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HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

Richmond Research Center  
Richmond, California

AD 424714

STAUFFER CHEMICAL COMPANY  
Richmond Research Center  
Richmond, California

"HIGH ENERGY OXIDIZERS"

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WASHINGTON, D. C.

Quarterly Technical Summary Report  
for the Period August 1, 1963 to November 1, 1963

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Summary

One compound,  $\text{ClF}_2^+\text{AsF}_6^-$ , was selected from the chlorine-trifluoride based complexes and investigations were concentrated on this single compound. Low temperature NMR, X-ray investigations, conductometric titration and molecular weight determinations were carried out and the ionic structure seems to be proven with reasonable certainty.

Abstract

This is the third Quarterly Technical Summary Report on our investigation on chlorinetrifluoride based complexes.

Some modification was made on the vacuum line to allow its use in conductometric titration and molecular weight determination. At the same time a dry-box was assembled for use with chlorine-trifluoride and similar corrosive materials.

Low temperature NMR work was repeated, but only qualitative proof was obtained for the ionic structure. The dissociation of the complex was measured in  $\text{IF}_5$  and found to be complete within the error of the measurement. The ionic structure was proved by conductometric titration too.

The Debye-Scherrer powder diagram was obtained for both  $\text{KAsF}_6$  and  $\text{ClF}_2^+ \text{AsF}_6^-$ . ~~Investigations are not yet finished on this field.~~

### Introduction

In order to prove the ionic structure of chlorinetrifluoride based complexes NMR and IR investigations were made in the previous quarter. Only qualitative observations could be made from the results because of the fast fluorine exchange between the solvent,  $\text{ClF}_3$ , and the complexes. Investigations were continued at lower temperatures but no quantitative conclusions could be made from the results. Other methods, such as classical molecular weight determinations and conductometric titration, were the most promising ones to show the dissociation of these complexes.

### Discussion

#### Vacuum Line and Dry-Box

The vacuum line was modified to adapt it to molecular weight determination and conductometric titration. A Dry-Box was set up for handling the necessary chemicals under anhydrous conditions because of their hygroscopic nature. The transparent parts of the Dry-Box were covered by thin Teflon sheet. The metal parts were covered by a thin film of heavy Fluorocarbon-oil in order to prevent corrosion. Satisfactory results could be obtained under such conditions.

#### Nuclear Magnetic Resonance

The  $\text{ClF}_2^+\text{AsF}_6^-$  complex was prepared again in chlorinetrifluoride as solvent for low temperature NMR investigations. A sample of pure  $\text{ClF}_3$  also was submitted. Earlier investigations<sup>(1)</sup> claim a triplet and a doublet for pure  $\text{ClF}_3$  at low temperature which transforms to one broad peak if the smallest impurity was present. Chlorinetrifluoride was purified repeatedly, but only one broad unresolved peak could be obtained even at  $-83^\circ\text{C}$ ., its freezing point. No fine structure could be observed with the complex in chlorinetrifluoride solution. The splitting was obtained by the authors cited above in Teflon tubes and metal vacuum line. This procedure might assure less impurities in the samples, but no proof is available that the glass is responsible for not obtaining the fine structure.

#### Solubility

One of the biggest problems in the investigation of  $\text{ClF}_3$  based complexes is the lack of inert solvents other than halogenfluorides, since it reacts with almost anything. Commercial iodinepentafluoride was purified and the solubility of different compounds in it was investigated. It is miscible with  $\text{ClF}_3$ , it dissolves considerable amount of  $\text{AsF}_5$  and even more  $\text{ClF}_2^+\text{AsF}_6^-$ . Potassium fluoride has limited solubility, while forming  $\text{KIF}_6$ , but  $\text{NaF}$  is almost completely insoluble. Some solubility was observed in the case of  $\text{KAsF}_6$ , but

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(1) Hamer, A. N., Leece, J., Bentley, P. G., United Kingdom Atomic Energy Authority, Industrial Group, 1 GR-TN/CA-1048 p. 10

less than with KF. In the case of  $\text{BrF}_3$ , similar solubilities were observed, but the main problem was the purification of  $\text{BrF}_3$ . In glass a relatively fast reaction was noted and the influence of the impurities on the conductivity can not be excluded. Therefore,  $\text{IF}_5$  was used in the following experiments.

