

SOME STUDIES IN INORGANIC FLUORINE CHEMISTRY

by

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I. INTRODUCTION

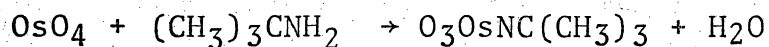
This research consists essentially of three parts. The first part describes attempts to prepare a compound of osmium containing multiple-bonded nitrogen. From a study of the existence of n-t-butyl osmiamate, it was our belief that pentafluorosulfanylamine and osmium tetroxide would also form pentafluorosulfanyl osmiamate through the maximum possible use of all available bonding orbitals. The second part describes attempts to prepare the known mercuric iminosulfur difluoride by using a novel method of synthesis. Reaction of mercury isocyanate with sulfur tetrafluoride was hoped to prove a simpler and more direct method for the reaction. Many organoiminosulfur difluorides have been obtained from the reaction of SF₄ with covalent isocyanates. The third part describes the investigation of the reaction of molybdenum hexacarbonyl with CsF in ethanol under reflux condition, where a metal carbonyl fluoride was believed to be formed.

PART A:

THE ATTEMPTED PREPRATION OF SF₅NOsO₃

I. INTRODUCTION

The purpose of this portion of this work was to investigate the possibility of preparing pentafluoro-sulfanyl osmiamate, SF_5NOsO_3 . Since the compound N-t-butyl osmiamate (1), $\text{C}_4\text{H}_9\text{NOsO}_3$, was prepared quite readily by the reaction of osmium tetroxide with t-butylamine as shown by the following chemical equation:



the reaction was expected to be an easy one. An attempt was made to react OsO_4 with SF_5NH_2 in order to prepare the analogous compound pentafluorosulfanyl osmiamate in a similar manner. In the expected compound the osmium atom would be bonded to three oxygen atoms by means of double bonds and to a nitrogen atom which is attached to a pentafluorosulfanyl- group by means of a double or triple bond.

II. EXPERIMENTAL SECTION

A. EQUIPMENT

1. Reactors

The preparation of some of the starting materials was carried out in stainless steel cylinders (Hoke, Inc., Cresskill, N. J.) of either 35 ml. or 75 ml. capacity. These were equipped with Hoke Model M327A series needle valves. Teflon tape (Hercules Chemical Co., Inc., New York, N. Y.) was applied to the threads on the fittings to provide leak-tight seals. The reaction of OsO_4 with SF_5NH_2 was run in a Pyrex vessel equipped with a male 24/40 tapered joint. A high vacuum stopcock, fitted with a female joint at one end and a 18/9 ball joint at the other end, was used to close the reaction vessel. Halocarbon wax was applied on the joints.

Kel-F reaction tubes, 6 in. by 3/4 in., were fitted with a brass female flare nut. A Kel-F tapered plug was drilled and threaded to provide a vacuum tight seal when the Kel-F plug was screwed into the brass nut.

2. Storage Vessels

Materials of high volatility were stored in the Hoke stainless steel cylinders. Less volatile materials were stored in glass vessels fitted with high vacuum

stopcocks.

3. Connections

Brass Swagelok unions (Crawford Fitting Co., Cleveland, Ohio) fitted with Teflon Swagelok ferrules were normally used for metal-to-glass connections. Quarter inch Swagelok unions fitted with brass Swagelok ferrules were also used for vacuum tight connections when connected to $\frac{1}{4}$ in. O.D. Kovar-Pyrex tubing. A Teflon tape manufactured by the Crawford Fitting Co. was applied to all thread fittings before connections were made.

The Hoke reactor valves were adapted to $\frac{1}{4}$ in. Swagelok fittings, and the reactors were attached to a Pyrex glass vacuum system through a ball or a socket joint connected to it.

4. Vacuum System

A typical system is shown in Figure 1 and consists of a manifold constructed from $1\frac{1}{4}$ in. O.D. Pyrex tubing to which various parts of the vacuum system were joined by vacuum tight connections. An all Pyrex glass vacuum system was used for measurements, handling and purification of volatile reactants and products. Volatile materials were added to and removed from the vacuum line by using containers attached to the lower manifold with ball-and-socket joints.

All vacuum stopcocks and ground glass joints were lubricated with Kel-F 90 brand stopcock grease manufactured by the Minnesota Mining and Manufacturing Co. or with Halocarbon wax manufactured by Halocarbon Products Corp.

5. Infrared Spectra

Infrared spectra in the 4000 cm^{-1} to 600 cm^{-1} regions were recorded using a Beckman IR-5 Infrared Spectrometer, and in the far infrared region, $600 - 200\text{ cm}^{-1}$ were recorded using Perkin-Elmer 621 Grating Spectrophotometer. The spectra were used routinely to determine the purity of materials and the efficiency of separations.

Spectra of the gas samples were taken using 10-cm gas cells fitted with NaCl or AgCl windows (Harshaw Chemical Co.). The windows were attached to the cell body using Pliobond (The Goodyear Tire and Rubber Co.).

B. STARTING MATERIALS

Silicon Isocyanate. $\text{Si}(\text{NCO})_4$ was purchased from Alfa Inorganics, Inc., and was used directly.

Silver Difluoride. AgF_2 , technical grade, was purchased from the Harshaw Chemical Co., and was used without further treatment.

Sulfur Tetrafluoride. SF₄ (Olin Mathieson Co.) was used directly from the cylinder since the presence of only thionyl fluoride as an impurity could be detected in the infrared spectrum of the material.

Hydrogen Fluoride. HF, furnished by the Blockson Chemical Division of Olin Mathieson Corp. was used without further treatment.

