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Union Carbide Corporation

FLUORINE OXIDIZERS

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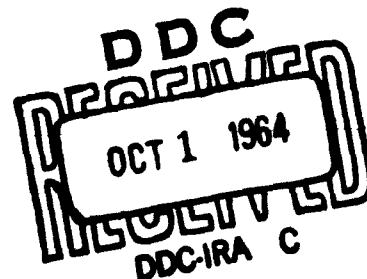


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I. ABSTRACT

Chloryl fluoride reacts with cesium fluoride at 0-25° to produce a solid having a limiting composition near "CsF₂". The solid, however, possesses little oxidizing strength. Reaction of chloryl fluoride with cesium oxide gives a solid product containing cesium, fluorine and chlorine in variable composition. These experiments gave no evidence indicating the formation of a stable fluorochlorate salt, Cs₂ClO₃F, or of a difluorochlorate salt, CsClO₂F₂.

Chloryl fluoride and chlorine trifluoride react with cesium azide with formation of fluorine-containing solids. These reactions are being studied as possible routes to fluorine-nitrogen anions.

The reaction of potassium perchlorate with bromine trifluoride gives nearly quantitative yields of chloryl fluoride and only minor amounts of perchloryl fluoride.

Platinum hexafluoride and chlorine trifluoride react to form chlorine pentafluoride and the solid compound ClF₃·PtF₅. Thermal decomposition of this substance produces fluorine, chlorine trifluoride and platinum tetrafluoride.

II. INTRODUCTION

Work during this quarter has been aimed principally at elucidating the chemical properties of chloryl fluoride and of platinum hexafluoride. The initial effort with chloryl fluoride has been a study of chemical reactions which might lead to formation of fluorochlorate ions or provide evidence concerning the stability of such ions. The reactions chosen were those between chloryl fluoride and alkali metal fluorides and oxides, viz., CsF and Cs₂O, which could provide routes to cesium difluorochlorate, CsClO₂F₂, and to cesium fluorochlorate, Cs₂ClO₃F, respectively. As part of our overall objectives of investigating the chemistry of chloryl fluoride and of synthesizing new, solid oxidizers, the reaction of chloryl fluoride with cesium azide has been investigated as a possible route to nitrogen-fluorine anions. Preliminary results also are reported of a study of the related reaction between chlorine trifluoride and cesium azide.

Platinum hexafluoride has been shown to be a very powerful oxidizing agent as evidenced by its ability to oxidize molecular oxygen¹ to O₂⁺ PtF₆⁻¹ and xenon² to Xe⁺ PtF₆⁻¹. This great oxidizing strength of platinum hexafluoride suggests its utility as a reagent for synthesis of other highly oxidized species. Our program is directed towards a broad investigation into the reactions of PtF₆ with various fluorine compounds. During this quarter the reaction between platinum hexafluoride and chlorine trifluoride has been investigated in detail.

One further aspect of this quarter's work carries over from our previous study of bromine trifluoride as an electrolytic solvent. This has been a study of the reaction between potassium perchlorate and bromine trifluoride, the detailed stoichiometry of which is herein reported.

III. RESULTS AND DISCUSSION

Reaction of Chloryl Fluoride with Cesium Fluoride

The reaction of chloryl fluoride with cesium fluoride was studied as a possible route to CsClO_2F_2 . Stoichiometric data obtained from eleven experiments are summarized in Table I. As can be seen, a wide scatter of results was obtained for the chloryl fluoride to cesium fluoride reacting ratio, with values for this ratio ranging from 0.31 to 1.04. With but one exception (Exp. No. 1) the reaction was found to produce only minor amounts of oxygen. Regardless of the observed reacting ratio and other reaction variables, however, the weight gain of the solid reactants was fairly constant at about 17%. Based on the total weight of solid product obtained and the number of mmoles of cesium fluoride taken for reactions, the average molecular weight of the product was calculated as 179^{+5} .

