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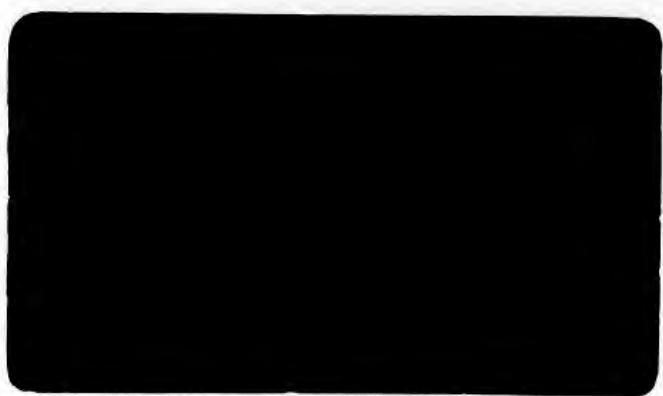


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HIGH ENERGY OXIDIZERS

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Project NR 093-035

Richmond Research Center  
Richmond, California

STAUFFER CHEMICAL COMPANY  
Richmond Research Center  
Richmond, California

"HIGH ENERGY OXIDIZERS"

CONTRACT Nonr-4019(00)

Project NR 093-035

*QTR No. 399.42*

OFFICE OF NAVAL RESEARCH

WASHINGTON, D. C.

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

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TABLE OF CONTENTS

|                                    | <u>Page No.</u> |
|------------------------------------|-----------------|
| Technical Report Distribution List | 1               |
| Summary                            | 1               |
| Abstract                           | 2               |
| Introduction                       | 3               |
| Discussion                         | 3               |
| Vacuum Line                        | 3               |
| Solubility                         | 3               |
| Nuclear Magnetic Resonance         | 3               |
| Infrared Spectrum                  | 4               |
| Experimental                       | 5               |
| Vacuum Line                        | 5               |
| Purification                       | 5               |
| Solubility                         | 5               |
| Nuclear Magnetic Resonance         | 5               |
| Infrared Spectrum                  | 6               |
| Table I                            | 7               |
| Table II                           | 8               |

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Summary

Investigations were continued to prove the ionic structure of chlorinetrifluoride based complexes. For this purpose NMR and IR studies were made. The former is hindered by the lack of a solvent, and further work is needed. Results obtained so far by both IR and NMR are in agreement with the ionic structure. Low temperature NMR studies will give the final proof for the ionic structure.

Abstract

This is the second Quarterly Technical Summary Report on our investigation on the complexes of chlorinetrifluoride.

Further modification was made on the vacuum line, mostly to make its operation more safe. This was necessitated by an explosion experienced during the last report period.

Oleum, fluorosulfonic acid, sulfurtrioxide and  $\text{BrF}_5$  were investigated as possible solvents for the complexes in the NMR studies. The first three gave chemical interactions, while  $\text{BrF}_5$  exchanged fluorine with the complexes. Low temperature NMR work was attempted, but the results were not reproducible because of mechanical difficulties with the NMR.

Infrared studies were made on  $\text{ClF}_3$ ,  $\text{AsF}_5$  (both in solid and gasphase),  $\text{KAsF}_6$  and  $\text{ClF}_2^+\text{AsF}_6^-$ . Different windows were used and the application of KBr coated with a thin Kel-F layer was found to be the most suitable among the possible solutions. Definite proof was obtained for the presence of the  $\text{AsF}_6^-$ .

### Introduction

The preparation and physicochemical properties of the chlorine-trifluoride complexes were reported in the last Quarterly Technical Summary Report. Conductivity measurements indicated an ionic character. Similar conclusion could be made by vapor pressure and preliminary NMR investigations. For the final proof, however, complete NMR and IR investigations were needed.

### Discussion

#### Vacuum Line

The vacuum line was further improved from safety reasons. Additional cold traps were applied to insure a more efficient trapping of any waste material. The vacuum pump was filled with an inert Kel-F oil and the whole vacuum line was surrounded completely with sliding safety shields. No difficulties were experienced in this way. The addition of a separate exhaust system is considered to obtain complete protection against any danger.

