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Propulsion Research Program

Hydride and Fluoride Investigations

SEMIANNUAL TECHNICAL REPORT

(1 January-30 June 1962)

1 AUGUST 1962

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Prepared for DEPUTY COMMANDER AEROSPACE SYSTEMS
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Inglewood, California



LABORATORIES DIVISION •

AEROSPACE CORPORATION

CONTRACT NO. AF 04(695)-69

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El Segundo, California

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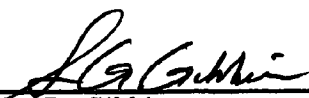
Hydride and Fluoride Investigations

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ABSTRACT

The complex formed between sulfur tetrafluoride and tetramethyl ammonium fluoride has been almost completely characterized. It has also been shown that an analogous complex between SF_4 and $(CH_3)_4NCl$ either does not form or is very weakly bound, and that phenyltrimethylammonium fluoride fails to react with SF_4 . The compound believed to be $(CH_3)_4N^+SF_5^-$ is stable to 70 to 100°C and reacts with water, nitrobenzene, formamide, and monomethyl formamide; it is generally insoluble in organic solvents but is soluble in dimethyl formamide. The fluorine nuclear magnetic resonance spectrum of the compound in dimethyl formamide solution exhibits a single line quite different from that of F^- or SF_4 . The thermal decomposition products of the complex are the reactants SF_4 and $(CH_3)_4NF$. Variations in the rate of complex formation are believed to be attributable to bifluoride impurities in the initial $(CH_3)_4NF$ reagent.

The reaction between ferric chloride, phenyl magnesium bromide and hydrogen to form iron hydrides has been studied. Results are not complete, but the products have been separated into at least five separate solid components, based on differential solubility in various basic solvents. These components are being studied.

Considerable effort has been spent in eliminating operational difficulties with the various vacuum apparatus associated with the time-of-flight mass spectrometer studies, and in performing preliminary calibration experiments with hydrogen atom generation by radio-frequency discharge. A stainless steel inlet system has been constructed for the vapor chromatograph that is used in conjunction with the mass spectrometer, to permit operation of the chromatograph under high vacuum injection conditions.

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I. HYDRIDE INVESTIGATIONS

A. ATOMIC SYNTHESSES

1. Introduction

The objective of this program is to ascertain the maximum number of metal to hydrogen bonds that various metals can form, even if some of the bonds are relatively unstable. The principal method of attack is to react metal vapors and the vapors of volatile compounds containing metal atoms with atomic hydrogen; and, subsequently, to analyze the complex reaction mixtures mass spectrometrically, applying the time-of-flight principle. Details of the proposed techniques and the associated apparatus were described in earlier reports.^{1, 2} The data collected in this study will aid in considering the feasibility of future suggestions pertaining to the synthesis of new metal hydrides for composite solid propellants.

2. Discussion of Results

Several experiments were conducted using $B_{10}H_{14}$ as a reactant with the atomic hydrogen stream; these were performed before the mass spectrometer was installed. A small thimble well of $B_{10}H_{14}$ was heated to $100^{\circ}C$ by a copper jacket. The atomic hydrogen stream intersected the $B_{10}H_{14}$ vapor at right angles. Mixing was considered adequate at the low pressure and the high velocity gas flow. The products were immediately impacted upon a trap surface at $-195^{\circ}C$ for further analysis. Some products were found and are now held in a solvent. This experiment is to be repeated in the line-of-sight inlet system and in the mercury photosensitized reaction cell.

The newly acquired mass spectrometer was installed during the first quarter of 1962. Performance tests were made during this period. Many anticipated difficulties arose and were systematically eliminated. Principal problems encountered were with the electronics and inlet systems. Redesign of the latter for direct line-of-sight sampling and photolytic studies has been performed;

details of operation are given in Fig. 1. The line-of-sight sampling system is terminated on the fast reaction inlet chamber by a greaseless bellows seal low impedance Granville Phillips shutoff valve. This permits the execution of atomic beam reactions ahead of this valve.

Several preliminary tests were conducted to check the performance of the radio-frequency discharge apparatus used to dissociate molecular hydrogen. Various well-known wall poisoners were used in attempts to produce the highest concentration of atoms for a given set of operating parameters. It was found necessary to monitor the total energy input into the reaction vessel to maintain constant atom concentration. Our interest in the absolute atom content is not great except that maintenance of a minimum percentage is necessary.