The non-volatile reaction product is a white to pale yellow solid which fumes and deliquesces in air. When added to water, the solid reacts with moderate vigor and apparent evolution of a gas with a pungent fluorine-compound odor. Similar behavior was noted when the hydrolysis was carried out on the vacuum line but no gases volatile at -78° were produced, thus showing the absence of F_2 , OF_2 or O_2 . Essentially the same results were obtained when hydrolysis was carried out in acid or alkaline solution. Solutions of the substance always possessed sufficient oxidizing strength to colorize acid iodide solution but quantitative analysis showed that not more than a trace of oxidant was present.

In a capillary tube, the solid product melted over the range 130 to 150° to an opaque, viscous fluid which was stable at 300° . When

heated strongly with a flame in a quartz tube, the material either boiled or evolved gases and then solidified. However, only trace amounts of gases were found after cooling the quartz tube to 25°. The x-ray diffraction pattern (Table II) of the substance appeared unique except possibly for a poorly defined cesium fluoride phase. An infrared spectrum of the substance, obtained on a pressed KBr disc, showed broad bands centered at 3.0, 4.85, 5.45, 6.8, 8.15, 10.5 and 12.5 μ . The results of numerous elemental analyses of the product are shown in Table I. In general, the highest fluorine results were obtained when the samples were hydrolysed in closed systems or on the vacuum line. The lower results, obtained on samples hydrolysed in open containers, suggest loss of volatile fluorine-containing materials.

The solid product obtained from Exp. 6 was treated directly with excess BF_3 in an effort to liberate $\text{ClO}_2\text{F}\cdot\text{BF}_3$. The total amount of BF_3 absorbed corresponded very closely to the sum of CsF taken and ClO_2F consumed but no $\text{ClO}_2\text{F}\cdot\text{BF}_3$ was formed; only a small amount of ClO_2 was obtained. The weight of the solid product was very close to that expected for total conversion to CsBF_4 and this identity was confirmed by the x-ray pattern.

Although the wide scatter of results obtained prohibit definitive interpretation, it does seem clear that no stable cesium difluoro-chlorate compound forms in this system. Beyond that deduction only a few trends may be noted. There is a definite and fairly constant weight increase of the solid reactant due to the reaction. The analyses indicate that this weight increase is principally due to an increased fluorine content, and that the limiting F/Cs ratio is 2. This excess fluorine content cannot be accounted

for in terms of CsClO_2F_2 , CsClF_4 , or other fluorochlorate species, since the determined chlorine content (as ClO_4^- , ClO_3^- , ClO_2^- , ClO^- and Cl^-) is inadequately low. It is probable, however, that the solid contains oxygen in the form of an oxyanion of chlorine and this could account partially for the low total analytical figures. If it is assumed that the fluorine analyses are low for those samples hydrolysed in open systems, then the analytical results suggest a limiting composition of CsF_2 for the solid reaction product. The lack of significant oxidizing strength of the material is difficult to reconcile with such a formulation.

Reaction of Chloryl Fluoride with Cesium Oxide.

The reaction of chloryl fluoride with cesium oxide occurs rapidly at temperatures of -78° or lower with evolution of oxygen and chlorine. Stoichiometric data obtained for the reaction are summarized in Table III (Exps. 1 through 4). The molar ratio of chloryl fluoride consumed to cesium oxide taken varied from 1.07 to 2.39 for four experiments, whereas the molar ratio of oxygen evolved to chloryl fluoride consumed was close to unity. Approximately two-thirds of the chlorine content of the chloryl fluoride entering reaction was liberated as elemental chlorine. The solid, non-volatile product contained cesium, chlorine and fluorine but the composition was variable, and no formulation such as that of the fluorochlorate salt could be deduced.

During two of the experiments (Exps. 5 and 6, Table III), the reaction of chloryl fluoride with cesium oxide occurred as a rapid, luminescent reaction. This phenomenon, which occurred as the reaction mixtures were being warmed from -196° to -78° , appeared as a flash of bright, white light of a few seconds duration. It was readily visible through the walls of the

Kel-F reactor and seemed to occur at temperatures close to -78° but was not accompanied by pressure damage to the reactor. Examination of the volatile reaction products showed that all of the chloryl fluoride had been consumed with liberation of one mole of oxygen per mole of chloryl fluoride. The only other volatile product was chlorotrifluoromethane, which must have resulted from attack of the reactants, or reaction intermediates, on the Kel-F reactor. The solid reaction products were found to contain cesium, fluorine and chlorine in non-stoichiometric ratios.