#### Solubility

So far in our investigations chlorinetrifluoride was the only solvent for our complexes. However, this was found to be unsuitable for NMR studies around room temperature, since strong fluorine exchange was observed between the solvent and the complexes. Because of the high reactivity of the complexes the number of available inert solvents is very limited. The following solvents have been tested for inertness: 60% oleum, fluorosulfonic acid and sulfurtrioxide. The conductivity of the solvents increased 50-100 times in each case after the addition of the complexes, but at the same time color formation and gas evolution was observed, indicating reaction between the solvents and the complexes.

Another possibility was the application of another halogenfluoride as a solvent. It was reported earlier, that  $\text{BrF}_5$  was the only halogenfluoride which was NMR inactive toward  $\text{ClF}_3$ <sup>(1)</sup>. Brominepentafluoride itself was found to form solid complexes with Lewis acids. In our studies we found that the chlorinetrifluoride complexes dissolved in  $\text{BrF}_5$  without any sign of reaction. The conductivity of  $\text{BrF}_5$  increased 50-100 times. This indicated that  $\text{BrF}_5$  could be used as a solvent for our NMR studies if it is NMR inactive towards our complexes too.

#### Nuclear Magnetic Resonance

Samples of pure  $\text{ClF}_3$ ,  $\text{BrF}_5$ ,  $\text{BrF}_5 \cdot \text{AsF}_5$  in  $\text{BrF}_5$  and  $\text{ClF}_3 \cdot \text{AsF}_5$  in  $\text{BrF}_5$  were prepared for NMR studies with some difficulties. The samples, however, showed rapid fluorine exchange between the solvent and the complexes. This indicates that although  $\text{BrF}_5$  does not exchange fluorine with  $\text{ClF}_3$ , the  $\text{ClF}_2^+$  cation is more reactive than  $\text{ClF}_3$  from this

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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

point of view. This is an indirect proof for the existence of the  $\text{ClF}_2^+$ , since such a rapid fluorine exchange could not be explained by the formation of any other type of complexes, if  $\text{ClF}_3$  and  $\text{BrF}_5$  are NMR inactive towards each other as earlier investigations showed.

The samples were prepared again in chlorinetrifluoride solution and they were subjected to low temperature NMR studies. The qualitative results indicated again the ionic structure, but the repetition of the experiments with the same samples gave different quantitative values. This was decided to be the fault of the method and presently the possibility of adjustment of the NMR spectrometer is being studied, before further NMR work will be done.

#### Infrared Spectrum

We have reported earlier, that IRTRAN-2 windows were resistant towards chlorinetrifluoride. However, their use is limited by their absorption, starting from  $710 \text{ cm}^{-1}$ . When they were used with  $\text{ClF}_3$  and  $\text{AsF}_5$  only very poor spectra were obtained since most of the fundamental vibrations appear around or under  $700 \text{ cm}^{-1}$ . Therefore, a search was made for other windows which had transmission even under this value and were resistant against the materials used in these studies. It was found that KBr windows could be coated by a very thin layer of Kel-F grease and they still gave acceptable transmission in the most important ranges. The spectrum of  $\text{ClF}_3$ ,  $\text{AsF}_5$  (both in solid and gas-phase),  $\text{KAsF}_6$  and  $\text{ClF}_2^+\text{AsF}_6^-$  was taken down to  $400 \text{ cm}^{-1}$ . The presence of the  $\text{AsF}_6^-$  anion could be proven easily by the spectrum of  $\text{KAsF}_6$ . The presence of a  $\text{ClF}_2^+$  cation can be established only by theoretical consideration since nothing is known so far about  $\text{ClF}_2^+$  cation in the IR literature. Unfortunately the fundamental vibration of the  $\text{ClF}_2^+$  cation can not be assigned without doubt; therefore, its definite structure determination can not be done by this IR investigation. The presence of the  $\text{AsF}_6^-$  anion and the known 1:1 mol ratio between the components leave no other possibility in any case. The comparison of the different spectra can be seen in Table I.

## Experimental

### Vacuum Line

The explosion which was experienced during the last report period necessitated further improvements in the set-up of the vacuum line in order to assure even safer working conditions.

First more cold traps were inserted between the system and the vacuum pump, which enables us to evacuate the vacuum line without a direct connection to the pump. All traps are cooled by liquid  $N_2$ . In addition, the vacuum pump was cleaned, rinsed and then it was filled by a high boiling Kel-F based Halocarbon oil (Series No. 13-21). The pump operates satisfactory with this oil. Finally, the whole system was surrounded by sliding safety shields, which allows its operation with minimum exposure of hands and face to danger. The only problem remaining is the exhaust system, which would not be too efficient in the case of an unexpected explosion. The solution of this problem is being investigated.