Current major effort is with the mercury photosensitized reaction cell shown in Fig. 1. Adequate precautions have been taken to assure that proper pressure measurements can be made in the presence of condensables or noncondensables and mixtures of these. After initial checks with known noncondensable reaction mixtures (such as ethane- H_2 and ethylene- H_2) experiments with either $TiCl_4-H-Hg^*$ or $Ti(OCH_3)_4-H-Hg^*$ will be undertaken. The titanium system is important to our study of the transition metal hydrides. Mass numbers are determined by correlation with the mass numbers as taken from appropriate compounds listed in our recently acquired American Petroleum Institute tables of mass spectra.

Effort has also been expended in building an all-stainless steel inlet system for the vapor chromatograph. The principal limitation of vapor fractometers is their inability to operate under high vacuum injection conditions. The valve supplied by the Perkin-Elmer Corporation is not, under normal conditions, vacuum tight. Proper alterations have been made to eliminate this difficulty. All rubber and tygon connectors have been eliminated to prevent tedious outgassing. The instrument is now ready for connection to the mass spectrograph for analysis of eluents. This will be needed for cases where series of stable but difficultly separable compounds are formed in the atomic hydrogen studies.

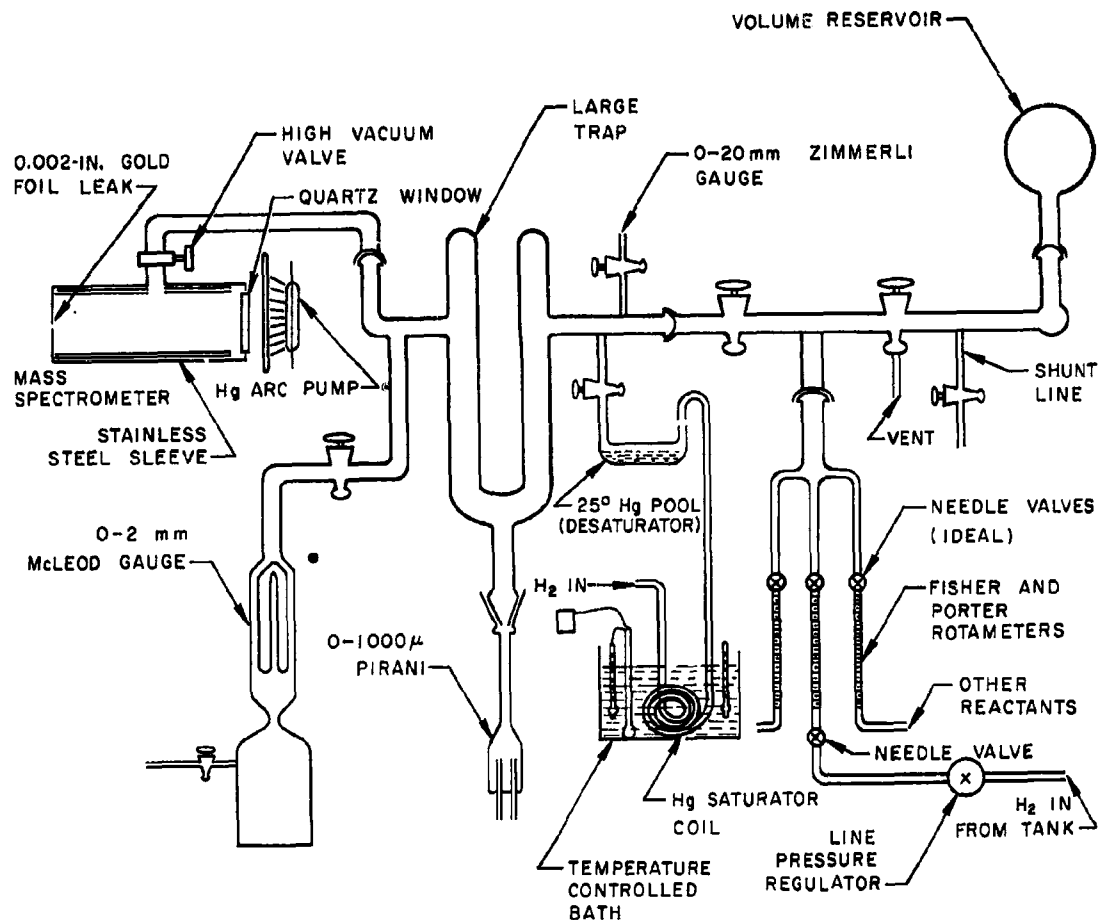


Fig. 1. Inlet System for Photolytic Studies.