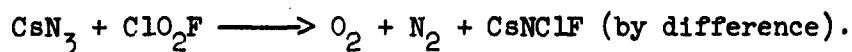
In summary, the reaction of chloryl fluoride with cesium oxide was found to be unpredictable and gave solid products of varying composition. The luminescent reaction was originally observed during our second attempt to carry out the reaction of cesium oxide with chloryl fluoride. The succeeding experiments were carried out in an effort to reproduce consistently this result, but the luminescent reaction occurred in only one other experiment. No evidence suggestive of special conditions or catalysts necessary for initiating this reaction was obtained.

The fast rate of the luminescent reaction and the fact that one mole of oxygen evolves per mole of chloryl fluoride suggests that the overall reaction may simply be decomposition into O_2 and ClF. Subsequent reaction of ClF with the solid reactant could then account for the composition of the non-volatile product.

Reaction of Chloryl Fluoride and Chlorine Trifluoride with Cesium Azide.

The reaction of chloryl fluoride with cesium azide takes place vigorously at 25° but smoothly at -78° . The reaction proceeds in a 1:1 reacting ratio with evolution of one mole each of nitrogen and oxygen per mole of chloryl fluoride taken. The stoichiometric data, therefore,

may be summarized by the equation:



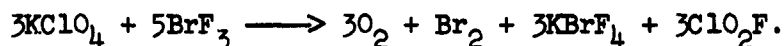
Analysis of the non-volatile reaction product gave the ratio Cs/F/Cl = 1.0/0.49/0.63; the nitrogen analysis has not yet been obtained. The white, solid product did not melt below 300°. An x-ray diffraction pattern showed a clearly defined CsCl phase but no other crystalline phase. Infrared bands at 3.0, 4.75, 6.55, 7.22, 7.97, 8.34, 8.90 and 10.3 μ were observed on a KBr disc of the material. A concentrated solution of the solid in water was deep yellow in color but on dilution the color faded completely. These aqueous solutions possessed no oxidizing strength towards acid iodide solution.

The reaction of chlorine trifluoride with cesium azide also takes place smoothly at -78° with liberation of one mole of nitrogen per mole of cesium azide taken. Chlorine and possibly chlorine monofluoride were also produced in the reaction. The solid residue was found to contain cesium, fluorine and chlorine in the ratio Cs/F/Cl = 1.0/1.56/.11 and a nitrogen content by difference of 4.86%.

These results on the reactions of chloryl fluoride and chlorine trifluoride with cesium azide require verification and refinement. Nevertheless, the results indicate that the solid products contain nitrogen and fluorine, possibly in the form of a nitrogen-fluorine anion.

Reaction of Potassium Perchlorate with Bromine Trifluoride.

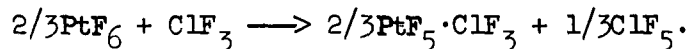
The reaction of potassium perchlorate with bromine trifluoride takes place slowly at 25° with liberation of oxygen, bromine, chloryl fluoride and minor amounts of perchloryl fluoride. The principal reaction may be represented by the equation:



Our early interpretation of the reaction as leading to the formation of stable fluorochlorate species in solution must be withdrawn since experimental data has been obtained which nicely confirms the stoichiometry of the above equation. Nevertheless, it has been observed that when the reacting ratio of KClO_4 to BrF_3 is large, i.e., when the solution is concentrated, the reaction proceeds beyond the 50% completion stage only very slowly. The reasons for this behavior are not clear.