### Purification

All fluorine compounds were purified as described in our previous report. Oleum, fluorosulfonic acid and sulfurtrioxide were pure commercial products.

### Solubility

The solubility of the complexes in different solvents was determined in the conductivity cell described in the previous report. The general procedure was to fill the cell with the solvent studied and its conductivity was measured. Then the solid complex was introduced through the sidearm of the cell in an approximate quantity of 20-30 mg. Since the exact values were not important as far as the solubility is concerned, no quantitative measurements were made. In each case a 50-100 fold increase of the conductivity was observed. This indicated not only the dissolving of the complexes, but also the ionic character of the solution. Unfortunately, in the case of oleum, fluorosulfonic acid and sulfurtrioxide immediate gas formation was observed and a pale yellow color formed in the clear solution.

When the complexes were added to  $BrF_5$  no gas evolution or change of color was observed. The conductivity, however, increased in the usual order. When only the Lewis acids were added to  $BrF_5$  an increase of the conductivity was observed again, but a crimson solution was obtained. No essential change of conductivity was observed when some  $ClF_3$  was added to  $BrF_5$ .

### Nuclear Magnetic Resonance

The complexes in  $BrF_5$  solution were prepared for NMR study in the vacuum line using the set-up described in the previous report. The  $BrF_5$  reacted slowly with the NMR tubes at room temperature and built up some pressure overnight, which resulted in the explosion of the tubes. The second time the samples were stored in Dry-Ice overnight and transferred next day immediately to the NMR spectrograph.

One of the samples blew up again, but the rest could be studied.

The samples in excess  $\text{ClF}_3$  as solvent were prepared similarly as reported earlier. The study was attempted at temperatures down to  $-80^\circ\text{C}$ . Absorption was obtained for  $\text{ClF}_3$ ,  $\text{AsF}_6^-$  and supposedly  $\text{ClF}_2^+$ , but the ratio of  $\text{AsF}_6^-$  and  $\text{ClF}_2^+$  was varying and therefore the quantitative determination could not be made.

#### Infrared Spectrum

The spectrum of  $\text{ClF}_3$  and  $\text{AsF}_5$  was studied with different windows. In the case of  $\text{NaCl}$  conversion to  $\text{NaF}$  was observed. With IRTRAN-2 windows no etching was observed, but the spectra could not be evaluated because of their limited range of useability. Potassium bromide windows in the cell described in the first report were used with coating on their surface. Teflon coating, obtained from a can of Fluoroglide, did not give a continuous cover, and therefore some attack was observed. The best results were obtained by Halocarbon's Kel-F based stopcock grease.