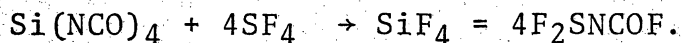
Sodium Fluoride. NaF pellets (Harshaw) were heated to 400°C to dry them before use.

Osmium Tetroxide. OsO₄ was obtained from the Eastern Chemical Corporation.

Diethyl Ether (Anhydrous), reagent grade (Fisher Scientific Co.), was used without further treatment.

Preparation of Fluoroformyliminosulfur Difluoride.

F₂SNCOF was prepared from Si(NCO)₄ and SF₄ (2) as shown by the following equation:

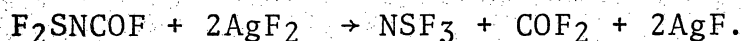


In a 75-ml. stainless steel cylinder 4.9g of Si(NCO)₄ was placed and 10.8g of SF₄ was condensed therein by cooling to -78°C (dry ice-trichloroethylene). The

reactor was then heated to 120°C in a three-inch tubular furnace and the temperature was held at 120°C for several hours. The products were purified by collecting at -78°C in a vacuum train.

PREPARATION OF THIAZYL TRIFLUORIDE.

Thiazyl trifluoride, NSF₃, was prepared from F₂SNCOF and AgF₂ according to the method of Clifford and Stanton (3). The reaction is



In a typical preparation, 37g of AgF₂ was placed in a 5-liter Pyrex bulb, the bulb was attached to the vacuum line and evacuated. The F₂SNCOF was introduced into the 5-liter bulb until the pressure reached approximately 200 mm Hg. The F₂SNCOF was then condensed in a trap with a dry ice-trichloroethylene slush bath. The F₂SNCOF was then allowed to expand into the 5-liter bulb and there reacted with the AgF₂. The reaction was allowed to take place for 16 hours. The products were purified by fractional condensation, and NSF₃ was collected at -131°C (n-pentane slush bath) after several purification passes. The purity of the NSF₃ was confirmed by comparing its infrared spectrum with the published spectrum (3).

Preparation of Pentafluorosulfanylamine.

SF₅NH₂ was prepared from NSF₃ and HF according to the method of Clifford and Duncan (4). A quantity of 1.41 g (13.7 mmoles) of NSF₃ and excess HF (78 mmoles) were allowed to react at room temperature for 18 hours in a Kel-F tube reactor. The contents of the reactor were then distilled under vacuum into another Kel-F tube containing dried NaF pellets, 21 g, which removed the unreacted HF from the product. The volatiles, after the treatment with NaF at room temperature for several hours, were passed through a -63°C (chloroform slush) trap to collect SF₅NH₂, the unreacted NSF₃ was collected in -196°C trap.

C. PROCEDURE FOR THE REACTION OF
OsO₄ WITH SF₅NH₂

Approximately 1 g (4 mmoles) of osmium tetroxide was placed in a Pyrex vessel and dissolved in 15 cc of anhydrous diethyl ether. This Pyrex reactor vessel was attached to the manifold of the vacuum line by means by a ball joint. With the reaction vessel in a -78°C bath (dry-ice slush), the mixture was degassed by pumping for about 5 minutes, then the -78°C bath was replaced with a -196°C bath (liquid nitrogen), and the reaction vessel was thoroughly evacuated.

About 4 mmoles of SF_5NH_2 was measured out and condensed into the vessel with liquid nitrogen, and the stopcock of the vessel was closed. The vessel was then placed in a -78°C slush bath and allowed to stand at -78° slush bath for 3 hours. The brownish red ether solution of OsO_4 after reacting for 3 hours at -78°C turned to a black color. The volatile material was collected in a liquid nitrogen-cooled trap. An infrared spectrum indicated the presence of SF_5NH_2 by the following absorptions: $3500\text{ cm}^{-1}(\text{w})^*$, $3400\text{ cm}^{-1}(\text{w})$ N-H stretch, $1580\text{ cm}^{-1}(\text{m})$ N-H bend, $1200\text{ cm}^{-1}(\text{w})$, $935\text{ cm}^{-1}(\text{vs})$ $885\text{ cm}^{-1}(\text{vvs})$ S-F stretch. There were pale yellowish crystalline materials left behind when the volatile materials had been condensed to the cooled trap. The infrared spectrum of these crystals in gas phase showed absorption at $1025\text{ cm}^{-1}(\text{s})$ Si-F stretch, $970\text{ cm}^{-1}(\text{s})$, $960\text{ cm}^{-1}(\text{s})$, $952\text{ cm}^{-1}(\text{s})$ Os-O stretch and $885\text{ cm}^{-1}(\text{w})$ S-F stretch. The volatile materials in the cooled trap were then fractionally condensed slowly in traps cooled to -23° , -78° , and -196° . After several passes of purification, the materials caught in -23° trap showed a trace of ether absorption peaks and strong absorption peaks at $1025\text{ cm}^{-1}(\text{s})$ Si-F stretch, and $970\text{ cm}^{-1}(\text{s})$, $960\text{ cm}^{-1}(\text{s})$, and $952\text{ cm}^{-1}(\text{s})$

* (s) -strong; (vs) -very strong; (vvs) -very very strong; (m) -medium; (w) -weak.

