0.84	0.42	0.12	0.06	2.2

a

G = number of ions or molecules produced per 100 e.v.

b

data from reference 3b.

2.2 Results and Discussion

The cobalt-60 gamma radiolysis of ammonium perchlorate was studied over the dose range of ca. 0-120 megarads (ca. 0-0.5 x 10²² electron volts). Reagent-grade ammonium perchlorate was recrystallized twice from deionized water, dried and then irradiated at 10-15°C. in stoppered test tubes with cobalt-60 gamma radiation. No precautions were taken to exclude air from the specimens prior to radiolysis. The irradiated ammonium perchlorate was dissolved in water and analyses performed for chlorate, chlorine dioxide, chlorite, hypochlorite, chlorine, chloride and the total of nitrite and nitrate. All of the analytical procedures were checked out with known mixtures of the various chemical species and it was ascertained that

interferences were not present. The details of the experimental procedures were previously described (see Report RAI 331).

Chlorine dioxide, chlorite, hypochlorite and chlorine were analyzed by their oxidation of iodide ion to iodine in a manner similar to that of Johnson and Prince.³ The iodine was determined spectrophotometrically at 350 μ . In basic media (pH 8-9), ClO^- and Cl_2 are reduced to Cl^- , ClO_2 to ClO_2^- while ClO_2^- is unaffected. On acidification (to pH 1-2), ClO_2^- (both ClO_2^- formed from NH_4ClO_4 radiolysis and from the reduction of ClO_2 in basic media) is also reduced (to Cl^-) in addition to ClO_2 , ClO^- and Cl_2 . Since no additional oxidation of iodide was observed on acidification, it is concluded that both ClO_2 and ClO_2^- are not products of ammonium perchlorate radiolysis. Thus, the basic oxidation of iodide ion was due to ClO^- plus Cl_2 . The yields of these two species were separated by performing the oxidation with and without prior "flash-boiling". "Flash-boiling" resulted in the expulsion of Cl_2 from the solution of irradiated ammonium perchlorate and was accomplished by heating the solution just to boiling.

The oxidizing power of the solution of irradiated ammonium perchlorate toward ferrous ion in acidic media was also observed in a procedure similar to that of Johnson and Prince.³ The ferric ion was determined spectrophotometrically at 305 μ . In addition to the ClO^- and Cl_2 , ClO_3^- is also reduced (to Cl^-) by ferrous ion. Thus, the ClO_3^- yield is obtained by the difference between the iodide and ferrous oxidations.

Chloride ion was determined by a modification of the Volhard procedure utilized by Burns and Muraca.⁵ An excess of silver nitrate was added to the sample and the excess silver ion

back titrated with thiocyanate ion. The yield must be corrected to take into account the fact that hypochlorite also reacts with silver ion (yielding $\text{AgCl} + \text{O}_2$).

The sum of nitrite plus nitrate was determined by a modification of the procedure used by Norwitz⁶ in the analysis of nitrate. This involved the reduction of both nitrate and nitrite to nitric oxide by ferrous ion (in concentrated sulfuric acid solution) followed by the formation of $\text{Fe}(\text{NO})^{2+}$ whose absorption at 525 μ was then determined.

As indicated above, ClO_2 and ClO_2^- were found not to be products of ammonium perchlorate radiolysis in any appreciable amount. The same was observed for NO_3^- plus NO_2^- . ClO_3^- , ClO^- , Cl_2 and Cl^- were found to be major products of the radiolysis of ammonium perchlorate and the results are shown in Table 2 and in Figure 1. The initial G values were calculated and are given in Table 3. It can be seen from Figure 1 that all yields except the ClO_3^- were essentially independent of dose over the range studied. The ClO_3^- yield, however, was observed to fall off and decrease at the higher doses. This probably indicates that the ClO_3^- is undergoing radiolytic decomposition. This is very similar to the results of Heal¹ on the radiolysis of potassium perchlorate although Johnson and Prince³ did not observe the effect.

It is interesting to compare the ammonium perchlorate radiolytic yields (Table 3) with the alkali and alkaline earth metal perchlorate radiolytic yields obtained by Johnson and Prince (Table 1). It is seen that the relative yields of the various radiolytic products are quite dissimilar in the two cases. The following points of comparison can be made:

Table 2
Radiolytic Yields of Ammonium Perchlorate

Radiation Dose ^a (Mrads)	Yields ^b in Micromoles per Gram Irradiated Ammonium Perchlorate				
	ClO ₃ ⁻	ClO ⁻	Cl ₂	Cl ⁻	NO ₂ ⁻ /NO ₃ ⁻
8.6	-	3.0	-	17	-
11	-	3.7	13	24	-
16	20	5.1	-	34	-
18	22	6.0	23	36	-
23	26	9.6	-	54	-
27	29	12	32	66	1.4
35	-	15	43	87	-
44	39	21	48	103	-
52	37	25	68	118	2.7
61	46	-	87	157	-
71	-	38	-	186	-
80	53	-	93	-	-
87	47	-	111	218	5.5
96	45	43	120	247	-
114	37	-	-	301	-
120	-	57	182	-	-
145	38	-	210	390	-
186	-	68	260	-	-

^a

All irradiations except the 11 Mrad one were performed at 0.36 Mrad/hr.; the 11 Mrad irradiation was performed at 0.17 Mrad/hr.