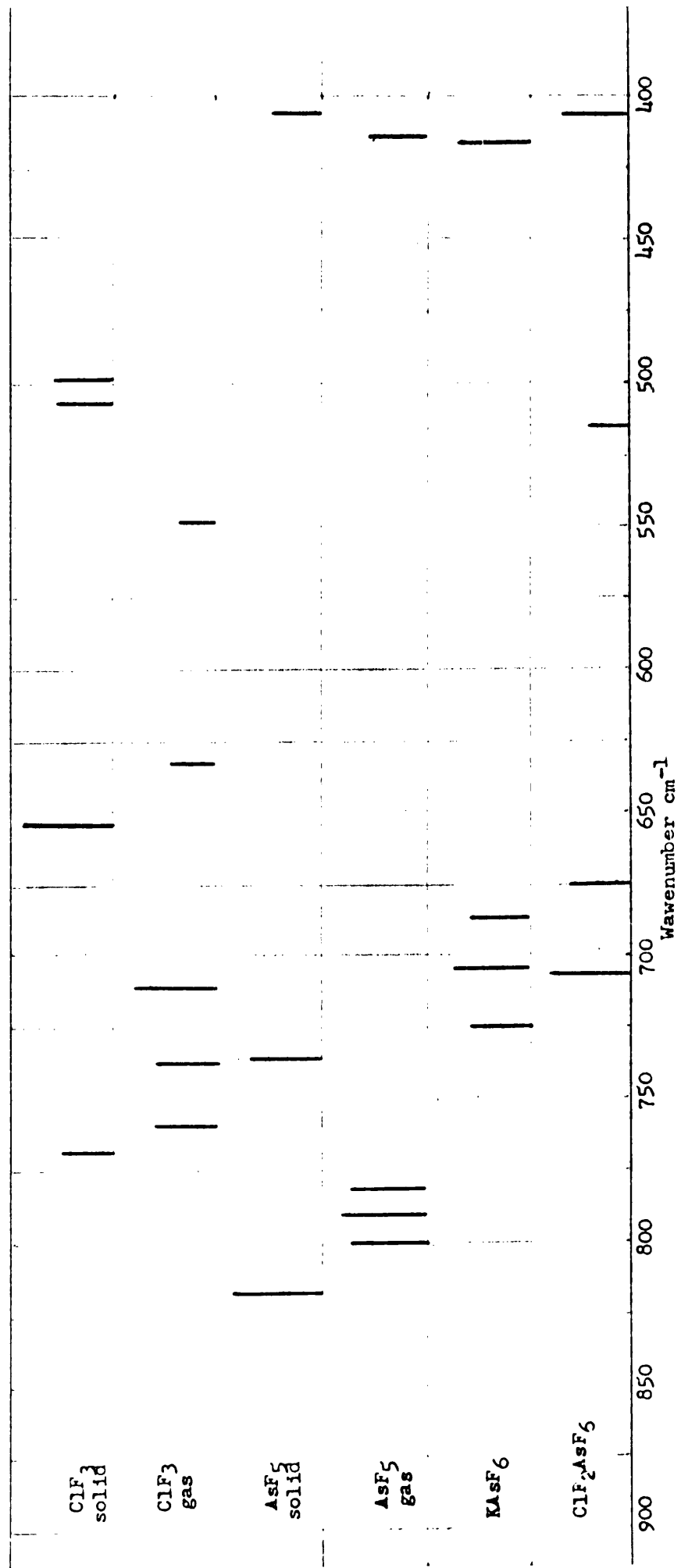
For comparison,  $\text{KAsF}_6$  was prepared in the following way. One gram of  $\text{KF}$  was placed in the vacuum line and 5 ml. of  $\text{AsF}_3$  was condensed on it. After an hour the excess  $\text{AsF}_3$  was pumped off and the remaining solid was treated very cautiously with an excess of  $\text{ClF}_3$ . A violent reaction took place first, which simmered down later. The excess  $\text{ClF}_3$  was pumped off and the  $\text{KAsF}_6$  was obtained in high purity.

#### Analysis:

|    | <u>Theor.</u> | <u>Found</u> |
|----|---------------|--------------|
| F  | 49.9%         | 48.8%        |
| K  | 17.3%         | 16.4%        |
| As | 32.8%         | 31.7%        |

Its IR spectrum was taken as a  $\text{KBr}$  pellet.

AEP:ls  
August 23, 1963



T A B L E I.

Table II

|                                   | <u>Wave number (cm<sup>-1</sup>)</u> | <u>Intensity</u> |
|-----------------------------------|--------------------------------------|------------------|
| ClF <sub>3</sub> gas              | 549                                  | mw               |
|                                   | 631                                  | m                |
|                                   | 710                                  | vs               |
|                                   | 742                                  | ms               |
|                                   | 759                                  | ms               |
| ClF <sub>3</sub> solid            | 499                                  | m                |
|                                   | 507                                  | m                |
|                                   | 654                                  | vs               |
|                                   | 766                                  | m                |
| AsF <sub>5</sub> gas              | 410                                  | ms               |
|                                   | 780                                  | vs               |
|                                   | 790                                  | vs               |
|                                   | 800                                  | vs               |
| AsF <sub>5</sub> solid            | 404                                  | m                |
|                                   | 739                                  | s                |
|                                   | 814                                  | vs               |
| KAsF <sub>6</sub>                 | 413                                  | ms               |
|                                   | 685 (sh)                             | m                |
|                                   | 705                                  | vs               |
|                                   | 725 (sh)                             | m                |
| ClF <sub>2</sub> AsF <sub>6</sub> | 405                                  | s                |
|                                   | 514                                  | w                |
|                                   | 675                                  | m                |
|                                   | 707                                  | vs               |

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