Os-O stretch. The material caught in -78° and -196° traps were yellow solutions at room temperature, infrared spectrum showed strong ether bands, a Si-F band at 1030 cm^{-1} , Os-O bands at $970 - 952\text{ cm}^{-1}(s)$, and SF_5NH_2 absorption bands.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Initial attempts at preparing the osmiamate compound from pentafluorosulfanylamine and osmium tetroxide were made in diethyl ether at -78°C (dry ice slush bath). Since SF_5NH_2 was soluble in diethyl ether at -78°C , it was suspected that the reaction would take place easily under these conditions. After the reaction was terminated, the mixture in the Pyrex glass vessel appeared black in color. This black substance was not investigated further after all the volatile materials were vacuum distilled into a cooled trap. Probably a reduction of the osmium tetroxide took place during the reaction. The pale yellow volatile substance in the cooled trap was first thought to be the expected osmiamate, but after taking infrared spectrum of this volatile material, it was found to exhibit diethyl ether absorption bands, osmium-oxygen bands, pentafluorosulfanylamine absorption bands and a band at 1030 cm^{-1} (Si-F). Isolation of the pale yellow crystalline solid from the diethyl ether solvent was done by fractional condensation with difficulty. The separation was effected after several passes of slow condensations. It was observed that the crystals attacked grease quite readily forming a black residue in all the stopcocks. Probably black Os(IV) oxides were formed.

The pale yellow crystalline material was believed to be OsO_4 , since the infrared examination of this substance showed Os-O bands at 970, 960 and 950 cm^{-1} , these represent the absorption bands of OsO_4 . Other impurities appeared in the spectrum, one band at 1030 cm^{-1} which both by the shape and intensity appeared very similar to the strong SiF_4 absorption at this energy. SiF_4 is produced when SF_5NH_2 hydrolyzes and attacks glass. Another band at about 885 cm^{-1} was ascribed to the S(VI)-F stretch of SF_5NH_2 . Mass spectrometric data also furnished strong support for the presence of OsO_4 . A peak with a mass/charge ratio of 258, corresponding to the parent molecule ion was observed.

The foregoing reaction did not allow the preparation of the desired product under the conditions described. Since hydrocarbon solvents, such as pentane, were used in the preparation of N-t-butyl osmiumate, it is suspected that the reaction of OsO_4 with SF_5NH_2 would probably be favored by non-polar solvents rather than polar solvents such as the diethyl ether used. The choice of diethyl ether as a solvent system was dictated by the reported solubility of SF_5NH_2 .

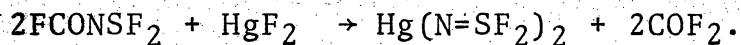
The unavailability of starting materials prevented the further investigation of this reaction.

PART B:

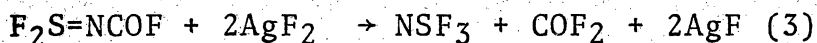
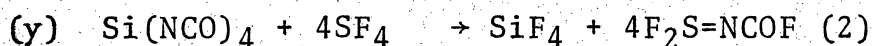
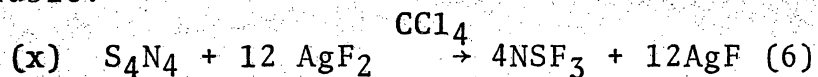
THE ATTEMPTED PREPARATION OF $\text{Hg}(\text{NSF}_2)_2$

I. INTRODUCTION

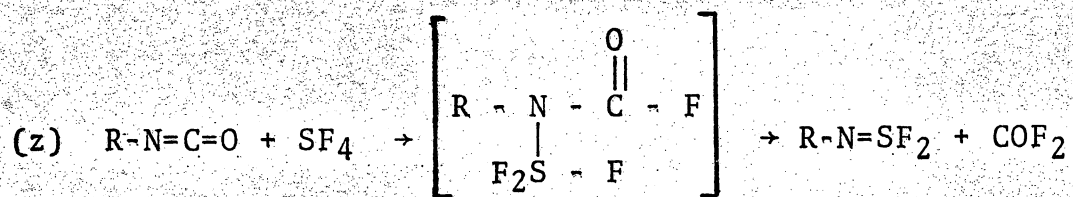
The synthesis of mercuric iminosulfur difluoride, $\text{Hg}(\text{N}=\text{SF}_2)_2$ has been reported by Glemser and his coworkers (5). This new compound has been obtained by the reaction of fluoroformyliminosulfur difluoride and mercury difluoride at room temperature as shown by the following equation:



It was the purpose of this study to investigate the possibility of preparing mercuric iminosulfur difluoride by the reaction of mercuric isocyanate with sulfur tetrafluoride as a better route to NSF_3 than the ones currently available.^{x,y}



From an investigation of sulfur tetrafluoride as a fluorinating agent for several organic and inorganic compounds, Smith, Tullock, et al. (7) obtained organoiminosulfur difluorides by the reaction of organic isocyanates with sulfur tetrafluoride. The proposed mechanism by which the reaction of isocyanates with sulfur tetrafluoride gave iminosulfur difluorides and carbonyl fluoride as a by-product is illustrated in equation (z).



The first step involved the addition of the elements of SF₄ across the carbon - nitrogen bond of the isocyanate group and then the elimination of carbonyl fluoride.

II. EXPERIMENTAL EQUIPMENT AND MATERIALS

A. EQUIPMENT

The reactions were carried out in the vacuum line using a 6-in. long Pyrex or quartz vessel, 5/8 -in. O.D., equipped with 24/40 inner taper joint, a 24/40 outer taper joint, fitted with a high vacuum stopcock. A 18/9 ball joint was used to attach the Pyrex or quartz vessel to the vacuum line. All ground joints were greased with a mixture of Kel-F brand no. 90 grease and Halocarbon wax. All vacuum stopcocks were lubricated with Kel-F 90 brand stopcock grease.

The infrared absorption spectra were taken on Nujol mulls between NaCl or CsBr disks with a Beckman IR-5 spectrometer (4000-600 cm^{-1}) or a Perkin-Elmer 621 grating spectrophotometer (600-200 cm^{-1}). The infrared spectra of gas samples were recorded using 10-cm gas cell equipped with NaCl windows (Harshaw Chemical Company).