^b

Each reported yield is the result of 2-5 determinations. The precision of yields was ±5-15%.

Table 3
Ammonium Perchlorate Radiolysis

Product	G Value
ClO ₃ ⁻	1.3
ClO ₂	<0.02
ClO ₂ ⁻	<0.02
ClO ⁻	0.45
Cl ₂	1.2
Cl ⁻	2.5
NO ₃ ⁻ + NO ₂ ⁻	<0.05

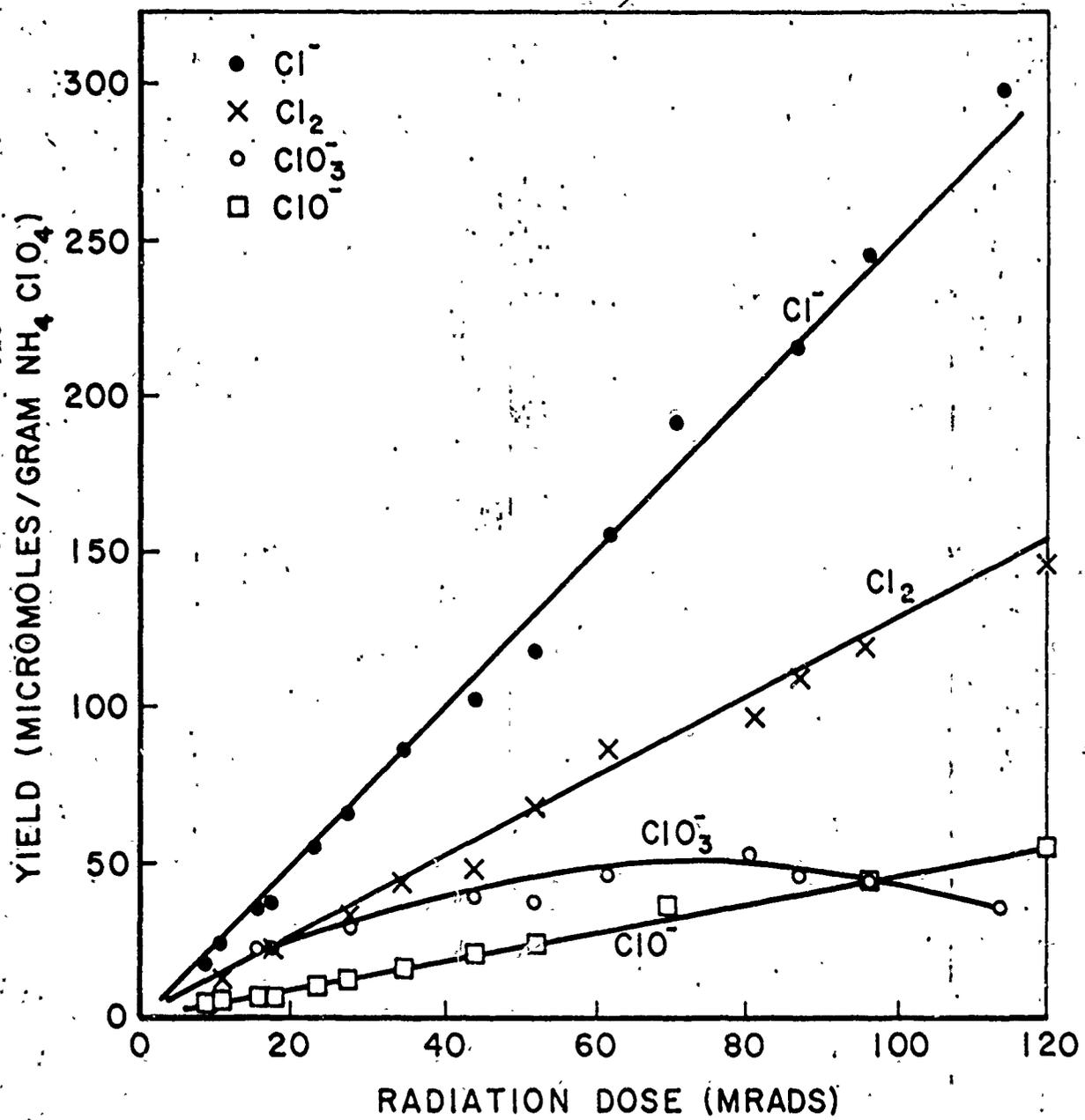


FIGURE 1. YIELDS IN AMMONIUM PERCHLORATE RADIOLYSIS.

1. The G for total yield of products of ammonium perchlorate radiolysis is larger by a factor of 2-5 than from the metal perchlorates.

2. Aside from oxygen, chlorate is the major radiolytic product of the metal perchlorates by a large factor. The other products (chlorite, chlorine dioxide, hypochlorite and chloride) are produced with much lower G values. This is not the case for ammonium perchlorate radiolysis.