Reaction of Platinum Hexafluoride with Chlorine Trifluoride

Platinum hexafluoride reacts with chlorine trifluoride with formation of chlorine pentafluoride and the compound $\text{PtF}_5 \cdot \text{ClF}_3$. Data for the reaction, shown in Table IV, are best interpreted in terms of the equation:

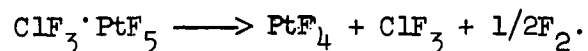


For the first five experiments shown in Table IV, the yields of $\text{PtF}_5 \cdot \text{ClF}_3$ and ClF_5 were somewhat greater than required by the above equation. Since the reacting ratio chosen for these experiments was $\text{PtF}_6:\text{ClF}_3 = 1:1$, it is thought that some further reaction between PtF_6 and the adduct $\text{PtF}_5 \cdot \text{ClF}_3$ must also occur. When the reacting ratio of $\text{PtF}_6:\text{ClF}_3$ was 2:3 (Exps. 6 and 7) the yields of $\text{PtF}_5 \cdot \text{ClF}_3$ and ClF_5 were very close to those required by the proposed equation. Furthermore, when an excess of chlorine trifluoride was used, all of the platinum hexafluoride was converted to the adduct.

The compound $\text{PtF}_5 \cdot \text{ClF}_3$ is a bright yellow solid which reacts violently with water to produce foul-smelling gases. In these respects, the compound appears identical to that obtained by Bartlett³ from

PtF_5 and ClF_3 , although our material appears to decompose rather than melt at 170° as did the compound described by Bartlett.

Thermal decomposition of $\text{PtF}_5 \cdot \text{ClF}_3$ at temperatures up to 620°C gives platinum tetrafluoride, chlorine trifluoride and fluorine. The experimental data, shown in Table V, are adequately described by the equation:



The validity of this equation is based on four experiments, which involved measurement of the quantities of ClF_3 and F_2 evolved, and of the changes in weight of the solid reactants, during decomposition. Platinum tetrafluoride was identified through its x-ray diffraction pattern and by chemical analysis.

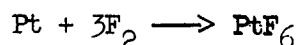
IV. EXPERIMENTAL

Apparatus

High vacuum systems, constructed from nickel tubing and traps, monel fittings and storage bulbs, Hoke TM440 valves, and Helicoid Monel Compound Gauges, are now in use. All reactions were carried out either in nickel or Kel-F reactors.

Chemicals

Platinum Hexafluoride was prepared by the reaction



using the procedure described by Weinstock, Malm and Weaver.⁴ Generally from 7 to 15 grams of PtF_6 were prepared in each run, purified, and stored in a monel flask on the vacuum system.

Chloryl fluoride was prepared from bromine trifluoride and potassium chlorate as described by Woolf.⁵ It was purified by trap to trap fractionation until vapor pressure measurements agreed with those reported in the literature.⁶ Storage in a monel bulb at 25° was satisfactory although slow decomposition occurs with formation of non-condensable gas.

Chlorine trifluoride (Matheson Co.) was purified by repeated trap to trap distillation until vapor pressure measurements indicated a high state of purity.⁷

Cesium fluoride and cesium azide were obtained from K&K Labs., Inc. For a few experiments cesium fluoride was converted to the bifluoride which was then decomposed at 500°. Cesium fluoride prepared in this manner gave essentially the same results in the chloryl fluoride experiments as did the untreated compound. Cesium oxide was obtained from the Rare Metals Chemical Co. Analysis of this material for cesium and alkalinity indicated 95% purity as Cs_2O .

Reaction of Chloryl Fluoride with Cesium Fluoride. These reactions were carried out in nickel or Kel-F reactors of 8-20 cc volume. The cesium salt was transferred to the reactor inside of a dry box, and then thoroughly pumped out on the vacuum line. Four-to-five-fold excesses of chloryl fluoride were taken for reaction in order to insure the presence of some liquid phase in the reactor. The pressures recorded in Table I are the estimated vapor pressures of chloryl fluoride at the temperatures of the reactions.

Attempts were made to follow changes in the composition of the gaseous reactants by infrared spectroscopy but no bands other than those attributable to chloryl fluoride were detected. However, the spectrum of chlorine dioxide coincides with part of the spectrum of chloryl fluoride, so that the formation of ClO_2 could have gone undetected in the presence of the large excess of chloryl fluoride. The gases recovered from the reactions always contained materials more volatile than chloryl fluoride as was shown by an increase in vapor pressure from 9 mm (before reaction) to 20-40 mm (after reaction). Attempts to separate these substances by fractionation were unsuccessful.