B. REACTION MATERIALS

Sulfur tetrafluoride, purchased from Olin Mathieson Company, and mercuric isocyanate* were used without

* Mercuric isocyanate, $\text{Hg}(\text{NCO})_2$, was prepared by James W. Thompson, by reacting HgCl_2 with KNCO in methyl alcohol solvent and dried under vacuum.

further treatment.

The organic solvents used in this study were of reagent grade, they were dried and distilled prior to use. Tetrahydrofuran was dried by refluxing over lithium aluminum hydride overnight and was then distilled. Dimethylsulfoxide was dried with type 4A molecular sieve and distilled at reduced pressure. Tributyl phosphate was dried over calcium hydride for several hours and distilled at reduced pressure, 2 mm Hg. Chloroform was dried over calcium chloride.

III. EXPERIMENTAL PROCEDURES

A. REACTION OF MERCURIC ISOCYANATE WITH SF₄ IN THF

Mercuric isocyanate (250 mg.) was loaded into a Pyrex vessel containing a small magnetic stirring bar, the reactor was then attached to the vacuum line and evacuated. A 50-ml round bottomed flask filled with dried tetrahydrofuran was attached to the vacuum line, cooled in -78°C bath, and evacuated. About 13-ml of THF was then vacuum distilled into the reaction vessel. Then from the SF₄ cylinder about 125 mm Hg pressure of SF₄ was introduced into the reaction vessel cooled at liquid nitrogen temperature. The mixture in the reaction vessel was allowed to warm up to 0° (ice temperature) and then was stirred for about two hours at 0°. The infrared spectrum of the volatile materials showed the absorption peaks (Figure 2) of carbonyl fluoride at the following wavelengths: 1950 cm⁻¹(s), 1250 cm⁻¹(s), and 775 cm⁻¹(w). Other gases shown to be present were the excess SF₄, SOF₂, and THF absorption bands. Pale yellow solid materials were collected, the infrared spectrum of which is shown in Figure 3. A comparison of the spectrum of this material with that reported for mercuric iminosulfur difluoride showed that there was no absorption band at 1313 cm⁻¹ as reported by

Glemser for $\nu_{S=N}$. The pale yellow solids were purified further by dissolving in THF and separating the insoluble material from the THF solution by filtration. A Nujol mull of the insoluble material showed an absorption band at 2180 cm^{-1} (m) where isocyanate, $-N=C=O$, absorbs. Bands at 2050 cm^{-1} and 1840 cm^{-1} appeared to be characteristic of the carbon-oxygen linkage. In metal carbonyl complexes, bridged carbonyl groups usually occur in the 1830 cm^{-1} region, and the terminal carbonyls absorb around 2030 cm^{-1} (8). The band at about 1650 cm^{-1} may be attributed to the $-C=N-$ stretch, and at 1230 cm^{-1} was a band characteristic of the frequency and intensity of a (C-F) stretching mode.

The material soluble in THF was separated from the solvent by vacuum distillation from the solvent, and the white residue was vacuum dried. The infrared spectrum of this material taken in a mull and recorded in the NaCl region showed bands at 1200 cm^{-1} and 1125 cm^{-1} . These bands may be associated with the NSO stretching frequencies. They were in agreement with the generally assumed positions of the asymmetric and symmetric NSO bands (9) around 1240 and 1125 cm^{-1} , respectively, in alkyl thionylamines. Another possibility is the $=C-F$ group, which generally gives rise to a band in the region $1265 - 1200\text{ cm}^{-1}$ (10). The band at 970 cm^{-1} is in the region

of S=O stretch (11). The band at 900 cm^{-1} appeared to be the N-S stretching vibration. In several sulfonamide derivatives the N-S band appears as a medium intensity band in the region $912 - 866\text{ cm}^{-1}$. This material was not soluble in chloroform and only slightly soluble in diglyme.

B. REACTION OF $\text{Hg}(\text{NCO})_2$ WITH SF_4 IN DMSO

In a quartz reaction vessel, $\text{Hg}(\text{NCO})_2$ and SF_4 were allowed to react in dimethylsulfoxide. As the reaction proceeded for an hour at room temperature there was observed a precipitate and yellow orange solution. As the mixture was stirred for another hour, the solution turned more yellow. The reaction products obtained in this reaction included volatile materials, which showed no COF_2 absorption bands, a pale yellow precipitate and yellow non-volatile liquid. The pale yellow precipitate became gray slowly in air. Infrared studies of the products showed that DMSO had undergone chemical changes.

C. REACTION OF $\text{Hg}(\text{NCO})_2$ WITH SF_4 IN TRIBUTYL PHOSPHATE

About 13 ml of $(\text{C}_4\text{H}_9)_3\text{PO}_4$ was used for the reaction of $\text{Hg}(\text{NCO})_2$ and SF_4 . $\text{Hg}(\text{NCO})_2$ was slightly soluble in

$(C_4H_9)_3PO_4$. 50 mg. of $Hg(NCO)_2$ was used and about 30 mm Hg of SF_4 was introduced into the quartz reaction vessel. The reaction mixture was stirred at room temperature for two hours. About 3 mm Hg of gases were observed and the infrared absorption of these gases indicated the absorption bands of COF_2 and excess SF_4 and SOF_2 . The color of the reaction solution changed slowly from colorless to light brown, then to pink and finally to orange. Brown solids were isolated from the solution and dried. The infrared spectrum of this light brown material showed the absorption bands of tributyl phosphate and absorption bands at $2200\text{ cm}^{-1}(\text{vw})$, $2080\text{ cm}^{-1}(\text{w})$, and $1850\text{ cm}^{-1}(\text{w})$.