3. Chlorate is a major product of ammonium perchlorate radiolysis with a G which is approximately 1/2-1/3 that for the metal perchlorates. However, chlorate is by no means the only major radiolytic product of ammonium perchlorate.

4. Chloride is a major radiolytic product of ammonium perchlorate with a G which is greater by a factor of 2-20 than in the case of the metal perchlorates.

5. Chlorine (Cl_2) is a major radiolytic product of ammonium perchlorate although it is not a product of the radiolysis of metal perchlorates.

The above points of comparison between the products of metal and ammonium perchlorate radiolysis are shown in Table 4.

As we have seen there are drastic differences in the radiolysis of ammonium perchlorate as compared to that of the alkali and alkaline earth metal perchlorates. One possible reason for this may be the participation of the ammonium ion in the radiation decomposition of ammonium perchlorate. As part of our effort to search for changes in the oxidation state of nitrogen in ammonium perchlorate, we have analyzed for nitrite/nitrate. The very low yields observed for nitrite/nitrate also preclude the presence of a variety of nitrogen compounds

such as NO_2 , NO , N_2O_3 , etc., since these would show up in our nitrite/nitrate analysis. Essentially the only nitrogen compounds which would not have been analyzed by our procedure for $\text{NO}_2^-/\text{NO}_3^-$ are N_2 and possible also N_2O .

Table 4

Comparison of Radiolytic Yields of Metal and Ammonium Perchlorates

Product	G for Alkali and Alkaline Earth Perchlorates ^{a,b}	G for Ammonium Perchlorate ^c
ClO_3^-	3.6 (1.8-5.3)	1.3
ClO_2	0.24 (0.07-0.59)	< 0.01
ClO_2^-	0.23 (0.00-0.84)	< 0.01
ClO^-	0.10 (0.03-0.17)	0.46
Cl_2	0	1.2
Cl^-	0.37 (0.06-1.1)	2.5

a

Data of Johnson and Prince, reference 3

b

The value noted is the average of the G values for all of the alkali and alkaline earth perchlorates. The range of G values for these perchlorates is shown in parentheses.

c

Data of RAI study.

Some annealing experiments were performed in order to ascertain whether any changes occur in the irradiated ammonium perchlorate on standing. Samples of ammonium perchlorate irradiated to doses of ca. 3, 10, 25 and 50 Mrads were analyzed immediately after irradiation and subsequently after various time intervals of storage in a constant temperature bath at 20°C. The analytical results for the stored samples showed greater variations than normal and made it difficult to draw any strong conclusions. However, it could be concluded that the chlorate yield decreased by

ca. 50% and the chlorite by ca. 20-30% after storage for 50 days. The chloride and chlorine yields generally appeared to remain constant although in many samples increases or decreases by 10-30% were observed. Some very preliminary work indicated that the presence of water was probably responsible for these sporadic results.

2.3 Experimental Details

a) Materials and Sample Preparation

Matheson, Coleman and Bell reagent-grade ammonium perchlorate was recrystallized twice from deionized water, dried and ground up prior to use. All other materials were reagent or analytical-grade chemicals which were dried but otherwise not further purified before use.

Samples of ammonium perchlorate were placed in ground glass test tubes, capped and then irradiated at 10-15°C. with cobalt-60 gamma radiation. (A few of the irradiations were performed at 6-10°C. with no significant differences being observed in the radiolytic yields.) Dosimetry was performed via the oxygenated Fricke ferrous sulfate dosimeter⁷ using a $G(\text{Fe}^{3+})$ of 15.6.

b) General Notes on Analytical Procedures

Many of the analyses were performed with and without prior "flash boiling". Flash boiling resulted in the expulsion of gases (Cl_2 , ClO_2) from the solution of irradiated ammonium perchlorate. It was accomplished by heating the solution in a flask with a Bunsen burner with swirling until (ca. 1/2 minute) the solution just began to boil. The flash boiling procedure was shown, via the analysis of standard solutions, not to affect

the yields of the non-gaseous products (ClO_3^- , ClO_2^- , ClO^- , Cl^- , NO_2^- , NO_3^-).

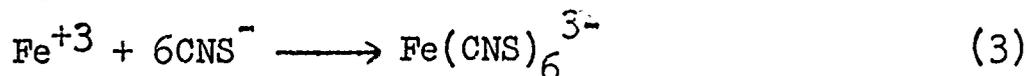
All spectrophotometric determinations were performed with a Beckman DU Spectrophotometer.

Analyses of irradiated samples were performed immediately after the completion of irradiation. In a few cases, samples were stored at dry ice-acetone temperatures overnight prior to analysis.