Operation of Mercury Photosensitized Reaction System

The system is completely evacuated to a pressure of at least 10^{-6} mm. A background spectrum is taken with the system open to the gold leak. Hydrogen and reactant are introduced through the rotameters. At this point all mercury is eliminated from contact with the reactants or the mass spectrometer inlet.

The gases are expanded into the large reservoir volume at the desired pressure. The latter is measured initially with the Pirani gauge; after the filling of the cold trap the pressure is measured accurately by the McLeod gauge. This, of course, is possible only when noncondensables are present. The mass spectrum of the reaction mixture prior to photosensitization is then obtained. The ultraviolet lamp is then turned on and, after an appropriate waiting period, another spectrum is obtained. This procedure eliminates the effect of thermal reactions. The system is again evacuated. Then, hydrogen is bubbled slowly through the saturator and equilibrator. After a few minutes, the Hg-saturated H_2 is expanded as before into the large reservoir volume. The pressure is recorded without trap-out of the McLeod gauge. The other reactant can be introduced as before from the rotameters or via a vent line. The mixture mass spectrum is retaken to insure proper mixture ratio. The lamp is then ready to be activated. After appropriate delay the mass spectrum is again taken.

The pressure in the system falls very slightly as the sample mixture is pumped through the leak. A very large volume reservoir will practically eliminate this effect.

Fractionation will then be accomplished in the chromatograph and identification in the mass spectrograph. Most of the eluted species can be trapped out for further studies, and only a small fraction actually will be diverted to the mass spectrograph.

B. SYNTHESIS OF TRANSITION METAL HYDRIDES BY CLASSICAL TECHNIQUES

1. Introduction

The possibility of forming transition metal hydrides with a large number of hydrogen bonds is an intriguing aspect in the consideration of metal hydrides as fuel additives for composite solid propellants. The existence of binary stoichiometric transition metal hydrides has been the subject of considerable controversy since Weichselfelder³ first claimed the synthesis of such compounds as FeH_6 , FeH_2 , and NiH_4 . Evidence both for and against these hydrides is weakened by the fact that of the six groups⁴⁻⁹ in this field, none isolated pure products. An objective of the present work is the unequivocal characterization of Weichselfelder's "hydride products," and the demonstration of whether binary hydrides can be synthesized by such reactions. A complete discussion of the techniques under consideration and the scope of the program has been published.¹

2. Discussion of Results

Weichselfelder's "iron hexahydride," prepared by the reaction of ferric chloride with phenyl magnesium bromide in diethyl ether under an atmosphere of hydrogen, was the starting point of the present synthesis program. A preliminary experiment reproduced Weichselfelder's observations. Specifically, the hydrogen consumed was 10 percent in excess of that necessary for FeH_6 . Hydrolysis of the reaction products in situ corresponded to $\text{Fe}/5.9\text{H}$.

Isolation of pure hydride products from the ferric chloride reaction was the next objective. A second reaction, carried out at room temperature was

terminated after 31 days when hydrogen consumption ceased.* The iron-to-hydrogen ratio was 1/5.4. The reaction mixture consisted of two phases, namely, a black viscous oil, and a yellow mobile supernatant liquid. For simplicity, the subsequent separation procedure is shown by a flow diagram, Fig. 2.