D. REACTION OF $Hg(NCO)_2$ WITH SF_4 IN CHLOROFORM

Using chloroform as the solvent for the reaction of $Hg(NCO)_2$ and SF_4 , after 24 hours of reaction at room temperature, the infrared absorption spectrum showed the absorption bands of SF_4 , SOF_2 and $CHCl_3$, no production of COF_2 . Neither was any reaction observed after heating the reaction mixture in a 75-ml Hoke stainless steel cylinder using a 3-in. tubular furnace at 100°C for two hours.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Attempts to prepare $\text{Hg}(\text{NSF}_2)_2$ by treatment of $\text{Hg}(\text{NCO})_2$ with SF_4 in a solvent have failed, apparently due to interfering side reactions and decomposition. From the results of the reactions attempted using different organic solvents, the reactions in THF and tributyl phosphate both had produced one of the products, carbonyl difluoride, but not enough of COF_2 formed to correspond to the amount of starting materials used. The solid products obtained were not the expected compound. The infrared studies showed that the solid products produced from the two reactions (THF and tributyl phosphate reactions) both had absorption bands at 2180 cm^{-1} , 2050 cm^{-1} , and 1840 cm^{-1} , which are the absorption bands of isocyanate and carbonyl group, and neither one of the two isolated solid products, which were produced from the THF reaction, indicated the formation of mercury imino-sulfur difluoride. This could be due to the instability of the nitrogen-sulfur bond toward the solvent and gross decomposition of the $-\text{N}=\text{SF}_2$ grouping taking place with the cleavage of both the sulfurfluorine and iminosulfur linkage. Other solvents might be tried such as dioxane, where $\text{Hg}(\text{NCO})_2$ is soluble, or nonpolar solvents that can dissolve the $\text{Hg}(\text{NCO})_2$ where no interaction with the

solvents could possibly be taking place. Irradiation of the reaction by UV light might cause the reaction to take place.

PART C:

THE ATTEMPTED PREPARATION OF MOLYBDENUM
CARBONYL FLUORIDE

I. INTRODUCTION

In recent years the study of the chemistry of the metal carbonyls has increased considerably, reviews have appeared on the metal carbonyls themselves and on such related topics as the anionic carbonylmetallates (12), metal-olefin complexes (13), tricarbonyl (diene) iron species (14), perfluoroalkylmetal compounds (15), and π -cyclopentadienyl and π -arene (16) metal derivatives. There have been no reports of metal carbonyl fluorides, and so far attempts to make them have been unsuccessful; e.g., the reaction between rhenium carbonyl iodide, $\text{Re}(\text{CO})_5\text{I}$, and iodine pentafluoride yields only the dimeric tetracarbonyl iodide $(\text{Re}(\text{CO})_4\text{I})_2$ (17), and the action of fluorine itself on the $\text{Mo}(\text{CO})_6$ yields lower fluorides (18). Peacock had also observed that metallic carbonyls seem to behave as starting materials for the preparation of lower fluorides, e.g., $\text{Mo}(\text{CO})_6$ dissolved in molybdenum hexafluoride yielded molybdenum pentafluoride (19).

Buslaev (20) obtained evidence which he considered to indicate that a metal carbonyl fluoride could be prepared by the reaction of molybdenum hexacarbonyl with cesium fluoride. $\text{Mo}(\text{OC}_2\text{H}_5)(\text{OH})_3$ and $\text{Cs}_3\text{Mo}_2(\text{CO})_4\text{F}_4(\text{OH})_3$

were two molybdenum compounds that were postulated by Buslaev to have been formed by the reaction of $\text{Mo}(\text{CO})_6$ and CsF in hot ethanol. This conclusion was based on the chemical analysis for the elements and on the infrared spectra. The preparation of the first was done by Buslaev by means of the reaction between $\text{Mo}(\text{CO})_6$ and ethanol under reflux conditions for 10-12 hours. This produced a green solution and a dark brown precipitate. Elemental analyses have showed that this dark brown precipitate had a composition corresponding to $\text{Mo}(\text{OC}_2\text{H}_5)(\text{OH})_3$. The infrared spectrum of this material in a KBr pellet was obtained from the first reaction was used to react with CsF at 60°C for 6-8 hours. A flocculant light brown precipitate was obtained and was postulated to be $\text{Cs}_3\text{Mo}_2(\text{CO})_4\text{F}_4(\text{OH})_3$ based on the results of the elemental chemical analysis. No infrared spectrum of this product was obtained by Buslaev.

The above work was repeated in order to confirm and characterize the compounds in more detail.

II. EXPERIMENTAL SECTION

A. REACTION MATERIALS

Molybdenum hexacarbonyl, purchased from Columbia Organic Chemicals Co., Inc., was used as received. Cesium fluoride was purchased from American Potash and Chemical Corp. All solvents used were reagent grade.

B. ELEMENTAL ANALYSES

(a) Molybdenum was estimated by reduction with a Jones reductor (21) and subsequent titration with standard permanganate solution. The procedure depends upon the reduction of hexavalent molybdenum to trivalent form by passing its acidified solution through a column of amalgamated zinc. Since the reduced molybdenum compound is sensitive to the oxygen of the air, resulting in partial oxidation, the reduced compound was caught in an excess of ferric solution, whereupon an equivalent amount of ferric compound was reduced to Fe(II) state. Titration of the reduced iron by standard potassium permanganate established the amount of molybdenum reduced by the zinc. The number of ml. of permanganate

(1 ml. of 0.1 N KMnO_4 = 0.0032 gram Mo), less the blank, multiplied by 100, and divided by the weight of sample taken, gave the percentage of molybdenum in the sample.