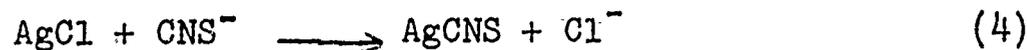
These two procedures yielded results which were indistinguishable from each other.

c) Chloride Ion

Chloride ion was determined by a modification of the Volhard procedure utilized by Burns and Muraca⁵ and by Johnson and Prince.^{3b} An excess of standard silver nitrate was added to the chloride-containing sample (equation 1) and the excess silver ion back titrated with thiocyanate ion (equation 2) in the presence of ferric ion which served as an indicator through the formation of the red-brown ferrithiocyanate ion (equation 3):

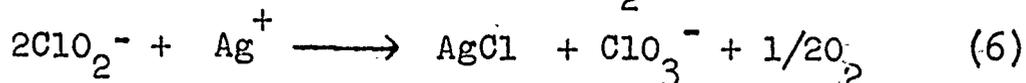
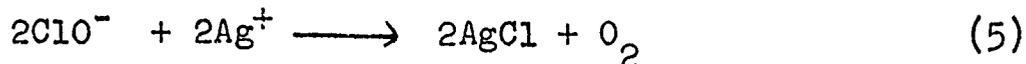


Benzyl alcohol or nitrobenzene was added after the addition of silver nitrate to coat the silver chloride precipitate and prevent its equilibration with thiocyanate ion (equation 4):



This analytical procedure was checked with known chloride solutions spiked with ClO_3^- , NH_4ClO_4 , ClO_2^- , ClO^- , Cl_2 , NO_2^- and NO_3^- and found to be free from interferences.

However, corrections had to be employed to calculate the Cl^- yield because ClO^- and ClO_2^- also react with silver ion. One mole of ClO^- reacts with one mole of silver ion while one mole of ClO_2^- reacts with only one-half mole of silver ion:

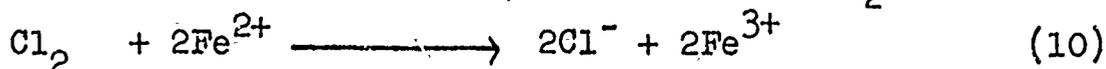
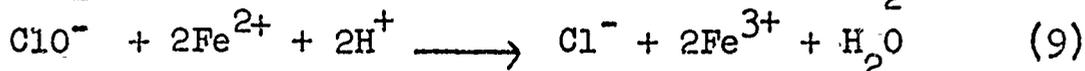
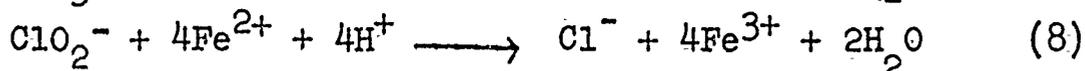
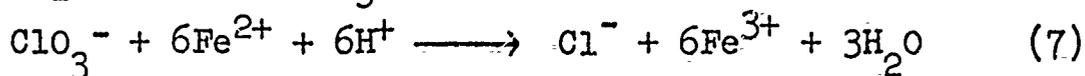


The chloride ion yield was found to be unaffected by flash boiling as would be anticipated since gaseous species such as Cl_2 and ClO_2 would not be expected to interfere.

The experimental procedure consisted of the addition of an appropriate portion (an amount which required a back titration with approximately 1 ml. of thiocyanate) of irradiated ammonium perchlorate to 5-10 ml. water and 0.1M sodium hydroxide (1 ml. per 50 mg. ammonium perchlorate) contained in an Erlenmeyer flask. (Optional: Flash boil and then cool.) One to 1-1/2 ml. of 1-1 nitric acid and then a 5 ml. aliquot of standard 0.01M silver nitrate were added followed by 10 drops of saturated ferric ammonium sulfate solution and 3 ml. of benzyl alcohol or nitrobenzene. After standing for 15 minutes the excess silver nitrate was back titrated with standard 0.01M potassium thiocyanate to the red-orange-brown end point.

d) Oxidation of Ferrous Ion : Cl_2 and ClO_3^- Yields

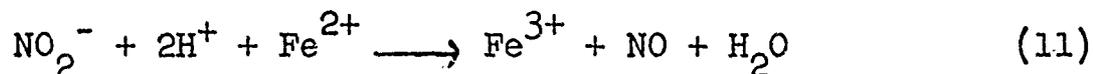
Ferrous ion was oxidized to ferric ion in acidic medium by Cl_2 , ClO^- and ClO_3^- according to equations 7-10:



These oxidations were employed to determine the yields of

Cl_2 , ClO^- , ClO_2^- and ClO_3^- in ammonium perchlorate radiolysis. The procedure was a modification of that of Johnson and Prince.^{3b} The analysis was performed by the UV spectrophotometric determination of ferric ion yield via its absorption at 305 m μ .

It was determined that NH_4ClO_4 , Cl^- , and NO_3^- did not interfere with this procedure although NO_2^- oxidizes Fe^{2+} according to eq. 11:



However, the yield of NO_2^- in ammonium perchlorate radiolysis was independently found [see f) below] to be so small as to make a correction for eq. 11 unnecessary.