The solid products were analysed for cesium by precipitation as the hexachloroplatinate (IV), for fluorine by thorium nitrate titration, and for chlorine by the Volhard method. Aqueous solutions of the $\text{CsF-ClO}_2\text{F}$ products gave negative tests for ClO_4^- by precipitation with nitron. All other oxidation states of chlorine were included in the analysis by reduction to chloride with SO_2 .

Reaction of Chloryl Fluoride with Cesium Oxide. The oxide was carefully pulverized and loaded into the Kel-F reactors inside of a dry box. After evacuation, chloryl fluoride was condensed into the reactor at -196° .

The molar ratio of chloryl fluoride to cesium oxide taken was between two and three in all experiments. Excess chloryl fluoride was recovered only from those experiments carried out at -78° .

The reaction gases were fractionated and identified by vapor pressure measurements. Chlorine was further identified by vapor density measurements, and the identity of chlorotrifluoromethane was confirmed by the infrared spectrum.

Reaction of Chloryl Fluoride with Cesium Azide. Chloryl fluoride, 2.37 mmoles, was condensed at -196° into a Kel-F tube containing 3.03 mmoles of CsN_3 . The reactor was kept at -78° for 18 hours, after which time 4.73 mmoles of non-condensable gas and a trace of condensable gas were recovered. Analysis by VPC using a molecular sieve column showed the non-condensable gas to contain 2.23 mmoles of O_2 and 2.50 mmoles of N_2 ; hence the ratios were $\text{O}_2/\text{ClO}_2\text{F} = 0.94$ and $\text{N}_2/\text{ClO}_2\text{F} = 1.05$. No additional gases were evolved after heating the reactor to 100° for 30 minutes.

The white solid residue did not melt below 300° . Analysis gave 75.7% Cs, 5.36% F, and 12.58% Cl which defines the ratios $\text{Cs:F:Cl} = 1.0:0.49:0.63$. The x-ray pattern showed a clearly defined CsCl phase with no unassigned lines. Bands at 3.0, 4.75, 6.55, 7.22, 7.97, 8.34, 8.90 and 10.3μ were observed in the infrared spectrum of the solid in a KBr disc.

Reaction of Chlorine Trifluoride with Cesium Azide. In a similar manner, the reaction of 2.48 mmoles of CsN_3 with 1.49 mmoles of ClF_3 for 5 hours at -78° produced 2.43 mmoles of N_2 and 0.43 mmoles of Cl_2 . Analysis of the white, solid residue gave 76.1% Cs, 16.9% F and 2.16% Cl: $\text{Cs:F:Cl} = 1.0:1.5:0.11$.

Reaction of Potassium Perchlorate with Bromine Trifluoride. Reaction

of 2.94 mmoles of KClO_4 with 2 ml of BrF_3 for 18 hours at 25° produced 3.23 mmoles of O_2 , 0.15 mmoles of ClO_3F , 2.85 mmoles of ClO_2F and 0.81 mmoles of Br_2 . The observed ratios are: $\text{O}_2/\text{KClO}_4 = 1.10$; $\text{ClO}_2\text{F}/\text{KClO}_4 = 0.97$; and $\text{Br}_2/\text{KClO}_4 = 0.28$; which define the equation



The identity of the solid residue remaining after evaporation of the excess BrF_3 was confirmed by x-ray analysis as KBrF_4 .

Reaction of Chlorine Trifluoride with Platinum Hexafluoride.

In a typical experiment, 3.39 mmoles of PtF_6 and 3.39 mmoles of purified ClF_3 were condensed into a nickel reactor equipped with a Hoke TM440 valve. The reactor was allowed to warm up slowly from -195°C to room temperature and remain overnight at this temperature. The reactor was then opened and the quantity of gaseous products measured. The gaseous products were fractionated using a -126°C trap. The material left in the -126°C trap was identified as ClF_5 by its infrared spectrum⁸ and by vapor pressure measurements.