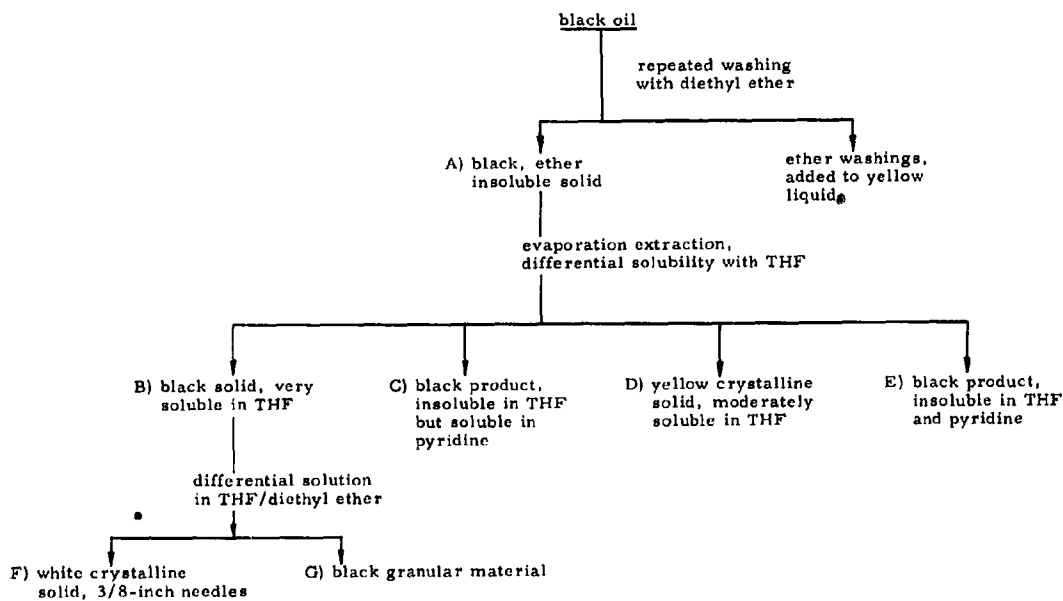


Fig. 2. Separation of Reaction Products.

*All operations were carried out in the absence of air and water. All reagents were rigorously dried. "Inert atmospheres" were not used.

Analysis of these fractions is still incomplete. At present, it is known that the yellow solid D contains Fe, Mg, Cl, and H, with the hydrogen in a hydride state. The insoluble product E is ferromagnetic and is presumed to be iron. Because of solubility differences in a tetrahydrofuran-diethyl ether mixture, solid B was separated into a white crystalline product and a black granular material. The product C was insoluble in tetrahydrofuran but dissolved in pyridine to form a red solution which was evidently a complex; upon evaporation of the solvent the red residue was soluble in both tetrahydrofuran and diethyl ether although C, itself, was insoluble in both. In the ether, the solute exhibited dichroism, and on evaporation of the solvent, the residue was blue. A preliminary analysis indicated that iron, magnesium, and chloride (but no bromide) were present; hydrogen has not yet been determined.

The original yellow supernatant mentioned above, to which was added the ether washings from the black oil, is known to contain iron, magnesium, hydrogen in a hydridic form, and organic matter.

Thus, various components of the black oil have been recognized, and methods have been devised that will effect their purification. The future program will include the physical and chemical characterization of the pure compounds. Conclusions are quite tentative, but it is worth pointing out that the apparent isolation of metallic iron indicates that if present earlier, FeH_6 has been transformed to another compound although with preservation of the hydridic hydrogen. The alternative is that FeH_6 was not formed. Whether the very considerable amount of hydride present is at least partially bonded to iron, either in a binary compound or as a complex one involving, e. g., magnesium, cannot yet be stated.

II. FLUORIDE INVESTIGATIONS

1. Introduction

Thus far, the program on fluoride synthesis has consisted of a systematic effort to prepare salts of anions of the type SX_5^{-1} . Simple anions of this type, in which sulfur exhibits a coordination number of five, were previously unknown. From the point of view of solid composite propellants, compounds of this type would be of interest as high energy oxidizer components if the X group were of the type OF or NF_2 and if the cation itself were energetic. Since the most readily conceivable compound of this type would be the fluoride, efforts have been expended to prepare the model anion SF_5^{-1} . In our last report on this subject¹⁰ it was stated that SF_4 will complex with $(CH_3)_4NF$ to form a compound which was believed to be the desired salt, $(CH_3)_4N^+SF_5^{-1}$. In the present report period, this reaction has been investigated thoroughly and the nature of the complex characterized.

2. Discussion of Results

a. Purifications

Characterization of the complex required the elimination of possible competing reactions by purification of the reactants. A method for purification of SF_4 was developed which can be summarized as follows. Sulfur tetrafluoride is introduced into the evacuated high-vacuum line and is condensed into a cooled flask containing NaF. An equivalent amount of BF_3 is introduced into the line and condensed into the flask. The closed flask is warmed to room temperature to allow the solid SF_4-BF_3 complex to form. Then the flask is cooled to $-70^\circ C$ and pumped on for 45 minutes. Dry reagent grade dioxane is distilled onto the complex; the mixture is then warmed to room temperature to liberate SF_4 . The evolving gas is expanded into an adjacent one-liter flask. The smaller flask is closed, and SF_4 is distilled from the one-liter flask at $-70^\circ C$ into another flask at $-190^\circ C$.