The yields of Cl_2 and ClO_3^- were obtained from eqs. 12 and 13

$$\text{Cl}_2 = 1/2 (\text{Fe}^{3+} - \text{Fe}_F^{3+}) \quad (12)$$

$$\text{ClO}_3^- = 1/6 \text{Fe}_F^{3+} - 1/3 \text{ClO}^- - 2/3 \text{ClO}_2^- \quad (13)$$

where Fe^{3+} , $\text{Fe}_F^{3+} = \text{Fe}^{3+}$ yields without and with flash boiling, respectively

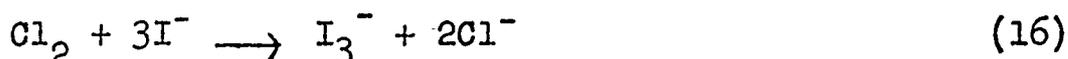
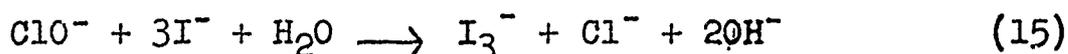
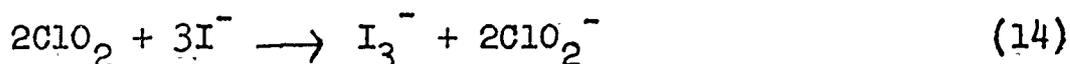
ClO^- , $\text{ClO}_2^- = \text{ClO}^-$ and ClO_2^- yields, respectively, from e) below.

The experimental procedure consisted of the addition of an appropriate portion (an amount which yielded an optical density of 0.2-0.5) of irradiated ammonium perchlorate to a 200 ml. volumetric flask containing 10 ml. water and 0.1M sodium hydroxide (1 ml. per 50 mg. ammonium perchlorate). (Optional: Flash boil and cool.) Twenty ml of 0.1M ferrous ammonium sulfate in 5% sulfuric acid, 20 ml. of 1.1-1 sulfuric acid, and then enough water to make up to volume were added. (For samples irradiated to very high doses, a 500 ml. volumetric flask was employed with appropriate adjustment of the amounts of the

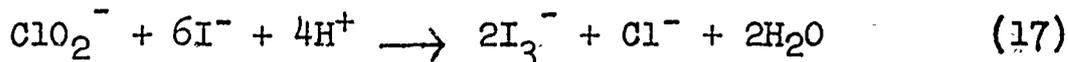
various reagents.) After standing for at least 4 hours, the optical density of the solution was determined at 305 μ against a blank solution made up in the same manner as above except that the irradiated ammonium perchlorate was omitted. The molar extinction coefficient of Fe^{3+} , E, was simultaneously determined by using standard KClO_3 solutions in place of the irradiated ammonium perchlorate in the procedure above. Our results showed an E value of 2166 as compared to the literature⁷ value of 2201.

e) Oxidation of Iodide Ion Cl_2 , ClO_2 , ClO^- and ClO_2^- Yields

The oxidation of iodide ion to iodine was the basis of the analysis of ClO_2^- , ClO^- , ClO_2 , and Cl_2 . The I_2 (actually I_3^-) was determined spectrophotometrically by its absorption at 350 μ . The analytical procedure employed was a modification of that employed by Johnson and Prince.^{3b} In basic (pH 8-9) media, ClO_2 , ClO^- and Cl_2 oxidize iodide according to eqs. 14-16 while ClO_2^- does not.



In acidic (pH 1-2) solution, ClO_2^- also oxidizes iodide (eq. 17).



It should be noted that the reaction in eq. 17 is due to ClO_2^- formed directly from ammonium perchlorate radiolysis and via the oxidation of iodide by ClO_2 (eq. 14).

Nitrite ion interferes with this analytical procedure since it will also oxidize iodide ion in acidic media but not in basic media. However, the yield of nitrite was found to be negligible as evidenced both by negligible differences observed

between iodide oxidation performed in acidic and basic media and by the separate nitrate/nitrite analysis in f) below.

The separation of the total iodine yield into those attributable to the various species (i.e., Cl_2 , ClO_2 , ClO_2^- , ClO^-) was facilitated by analyzing with and without prior flash boiling. Flash boiling resulted in the expulsion of Cl_2 and ClO_2 . The yields of ClO^- , ClO_2^- , ClO_2 and Cl_2 were obtained from eqs. 18-21:

$$\text{ClO}^- = I_{2B,F} \quad (18)$$

$$\text{ClO}_2^- = 1/2(I_{2A,F} - I_{2B,F}) \quad (19)$$

$$\text{ClO}_2 = 1/2(I_{2A} - I_{2B}) - \text{ClO}_2^- \quad (20)$$

$$\text{Cl}_2 = I_{2A} - I_{2A,F} - 2\text{ClO}_2 \text{ or } I_{2B} - I_{2B,F} - 2\text{ClO}_2 \quad (21)$$

where I_{2B} , I_{2A} = iodine yields in basic and acidic media, respectively, without flash boiling.