(b) Cesium was determined as cesium hexachloroplatinate by decomposing the sample in acid solution, and adding chloroplatinic acid to the solution until no more yellow precipitate formed. The precipitate was transferred to a previously weighed filtering crucible and washed twice with 95% ethyl alcohol (cesium hexachloroplatinate is insoluble in concentrated alcohol). The cesium hexachloroplatinate was dried in an oven at 110°C for one hour, cooled in desiccator, and weighed as Cs_2PtCl_6 . Factor: $\text{Cs}_2\text{PtCl}_6 \times 0.3943 = \text{Cs}$.

(c) Fluorine was determined by precipitation of fluoride ion as lead (II) chlorofluoride. Sixteen drops of concentrated HCl were added to the neutral solution of the sample, then 10 drops of glacial acetic acid and 24 ml. of 10% lead acetate were added. The white granular precipitate of PbFCl was allowed to stand for one hour, and filtered through a weighed Gooch crucible. After washing three times with PbFCl solution and finally twice with cold water the residue was dried one hour at 110°C and weighed as PbFCl . Factor: $\text{PbFCl} \times 0.0726 = \text{F}$.

(d) Carbon and hydrogen analyses were done by using an F & M Analyzer Model 185.

C. PHYSICAL MEASUREMENTS

The infrared spectra were obtained using Perkin-Elmer Model 621 grating spectrophotometer. The KBr pellet technique and the Nujol mull methods were employed for the preparation of the sample in the NaCl and CsBr regions, respectively.

D. PROCEDURES

In a typical experiment, 1 g of $\text{Mo}(\text{CO})_6$ and 100 ml. of ethyl alcohol were heated under reflux in a round bottomed flask equipped with a reflux condenser. The solution soon appeared green and $\text{Mo}(\text{CO})_6$ slowly sublimed out of the reaction mixture and was returned to the reaction vessel by scraping with a wire which was inserted into the condenser. After three hours, all the $\text{Mo}(\text{CO})_6$ was consumed, as shown by the cessation of sublimation. The mixture was continued refluxing for 12 hours, and cooled to room temperature. The dark brown precipitate was isolated from the green solution by suction filtration. The dark brown precipitate was collected on a medium frit and was dried in a vacuum desiccator overnight.

The green solution was then introduced to a round bottomed flask filled with cesium fluoride. The reaction

mixture was heated to 60°C for 8 hours. The flocculant light brown precipitate was separated from the solution by filtration with a sintered glass disc, rinsed twice with ethanol and dried in a vacuum desiccator.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The dark brown precipitate obtained from the reaction of $\text{Mo}(\text{CO})_6$ and ethyl alcohol changed to navy blue at 70°C without melting. It was not soluble in organic solvents. The analysis for Mo was 51.3%, C = 6.74%, H = 1.49%. This compound had been postulated by Buslaev to be $\text{Mo}(\text{OC}_2\text{H}_5)(\text{OH})_3$, for which the calculated percentages are Mo = 50%, C = 12.5%, H = 4.2%. Spectra of the Nujol mull and KBr pellet of this dark brown compound have been examined and the O-H stretching frequency was found at 3420 cm^{-1} , and a band at 1625 cm^{-1} has been characterized as the bending frequency for the O-H group. The (C-O) stretching frequency was found at 1085 and 1038 cm^{-1} , as observed in the reference spectra of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (22) where absorption bands for C-O stretching were found at 1063 and 1029 cm^{-1} , and for $\text{Ti}(\text{OC}_2\text{H}_5)_4$ (22) 1064 and 1042 cm^{-1} were observed. The bands due to Mo-O stretching frequency have been reported in the region $903\text{-}966\text{ cm}^{-1}$ and $700\text{-}510\text{ cm}^{-1}$ (23), and bands at $976\text{-}945\text{ cm}^{-1}$ and 735 cm^{-1} were observed in the spectrum of this dark brown material. A carbon-hydrogen stretching vibration was observed at 2970 cm^{-1} .

Since the carbon and hydrogen analyses obtained were not in agreement with the formula of postulated compound, no conclusion could be made concerning the

chemical composition of this reaction product. It was suspected, however, to be $\text{Mo}(\text{OC}_2\text{H}_5)(\text{OH})_3$.

The light brown precipitate from CsF addition had a high melting point, and did not decompose at 360°C . This compound was suspected by Buslaev to be $\text{Cs}_3\text{Mo}_2(\text{CO})_4\text{F}_4(\text{OH})_3$, but the infrared studies have shown that no carbonyl group existed in this compound. The presence of O-H bonds have clearly shown in the spectra. A band at 380 cm^{-1} has been reported as Cs-F absorption frequency (24), and in the region between $700\text{-}510\text{ cm}^{-1}$ have been observed the Mo-O stretching vibration (23). The possibility of the presence of metal-fluoride stretching frequency was expected in the region between $800\text{-}300\text{ cm}^{-1}$ (25). A band at $880\text{-}850\text{ cm}^{-1}$ was ascribed to the carbonate out-of-plane deformation band. As a result of these possible complications, the interpretation of this spectrum is difficult. From the results of the chemical analysis: Mo = 22.92%, Cs = 30.17%, C = 3.12%, H = 0.39%, F = 10.50%, O = 32.90%, it was postulated as $\text{CsF}\cdot\text{H}_2\text{O}\cdot\text{MoO}_6\text{CO}_3\text{F}$, since the carbon, hydrogen analysis were not reliable for this type of metallic complex, no conclusion could be obtained.

The molecular weights for the two compounds obtained could not be estimated because of limited solubility in any suitable organic solvents, also because of their low volatilities molecular weights can not be done using

mass spectrometer.

SUMMARY

(1) The attempt to prepare SF_5NOsO_3 by the reaction in diethyl ether solution of OsO_4 and SF_5NH_2 was unsuccessful. Further work is necessary before any conclusions can be drawn as regards the feasibility of this reaction.