Sulfur tetrafluoride has previously been introduced to the vacuum line from its cylinder through washing towers of mercury and of NaF. It has now been found that using Kel-F tubing in this introducing system and covering all connections and joints with series 8-00 Halocarbon Wax results in getting the SF₄ into the vacuum line with less than five percent impurities. Previously SF₄ introduced to the vacuum line appeared to consist of as much as 50 percent impurities.

Solid-state infrared spectra of (CH₃)₄NF made from [CH₃]₄NOH and aqueous HF always contained some extra absorptions. Some of them were attributable to HF₂⁻.¹¹ Therefore, it was suspected that various impurities in the fluoride were inhibiting or altering its reaction with SF₄. Accordingly, an alternate way to prepare the fluoride was sought. Ultimately, [CH₃]₄NF was made from [CH₃]₄NCl and KF in methanol. It was recrystallized from isopropanol. In a similar way, [C₂H₅]₄NF was made from its bromide. There is, respectively, some chloride and some bromide (about five percent) left in the preceding products.

b. Reactions and Characterizations

The complex between (CH₃)₄NF⁸ and purified SF₄ was found to decompose at 70 to 100°C, under vacuum. The products were largely SF₄ and the initial starting solid. Some SiF₄ was also evolved, but it was shown that the latter was an accidental impurity that resulted from the hydrolysis of the evolved SF₄ upon standing. To determine the characteristics of the suspected impurity in the complex, [CH₃]₄NF and SiF₄ were combined. A complete, rapid reaction yielded ([CH₃]₄N)₂SiF₆, a white, nonhygroscopic powder ([CH₃]₄NF is highly hygroscopic). This fluorosilicate did not decompose at all up to 200°C under vacuum. Therefore, the SiF₄ found in the decomposition of the SF₄-[CH₃]₄NF complex must have formed from the reaction of the liberated SF₄ with a trace of water in the presence of glass.

Additionally, the fluorosilicate showed a characteristic peak in its solid-state infrared spectrum which was not found in the good samples of the complex. The complex is soluble in dimethyl formamide but not in most other organic

solvents. It reacts readily with water and nitromethane. It also reacts with formamide and monomethyl formamide, indicating that it reacts with acidic hydrogens. Apparently it is fairly stable at room temperature and can be exposed to air for several days before it is affected adversely. The fluorine nuclear magnetic resonance spectrum of the complex in dimethyl formamide shows one line which broadens at low temperatures. This line is not similar to that of F^- , SiF_6^{2-} , or SF_4 ; it is a unique fluorine resonance.

Since the NMR spectrum does not contain several lines, it can be presumed that the complex is in equilibrium with the decomposition products. The ionic character of the complex is indicated by its solubility properties. Dimethyl formamide, which is a high dielectric constant solvent, commonly dissolves ionic compounds.

Sulfur tetrafluoride was found to complex weakly with $[CH_3]_4NCl$ (decomposed at room temperature) and not at all with phenyltrimethylammonium fluoride. The latter compound was made from the corresponding hydroxide by neutralization with aqueous HF. Thus, the cation is also important in the complexing reaction. Apparently steric hindrance keeps the phenyl-substituted salt from forming a complex. A reaction that will be studied next to clarify this point is the reaction of the ethyl analog of the R_4NF compounds, with SF_4 . Another final point yet to be settled is the effect of small amounts of bifluoride on the complex formation.

Some work has begun on the reactions of SF_4 with ammonia and amines. In particular, SF_4 and n-butylamine were reacted at $-30^\circ C$ in the presence of NaF. Infrared spectra of the products from the rapid reaction showed only the N-H bonds of the amine were attacked. Some indication of the specific nature of the products was also obtained. Further work in this area is planned.

c. Conclusions

The conclusions are tentative, pending completion of the final experiments mentioned above. Nevertheless, it appears that compounds containing the SX_5^{-1} .

anion are possible, providing that the electronegativity of the X atom or grouping is close to that of fluorine (chlorine is ineffective but NF_2 or OF might be suitable). The choice of the cation is also important. It appears that the cation must be of the complex type, and, in addition, it may have to be symmetrical.

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