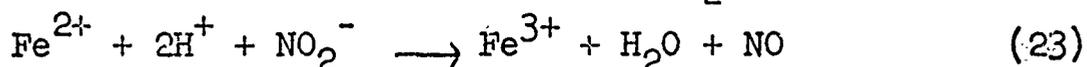
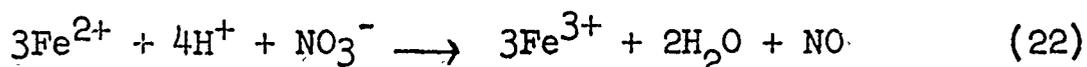
$I_{2B,F}$, $I_{2A,F}$ = iodine yields in basic and acidic media, respectively, with flash boiling

The experimental procedure consisted of the addition of an appropriate portion (an amount yielding an optical density of 0.2-0.5) of irradiated ammonium perchlorate to 10 ml. water and 0.1M sodium hydroxide (1 ml. per 50 mg. ammonium perchlorate) contained in a 200 ml. volumetric flask. (Optional: Flash boil and then cool.) Twenty ml. 10% potassium iodide solution and then enough water to make up to volume were added (For samples irradiated to very high doses, a 500 ml. volumetric flask was employed with appropriate adjustment of the amounts of the various reagents.) The optical density of the resulting solution was then determined at 350 m μ against a blank solution prepared in the same manner but without irradiated ammonium perchlorate. The solution from the UV optical cell was then poured back into its

volumetric flask, concentrated sulfuric acid (0.4 ml. per 50 mg. ammonium perchlorate) added and the optical density at 350 μ redetermined. The extinction coefficient, E, of iodine at 350 μ , was determined by using the same procedure as above with standard solutions of sodium chlorite. Our E value of 23,990 compared well with the literature^{3b} value of 24,940.

f) NO₂⁻/NO₃⁻ Yield

The analysis for NO₂⁻ plus NO₃⁻ was via a modification of the procedure used by Norwitz⁶ in the analysis of nitrate ion. It was based on the reduction of both nitrate and nitrite ions to nitric oxide (eqs. 22 and 23) by ferrous ion (in concentrated sulfuric acid solution) followed (eq. 24) by the formation of the red complex ion Fe(NO)²⁺ whose absorption at 525 μ was then determined.



We have determined that NH₄ClO₄, ClO₃⁻, Cl⁻, ClO⁻ and Cl₂ do not interfere with this analytical procedure.

The experimental procedure involved the addition of sufficient ferrous sulfate solution (2.5 g. ferrous sulfate heptahydrate in 3:1 by volume of concentrated sulfuric acid and water) to a 5 gram portion of irradiated ammonium perchlorate in a 10 ml. volumetric flask, to make up to volume. After standing for one hour, the optical density at 525 μ was determined vs. a blank of the ferrous sulfate solution. The extinction coefficient was determined to be 237 by using the above procedure with standard nitrate solutions.

3.0 BURNING RATES OF PROPELLANT SYSTEMS

3.1 Introduction

In order to clarify the observed effects of radiation on the deflagration rates of composite propellants, it was decided to study the effect of radiation on the binder and oxidizer components separately from each other and independent of other additives and substances. A novel laboratory "porous-plug" burner technique was recently developed which permits ready study of this problem.⁸

In principle, the "porous plug" burner simulates a strand burner. It essentially consists of a stainless steel tube into which solid oxidizer (e.g., ammonium perchlorate) can be packed, and then burnt while gaseous fuel (e.g., methane) is passed through it. Conversely, solid fuel (e.g., polystyrene) can be burnt while gaseous oxidizer (e.g., oxygen) is passed through. Fuze wires, located at precise intervals in the tube and connected to interval timers, allow the accurate measurement of burning rate. Details of the construction of this burner, which have been previously discussed,⁸ are summarized in Section 3.3.

Using this "porous-plug" burner technique, we studied the separate effect of radiation on the oxidizer and fuel components. Two types of experiments were performed:

1. Solid ammonium perchlorate oxidizer specimens, both irradiated and non-irradiated, were burnt in environments of gaseous methane fuel that had not experienced exposure to radiation and their burning rates measured as a function of dose level.
2. Solid polystyrene fuel specimens, both irradiated and non-irradiated, were similarly burnt in environments of

unirradiated gaseous oxygen oxidizer and their burning rates measured as a function of dose level.

3.2 Results and Discussion

Using the "porous-plug" burner, the effect of radiation on the burning rate of ammonium perchlorate (American Potash, 99.5% assay) was determined in an environment of methane gas. The burning rate was observed as a function of cobalt-60 gamma dose over the range 0-100 Mrad and at methane flow rates of 0.0072, 0.019 and 0.026 gm./cm.²/sec. The results are shown in Table 5. It is seen that the irradiation of ammonium perchlorate results in the acceleration of its burning rate. The effect of radiation is much greater at the higher methane flow rates.

Table 5

Effect of Radiation on Ammonium Perchlorate^a Burning Rate

Methane Flow Rate (gm./cm. ² /sec.)	Radiation Dose (Mrad)	Burning Rate (in./sec.)
0.0072	0	0.032
	30	0.033
	100	0.035
0.019	0	0.042
	40	0.048
	100	0.052
0.026	0	0.043
	40	0.049
	100	0.051

^a Particle size = 150-210 μ

There is essentially no difference in the burning rates of ammonium perchlorate at the two higher methane flow rates. This indicates that above a methane flow rate of 0.019 gm./cm.²/sec. the stoichiometric flow rate of methane (i.e., that rate required in order for the methane flow rate to be non-rate determining)

for the oxidation reaction between ammonium perchlorate and methane has been reached. At the low 0.0072 gm./cm.²/sec. methane flow rate, the mixture is too fuel-lean and the effect of radiation is not as noticeable.