(2) Several attempts at preparing $Hg(NSF_2)_2$ by the reaction between $Hg(NCO)_2$ and SF_4 in different solvents were not successful. No reaction took place in chloroform at room temperature or $100^\circ C$. In THF and tributyl phosphate reactions, only carbonyl difluoride was produced. No $Hg(NSF_2)_2$ in the solid product was observed.

(3) The reaction between $Mo(CO)_6$ and hot ethanol resulted in the formation of a dark brown precipitate, for which the carbon and hydrogen analysis were not in agreement with the formula postulated by Buslaev. The infrared spectrum of the light brown precipitate showed no carbonyl group absorption in the region at 2000 cm^{-1} . This should be observed for the compound to be postulated as $Cs_3Mo_2(CO)_4F_4(OH)_3$.

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APPENDIX

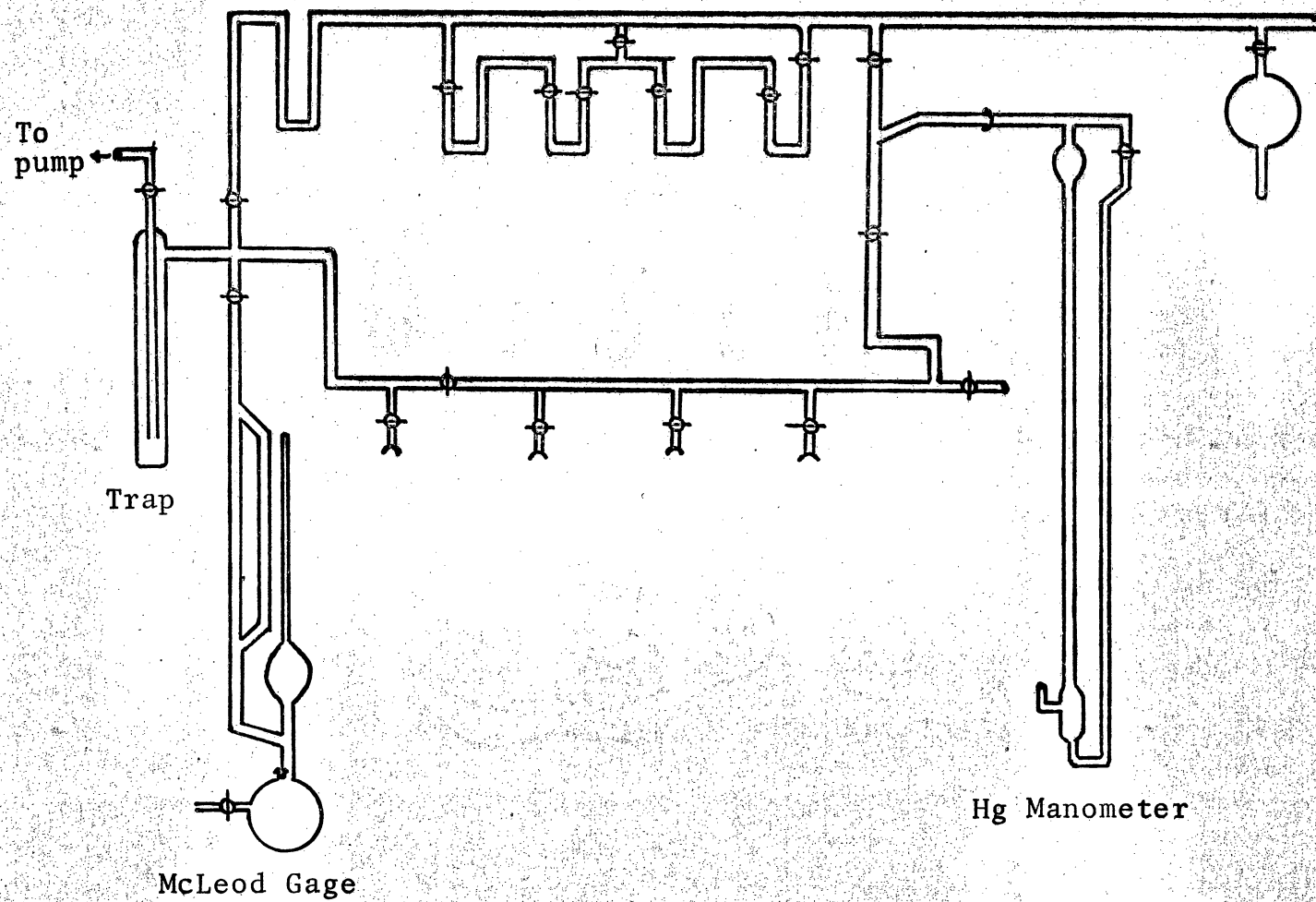


Figure 1. High Vacuum System

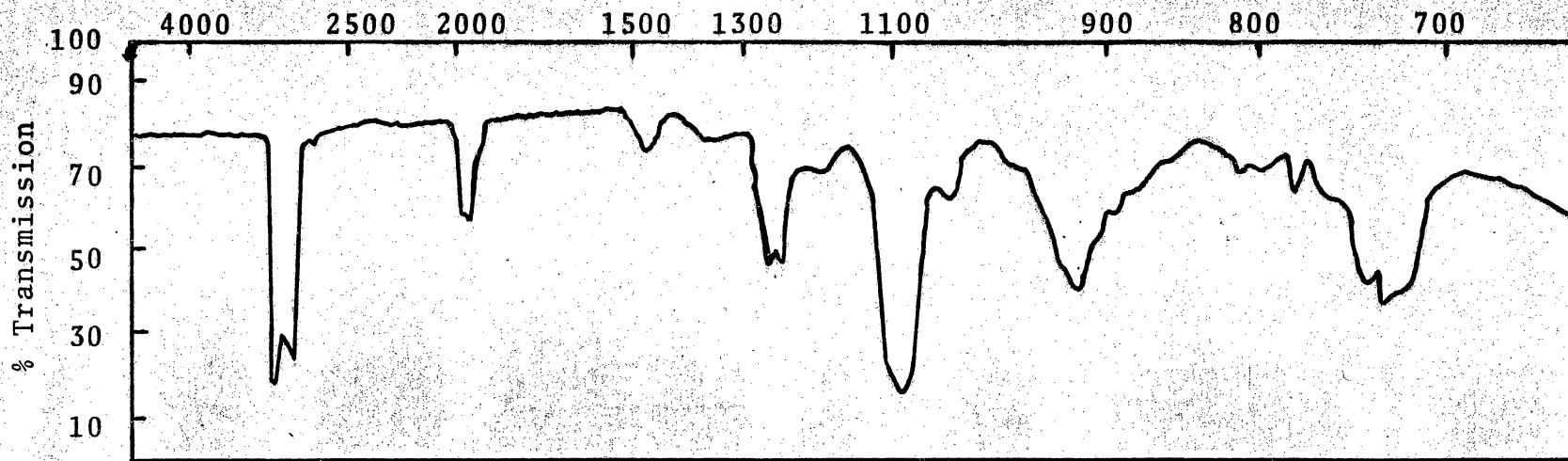


Figure 2. Infrared Spectrum of Gaseous Materials

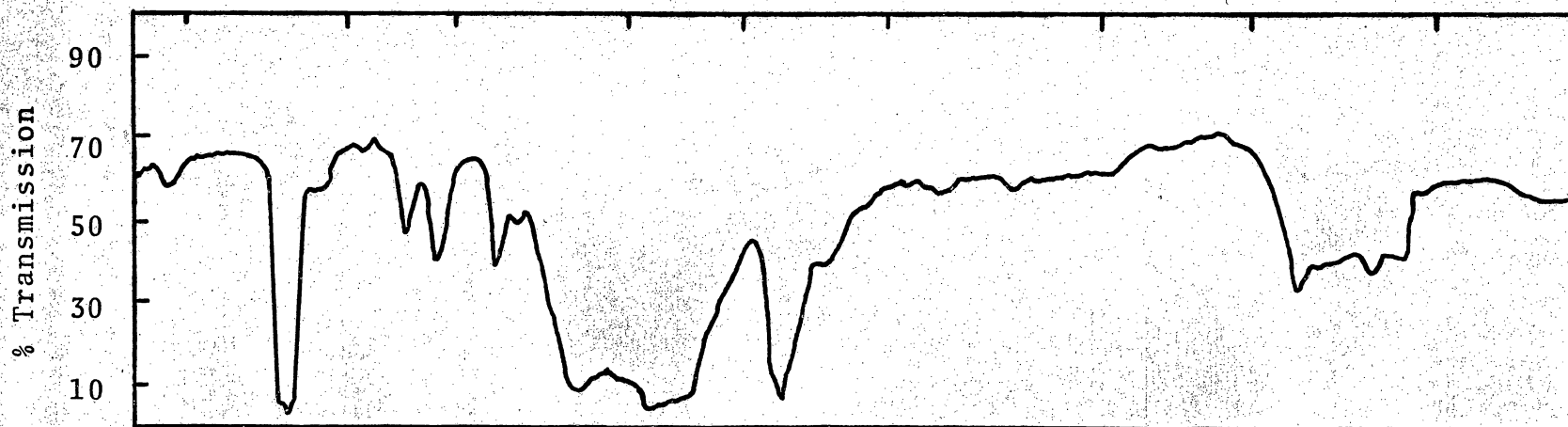


Figure 3. Infrared Spectrum of Pale Yellow Solid Materials

SOME STUDIES IN INORGANIC FLUORINE CHEMISTRY

by

Queng-Hui Tan

ABSTRACT