The bright yellow solid product was weighed and analyzed for platinum by reduction with hydrogen in a nickel boat. The average of three determinations gave 51.45% ($\text{ClF}_3 \cdot \text{PtF}_5$ requires 50.99% Pt). The adduct is very hygroscopic and difficult to handle. It reacts violently with water. The reduction in hydrogen can be facilitated by adding CCl_4 to the solid after weighing, and purging the reduction chamber with N_2 to eliminate the pressure of O_2 before passing H_2 into the system. This procedure eliminates the explosion which otherwise occurs. The temperature of the reduction tube was slowly increased from room temperature to 700°C . After reduction was completed the material was weighed as platinum metal.

The Thermal Decomposition of $\text{ClF}_3 \cdot \text{PtF}_5$

Weighed samples of $\text{ClF}_3 \cdot \text{PtF}_5$ were thermally decomposed in a nickel reactor. Decomposition begins at approximately 110°C . The temperature was increased to as high as 640°C where decomposition appeared to be complete. After cooling, the pressure of condensable and non-condensable gases were measured in standard volumes of the vacuum system. The F_2 produced in the reaction was absorbed by reaction with Hg and the amount of F_2 present determined by difference from the measurement of the total number of mmoles before and after absorption.⁹ ClF_3 was kept behind in the system by a -196°C trap. ClF_3 was identified by infrared spectroscopy and vapor pressure measurements of the gas.

The PtF_4 was identified by x-ray diffraction analysis (comparison with Bartlett's pattern³) and by chemical analysis for Pt (found 71.12% Pt, theoretical for PtF_4 : 71.96%).

V. FUTURE WORK

Major effort will be directed towards continuing study of the reactions of platinum hexafluoride with oxidized systems. The reactions of cesium azide with chloryl fluoride and chlorine trifluoride will be investigated in more detail in order to determine whether fluorine-nitrogen anions are formed.

Because of the complexity of the cesium oxide-chloryl fluoride reaction, it does not appear fruitful to continue this study. It would be of interest, however, to define the conditions necessary for producing the chemiluminescent reaction, and subsequently to examine the system spectroscopically. No further effort is planned for the chloryl fluoride-cesium fluoride reaction.

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TABLE I
Data for CsF-C1O₂F Reaction

Exp. No.	CsF taken mmoles	C1O ₂ F consumed mmoles	C1O ₂ F CsF	reaction tempera- ture °C.	time of reac- tion hrs.	pressure in reactor atm.	O ₂ obtained mmoles	Ave. M.W. of product per Cs g-atom taken	Analysis of product			Cs/F/Cl
									Cs %	F %	Cl %	
1	2.58	1.33	0.52	0	42	1.5	1.08	183	—	^a 15.5	1.54	-/0.82/0.04
2	2.38	2.16	0.91	0	44	1.5	0.09	181	76.5	^c 19.7	0.73	1.0/1.8/0.04
3	1.86	1.93	1.04	0	66	1.5	trace	182	—	—	—	—
4	6.62	3.52	0.53	0	44	1.5	trace	170	78.2	^d 16.2	—	1.0/1.4/—
5	6.59	2.03	0.31	25	144	3	trace	175	77.4	^a 13.6	—	1.0/1.2/—
6	6.57	2.07	0.31	25	144	3	trace	179	—	—	—	—
7	6.52	3.03	0.46	0	144	1.5	trace	177	74.6	^b 20.7	0.58	1.0/1.9/0.03
8	3.49	1.17	0.34	25	64	3	0.46	172	76.2	^a 14.6	2.30	1.0/1.4/0.11
9	2.25	2.12	0.94	25	42	3	0.39	184	70.7	^b 19.3	trace	1.0/1.9/-
10	1.88	—	—	25	90	3	0.36	190	^d 81.5	^b 26.4	2.72	1.0/2.2/0.13
11	2.59	—	—	25	44	3	trace	177	75.4	^b 23.0	3.51	1.0/2.1/0.17
Ave.			0.59					179 ⁺⁵				

- a). hydrolysis in open container
b). hydrolysis in closed system or on vacuum line
c). sample analyzed after fusion in quartz tube
d). high results due to incorrect sample weight

TABLE II

X-Ray Data for CsF-ClO₂F Reaction Product.