### Freezing Point Depression

The molar freezing point depression of  $\text{IF}_5$  was determined using KF. Attempts with NaF and  $\text{KAsF}_6$  failed because of their limited solubility in  $\text{IF}_5$  as mentioned above. Iodinepentafluoride forms  $\text{KIF}_6$  rapidly with KF, which is a known ionic compound. Therefore, it can be supposed with reasonable certainty that it is dissociated in  $\text{IF}_5$  completely, if it is present in small concentrations. Based on this assumption a value of  $7.165^\circ\text{C/mol}$  was found for the molar freezing point depression constant of  $\text{IF}_5$  in the following equation:

$$\Delta T = \frac{\Delta T_m \cdot g \cdot 1000 \cdot [1 + (n-1)\alpha]}{M \cdot G_0}$$

where  $\Delta T_m$  = molar freezing point depression constant

$g$  = weight of dissolved compound in gr

$G_0$  = weight of solvent in gr

$M$  = molecular weight of dissolved compound

$\alpha$  = dissociation coefficient

$n$  = number of particles forming at the total dissociation of one molecule of the dissolved compound

From this equation almost total dissociation was found in a nearly 0.1 molar solution. Since the solution is conductive the dissociation must give ionic particles and not  $\text{ClF}_3$  and  $\text{AsF}_5$  which could not contribute to the conductivity upon the solution of the complex in  $\text{IF}_5$ .

### Conductometric Titration

Since the solution of  $\text{ClF}_2^+ \text{AsF}_6^-$  in  $\text{IF}_5$  is conductive, a change in the conductivity could be observed while titrating with a suitable titer. If the complex reacts with  $\text{K}^+ \text{IF}_6^-$  in  $\text{IF}_5$  solution the following reaction will take place:



Chlorinetrifluoride and iodinepentafluoride are not conductive either separately or in mixture. Therefore, first the complex should be replaced by  $\text{K}^+ \text{AsF}_6^-$ . This actually involves the replacement of the  $\text{ClF}_2^+$  cation by a  $\text{K}^+$  cation, which process would not change too much the conductivity. When all the complex will be replaced a jump

is expected in the conductivity upon the addition of excess  $K^+IF_6^-$  solution.

The titration showed this jump at the place calculated from the concentration within the limit of experimental errors. First a small increase in the conductivity was observed which is also in agreement with the ionic structure, since the  $K^+$  cation should have a higher ionic mobility than the  $ClF_2^+$  cation. Figure 1 gives the titration curve. Since the titration was carried out with a relatively high increase of volume because of the limited solubility of  $KIF_6$  in  $IF_5$ , the results were corrected by a factor of  $V_0/V_0 + \Delta V$ , where  $V_0$  is the starting volume and  $\Delta V$  is the added volume of  $KIF_6$  solution. In such way almost completely straight lines were obtained.

#### Structure Investigation by X-Ray

The X-Ray investigation of the  $ClF_2^+$  complexes was limited to the Debye-Scherrer powder technique, since the growing of single crystals of the  $ClF_2^+$  based complexes from  $ClF_3$  solutions was connected with too many experimental difficulties.

The crystal structure of complex fluorides of general formula  $A^I B^V F_6$  is relatively well investigated<sup>(2)</sup>. It was found that these compounds fall into five structural types and that the structure adopted depends on the size of the ion  $A^I$  and  $B^V$ .

In the case of the hexafluoroarsenates the following structure type dependence of the cation radius was found:

TABLE I

|                               |                   |                                                                       |                 |
|-------------------------------|-------------------|-----------------------------------------------------------------------|-----------------|
| Increasing cation radius<br>↓ | Li $[AsF_6]$      | rhombohedral, $Li[SbF_6]$ type<br>(slightly distorted NaCl structure) | coord. number 6 |
|                               | Na $[AsF_6]$      |                                                                       |                 |
|                               | Ag $[AsF_6]$      | cubic facecentered, NaCl type                                         | coord. number 6 |
|                               | $O_2 [AsF_6]$ (3) |                                                                       |                 |
|                               | K $[AsF_6]$       | rhombohedral, $K[OsF_6]$ type<br>(distorted CsCl structure)           | coord. number 8 |
|                               | Tl $[AsF_6]$      |                                                                       |                 |
|                               | Rb $[AsF_6]$      |                                                                       |                 |
|                               | Cs $[AsF_6]$      |                                                                       |                 |

(2) A summary of all the work done is given by: R. D. W. Kemmitt, D. R. Russell, D. W. A. Sharp, J. Chem. Soc. 1963, 4408

(3) Thiokol, Report RMD 5009-Q3 (Oct. 1962-Jan. 1963)

If it could be found that the crystal structure of the  $[\text{ClF}_2^+][\text{AsF}_6^-]$  is in agreement with this radius dependency of the cation, this would be an additional proof that the  $[\text{ClF}_2^+][\text{AsF}_6^-]$  actually has a hexafluoroarsenate anion and therefore an ionic structure.