Since commercial ammonium perchlorate was employed in the above experiments, it was desirable to determine the burning rate of irradiated, recrystallized ammonium perchlorate. Ammonium perchlorate was purified by double recrystallization (as in Section 2.0) and then burnt as above. The effect of radiation on the burning rate of recrystallized ammonium perchlorate was found to be the same as that observed for the commercial, unpurified oxidizer.

The "porous plug" burner was next employed as a fuel burner. Solid polystyrene was packed into the steel tube and then burnt in an environment of gaseous oxygen. The effect of radiation on the burning rate of polystyrene was studied in this manner and the results are shown in Table 6. It is seen that radiation decreases the burning rate of polystyrene with the effect being greater at the lower oxygen flow rate. (This latter effect is similar to what was observed in the ammonium perchlorate burner.)

Table 6

Effect of Radiation on Polystyrene^a Burning Rate

Oxygen Flow Rate (gm./cm. ² /sec.)	Radiation Dose (Mrad)	Burning Rate (in./sec.)
0.55	0	0.092
	25	0.057
0.68	0	0.068
	25	0.059

^a Particle size = 300-350 μ

After having studied the effect of radiation on the burning rates of ammonium perchlorate and polystyrene separately, experiments were performed with solid mixtures of polystyrene and ammonium perchlorate. (In these experiments, of course, there is no flow of gaseous fuel or oxidizer through the burner.) These results are shown in Table 7 for various ammonium perchlorate-polystyrene mixtures in which the ammonium perchlorate has been irradiated. It is seen that just as irradiation of ammonium perchlorate increases its burning rate so does it increase the burning rate of ammonium perchlorate-polystyrene mixtures. That the effect is not as great in the latter case may be comparable to the former case at the low methane flow rate of $0.0072 \text{ gm./cm.}^2/\text{sec.}$

Table 7

Effect of Radiation on Burning Rate of Ammonium Perchlorate-Polystyrene Mixtures^a

<u>% Polystyrene</u>	<u>Radiation Dose (Mrad)</u>	<u>Burning Rate (in./sec.)</u>
10	0	0.041
	50	0.041
	100	0.045
16	0	0.044
	50	0.044
	100	0.050

^a
Particle size: Ammonium perchlorate = 60-65 mesh
Polystyrene = 65-100 mesh

3.3 Experimental Details

A schematic representation of the "porous plug" burner apparatus is shown in Figure 2. A description of the solid