The attempt to prepare SF_5NOsO_3 by the reaction of OsO_4 and SF_5NH_2 in diethyl ether was not successful. The product obtained was a pale yellow crystalline substance which was identified as OsO_4 by infrared spectra and mass spectrometric data. No indication of SF_5NOsO_3 was observed.

Several attempts to prepare $\text{Hg}(\text{NSF}_2)_2$ by the treatment of $\text{Hg}(\text{NCO})_2$ with SF_4 in a solvent, such as THF, DMSO, $(\text{CH}_3)_3\text{PO}_4$ or CHCl_3 , have failed, apparently due to interfering side reaction and decomposition. In THF and $(\text{CH}_3)_3\text{PO}_4$ systems, COF_2 was produced, but no $\text{Hg}(\text{NSF}_2)_2$ was produced in the solid product as shown by the infrared spectrum that there was no absorption band at 1313 cm^{-1} as reported by Glemser for $\nu_{\text{S}=\text{N}}$. No reaction was observed in CHCl_3 at room temperature or 100°C .

The reaction between $\text{Mo}(\text{CO})_6$ and hot ethanol produced a green solution and a dark brown precipitate, for which the C and H analyses were not in agreement with the formula postulated by Buslaev as $\text{Mo}(\text{OC}_2\text{H}_5)(\text{OH})_3$. The

product of the reaction of the green solution and CsF was a light brown precipitate which showed no carbonyl group absorption in the region at 2000 cm^{-1} . This should be observed for the compound to be postulated as $\text{Cs}_3\text{Mo}_2(\text{CO})_4\text{F}_4(\text{OH})_3$ by Buslaev.