The powder diagram of  $\text{K}[\text{AsF}_6]$  was taken and found to be in agreement with the literature<sup>(4)</sup>.

The powder diagram of  $[\text{ClF}_2^+][\text{AsF}_6^-]$  was also taken and attempts to index it were started. Table II gives the diffraction pattern of  $[\text{ClF}_2^+][\text{AsF}_6^-]$ .

TABLE II

Powder diagram of  $[\text{ClF}_2^+][\text{AsF}_6^-]$

$\text{Cu } \alpha$  rad., Ni Filter - 3 hr. 45 KV 20 mA

| Uncorr 2 $\theta$ |             | dA°   | ⊖     | sin <sup>2</sup> $\theta$ |
|-------------------|-------------|-------|-------|---------------------------|
| 106.7-90.1 = 16.6 | strong      | 5.34  | 8.30  | .0209                     |
| -88.4 = 18.9      | weak        | 4.84  | 9.15  | .0253                     |
| -85.6 = 21.1      | very strong | 4.21  | 10.55 | .0335                     |
| -83.4 = 23.3      | weak        | 3.81  | 11.65 | .0408                     |
| -82.8 = 23.9      | medium      | 3.72  | 11.95 | .0429                     |
| -78.9 = 27.8      | medium      | 3.21  | 13.90 | .0577                     |
| -77.1 = 29.6      | weak        | 3.02  | 14.80 | .0653                     |
| -74.2 = 32.5      | very weak   | 2.75  | 16.25 | .0783                     |
| -73.2 = 33.5      | very weak   | 2.67  | 16.75 | .0831                     |
| -70.7 = 36.0      | weak        | 2.49  | 18.00 | .0955                     |
| -69.6 = 37.1      | very weak   | 2.42  | 18.55 | .1012                     |
| -63.6 = 43.1      | very weak   | 2.097 | 21.55 | .1349                     |
| -63.0 = 43.7      | weak        | 2.070 | 21.85 | .1385                     |
| -61.7 = 45.0      | very weak   | 2.013 | 22.50 | .1464                     |
| -56.8 = 49.9      | weak        | 1.826 | 24.95 | .1780                     |
| -55.6 = 51.1      | weak        | 1.786 | 25.55 | .1860                     |
| -51.5 = 55.2      | very weak   | 1.663 | 27.60 | .2146                     |
| -50.2 = 56.5      | very weak   | 1.627 | 28.25 | .2239                     |

(4) R. B. Roof, Octa Cryst. (1955) 8, 739

## Experimental

### Dry-Box and Vacuum Line

A metal Dry-Box with plexiglass windows was modified in the following way: All plexiglass parts were covered with a transparent 0.05 mm thick Teflon sheet, which was held in place by Teflon tapes. The metal parts were covered by a thin film of Halocarbon 13-21 heavy oil. No vacuum was used, only purge with carefully dried nitrogen in both the working area and the inlet chamber. This precaution combined with the use of the vacuum line was sufficient to handle the reagents under anhydrous conditions.

### Nuclear Magnetic Resonance

Samples of  $\text{ClF}_2^+\text{AsF}_6^-$  in chlorinetrifluoride for NMR studies were prepared in similar way described in earlier reports. The investigations were carried out at low temperature (down to  $-80^\circ\text{C}$ .) with no quantitative proof for the ionic structure.

### Solubility

The commercial  $\text{BrF}_3$  and  $\text{IF}_5$  had the following specific conductance respectively:  $8.5 \cdot 10^{-3}$  and  $1.3 \cdot 10^{-4} \text{ cm}^{-1} \text{ ohm}^{-1}$ . Both were distilled under vacuum in the glass vacuum line. The conductivity of  $\text{BrF}_3$  did not change, but that of  $\text{IF}_5$  decreased to  $1.2 \cdot 10^{-5} \text{ cm}^{-1} \text{ ohm}^{-1}$ . Distilled  $\text{IF}_5$  was colorless and it could be kept in glass at dry-ice temperature for a long time without essential change in its conductivity. This distilled  $\text{IF}_5$  was used to determine the qualitative solubility of various inorganic compounds in it. Volatile materials such as  $\text{ClF}_3$  and  $\text{AsF}_5$  were condensed into it from the vacuum line. Solid materials such as  $\text{KF}$ ,  $\text{NaF}$ ,  $\text{KAsF}_6$  and  $\text{ClF}_2^+\text{AsF}_6^-$  were added to the  $\text{IF}_5$  in the conductivity cell and the liquid was stirred by a magnetic stirrer for half an hour.