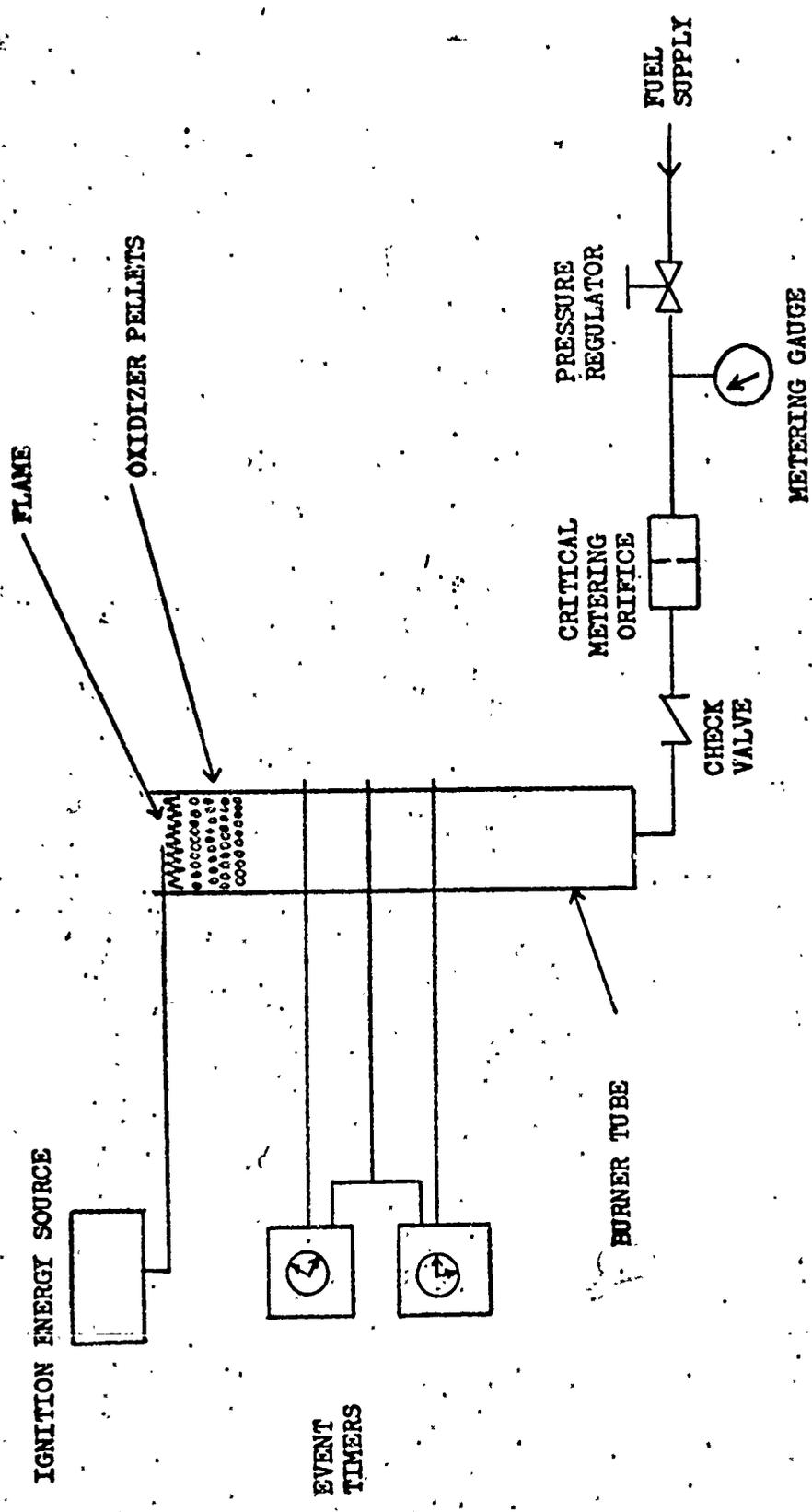


FIGURE 2. POROUS PLUG BURNER APPARATUS

oxidizer burner (i.e., solid oxidizer with gaseous fuel) is given below:

a) Burner Tube and Fabrication

The burner tube was constructed of type 304 seamless, stainless steel tubing of 17.8 cm. length and 1.02 cm. inner diameter. The tube was modified by drilling diagonally into it with a No. 60 drill bit at three two-inch axial intervals in the middle portion of the tube. Three eutectic tin-lead solder wires, 0.022 inch in diameter, were then inserted diagonally through the three axially drilled holes and fastened to, but electrically insulated from, the tube with a porcelain cement. Provision was also made for a nichrome ignition wire at the top of the tube.

A small ball of soft paper was stuffed into one end of the tube and then the tube loaded with ammonium perchlorate crystals. The oxidizer crystals were compacted into the burner tube by subjecting it to a series of sharp taps (ca. twenty times). In order to achieve point of contact bonding between oxidizer crystals and between the tube and oxidizer crystals, the fully loaded tubes were placed in a humidifier and subjected to moist air for ca. 5-10 hours. The tubes were then heated overnight in an oven at ca. 60°C. to dry the oxidizer. The soft ball of paper was then removed from the burner.

b) Fuel System

In operation, the oxidizer burner tube was placed in a vertical position and connected at the bottom via a pressure coupling to the methane fuel input system as shown in Figure 2. The methane throughput was measured by a critical flow orifice located upstream of the burner.

It was not possible to employ watchmaker jewels for critical orifices as the smallest size commercially available produced throughputs that were much too large for the desired burner operating conditions. A new technique was developed for making micro-orifices in conjunction with the John Kronheim Company of East Orange, New Jersey. This company makes orifices approaching 0.0015 inches in throat diameter by first drilling 1/32 inch thick aluminum discs with a 0.005 inch drill and then mechanically swedging the discs until the diameter was reduced. These orifices were still too large (> 0.002 inch diameter) for certain phases of the oxidizer burning operations. To overcome this, the swedged orifices were crimped even more by pressing down onto the disc face with a hand press. This procedure was one of trial and error but with patience did produce small orifices of ca. 0.0007 inch in diameter. These modified disc orifices were calibrated by a volumetric displacement method.

c) Event Timing and Ignition

The deflagration rate of the oxidizer porous plug burner was measured by determining the time required to burn through three equally spaced, longitudinally positioned wires in the burner. The first timing wire was located approximately three inches from the ignition wire as visual observations of the burning process revealed a flat burning surface was achieved within one inch of the ignition wire. The ignition wire was located parallel to the timing wires so that a smooth burning surface was initiated. An electrically heated, nichrome wire was used for ignition of the burner, and eutectic tin-lead wires of 0.022 inch in diameter were used for timing. The eutectic wire was found to have desirable rupture characteristics.

Stacked relays were employed in the timing circuit so that once the circuit was broken, short circuiting caused by melted timing wires contacting the metal tube could not reactivate the timing clocks.

Ignition was accomplished by using the current from a 12 volt battery to heat the 3 ohm resistance nichrome wire which ignited a polystyrene-ammonium perchlorate ignition mixture placed at the top of the burner. The heat generated from the ignition mixture was sufficient to ignite the ammonium perchlorate porous plug burner.

d) Test Procedure

During performance of a porous plug deflagration experiment, the following procedure was employed:

1. Porous plug burner was prepared and installed.
2. Timing wires were checked out for continuity.
3. Fuel gas was flowed at the desired rate through the porous plug burner.
4. Ignition was produced by the imbedded, electrically heated wire, and the propagating deflagration burned out the timing wires.
5. The burning rate was obtained from the measured duration between wire burnouts and the linear distance between wires.

e) Fuel Burner

The experimental procedure for the solid fuel burner (i.e., solid polystyrene with gaseous oxygen) was analogous to the above except for the appropriate substitutions of fuel for oxidizer and vice versa.

4.0

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