$d(\text{\AA})$	I/I ₀	$d(\text{\AA})$	I/I ₀
4.18	MW	1.418	W
3.79	W	1.362	VW
3.39	W	1.345	VW
3.21-3.09	W	1.329	VW
2.99	W	1.283	VW
2.91	VW	1.241	VW
2.82	MS	1.217	VW
2.37	M	1.191	W
2.24	VW	1.144	W
2.17	VW	1.118	W
2.12	VW	1.079	MW
2.08	VW	1.033	VW
2.06	VW	1.021	VW
1.91	MW	1.011	VW
1.86	W	0.997	VW
1.84	VW	0.967	VW
1.78	VW	0.944	VW
1.76	VW	0.923	VW
1.74	VW	0.907	VW
1.71	MW	0.884	VW
1.63	W	0.875	VW
1.52	VW	0.869	VW
1.481	VW		
1.439			

TABLE III
Data for $\text{Cs}_2\text{O}-\text{ClO}_2\text{F}$ Reaction

Exp. No.	Cs_2O taken mmoles	ClO_2F consumed mmoles	$\frac{\text{ClO}_2\text{F}}{\text{Cs}_2\text{O}}$	reaction temperature °C.	reaction time hrs.	O_2 obtained mmoles	Cl_2 obtained mmoles	Ave. M.W. of product per Cs g-atom taken	Analysis of solid product			
									Cs	F	Cl	Cs/F/Cl
1	2.57	5.06	1.97	-78	7	3.54	1.98	170	70.4	10.3	5.67	1.0/1.0/0.3
2	1.68	4.02	2.39	25	1	4.31	1.40	152	82.1	5.80	4.67	1.0/0.5/0.2
3	1.92	3.63	1.89	25	64	3.70	0.84	168	72.3	3.21	7.82	1.0/0.3/0.4
4	1.90	2.03	1.07	-78	18	2.19	.55	159	76.6	6.43	4.69	1.0/0.6/0.2
5	1.79	3.80	—	flash at < 78°		3.49	a 1.41	Wt. loss	-	-	-	1.0/0.6/0.2
6	1.67	3.44	—	flash at < 78°		3.52	b 0.41	Wt. loss	-	-	-	1.0/1.2/0.6

a). 2.32 mmoles of CClF_3 also found.

b). 2.37 " " " "

TABLE IV

Data for $\text{PtF}_6\text{-ClF}_3$ Reaction

Exp. No.	PtF_6 taken mmoles	ClF_3 taken mmoles	$\text{ClF}_3\cdot\text{PtF}_5$ obtained mmoles	$\text{ClF}_3\cdot\text{PtF}_5$ _____ ClF_3 taken	ClF_5 obtained mmoles	ClF_5 _____ ClF_3 taken
1	2.67	2.67	1.80	0.67	_____	_____
2	2.67	2.67	2.68	1.00	1.22	0.46
3	2.98	2.98	2.55	0.86	0.84	0.28
4	3.10	3.10	2.57	0.83	1.59	0.51
5	3.39	3.39	2.57	0.76	1.22	0.36
6	3.43	5.16	3.24	0.63	1.96	0.38
7	3.50	5.27	3.34	0.63	1.99	0.38

TABLE V
Thermal Decomposition of $\text{ClF}_3 \cdot \text{PtF}_5$

Exp. No.	$\text{ClF}_3 \cdot \text{PtF}_5$ taken mmoles	Dec. Temp. °C.	ClF_3 obtained mmoles	F_2 obtained mmoles	PtF_4 obtained mmoles	$\text{ClF}_3 \cdot \text{PtF}_5 / \text{PtF}_4 / \text{ClF}_3 / \text{F}_2$
1	2.43	520	2.49	_____	3.44	1.00/1.41/1.02/___
2	2.48	560	2.59	1.24	2.68	1.00/1.08/1.05/0.50
3	2.56	610	2.59	1.49	2.98	1.00/1.12/1.01/0.57
4	0.80	640	0.86	0.27	0.83	1.00/1.03/1.07/0.34

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