When chlorinetrifluoride was added no change was observed in the conductivity. With  $\text{NaF}$ , similarly only a minor change was noted. A slurry formed at less than 0.1 molar concentration. It was stirred by a magnetic stirrer for two hours but the  $\text{NaF}$  did not dissolve. With  $\text{KAsF}_6$  again a slurry was obtained at the beginning, which very slowly cleared up. Potassiumfluoride took only a short time, but it was not soluble in larger quantities. Finally,  $\text{ClF}_2^+\text{AsF}_6^-$  was dissolved instantaneously forming even a molar solution. This gives the following order of solubility:



### Freezing Point Depression

A standard all glass equipment with a glass joint connection to the vacuum line was used for these measurements. A magnetic stirrer insured a uniform temperature distribution. The freezing point of  $\text{IF}_5$  was determined with an accuracy of  $\pm 0.005^\circ\text{C}$ . The following experiments were carried out:



Potassium fluoride was powdered in the Dry-Box and 0.1137 g. of it was dissolved in 23.55 g. of  $\text{IF}_5$ . In repeated determinations a decrease of  $1.213^\circ\text{C}$  in the freezing point of  $\text{IF}_5$  was observed. Since  $\text{KF}$  forms  $\text{KIF}_6$  with  $\text{IF}_5$  only 23.12 g. should be counted as a solvent. Finally, it is known that  $\text{KIF}_6$  is an ionic compound and therefore it is logical to assume that it is completely dissociated to  $\text{K}^+$  and  $\text{IF}_6^-$  in diluted  $\text{IF}_5$  solutions. From these values the following equation can be written for the molar freezing point depression.

$$T_m = \frac{1.213 \times 58.1 \times 23.12}{0.1137 \times 1000 \times 2} = 7.165^\circ\text{C}$$

In another experiment 0.5748 g. of  $\text{ClF}_2^+\text{AsF}_6^-$  was dissolved in 24.99 g. of  $\text{IF}_5$  and  $1.250^\circ\text{C}$  freezing point depression was observed. The following freezing point depression and change in the conductivity should be expected in the case of:

|                                                       | <u><math>\Delta T</math> theory</u> | <u>Conductivity</u> |
|-------------------------------------------------------|-------------------------------------|---------------------|
| A. Ionic compound, completely dissociated             | $1.257^\circ\text{C}$               | conductive          |
| B. Coordination complex, undissociated                | $0.628^\circ\text{C}$               | non-conductive      |
| C. Decomposition to $\text{AsF}_5$ and $\text{ClF}_3$ | $1.257^\circ\text{C}$               | non-conductive      |

Since a freezing point depression of  $1.250^\circ\text{C}$  and a conductivity in the  $10^{-2}$  to  $10^{-3} \text{ cm}^{-1} \text{ ohm}^{-1}$  order was found, there is no doubt left that the possibilities B and C must be excluded. Therefore, it can be stated that the  $\text{ClF}_3 \cdot \text{AsF}_5$  complex exists in  $\text{IF}_5$  solution in the ionic form as  $\text{ClF}_2^+$  and  $\text{AsF}_6^-$ .

#### Conductometric Titration

An approximately 0.1 molar  $\text{KIF}_6$  solution in  $\text{IF}_5$  was prepared ( $f = 1.15$ ) by dissolving 0.1948 g. of  $\text{KF}$  in 93.46 g. of  $\text{IF}_5$ . The density of  $\text{IF}_5$  at the working temperature ( $296^\circ\text{K}$ ) was calculated (from the equation  $d = 4.38 - 0.004T$ ) to be  $3.20 \text{ g./cm}^3$ . This gives a concentration of 6.7 mg  $\text{KIF}_6/\text{ml}$ .

A standard conductometric cell was modified in such way that it could be connected to the vacuum line and the titration could be carried out with the exclusion of air moisture. A quantity of 0.1460 g. of  $\text{ClF}_2^+\text{AsF}_6^-$  was dissolved in 48.1 g. of  $\text{IF}_5$  (approximately 15 ml.). Under such conditions the equivalence point should be

$$\frac{58.1 \times 146.0}{262.4 \times 6.7} = 4.84 \text{ ml.}$$

The result of the conductometric titration is 4.93 ml., supposing ionic structure of the complex. The curve is shown in Figure 1 together with the corrected one which takes into consideration the dilution effect.

AEP:ls  
November 26, 1963

