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Contract No. 442
Task Order No. 12
Project No. MR 329 0211

Chemical Department
Solid Rocket and Chemical Division

~~George~~ *General*

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22 June 1957

Report No. 1288
(Quarterly)

INVESTIGATION OF
LIQUID ROCKET PROPELLANTS

Contract N7onr-462
Task Order III
Project IIR 220 023

Written by:

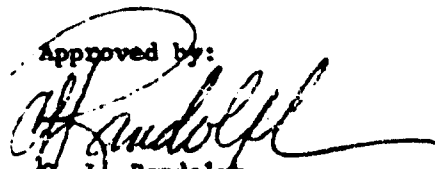
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No. of Pages: 41

Period Covered:

1 March through 31 May 1957

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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, Project NR 220 023.

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I. SUMMARY

A. Oxygen difluoride (OF_2) is currently being investigated as a prime fluorinating agent, both for the preparation of N-F containing compounds and for the preparation of other fluorinating agents containing the O-F linkage. Thermodynamic calculations have indicated that such compounds (e.g., CH_3NF_2) may exhibit unusually high specific impulses (Reference 1).

B. In an attempt to prepare N-F containing compounds (fluoramines), the action of oxygen difluoride on the following nitrogen compounds has been investigated: dimethylamine, tetramethyltetrazene, N-chlorethylenimine, and dimethylnitrosamine. No fluoramine has as yet been isolated from any of these reactions.

C. In an attempt to prepare O-F containing compounds (hypofluorites), the action of oxygen difluoride on t-butyl alcohol and on t-butyl peroxide has been investigated. It was found that t-butyl alcohol gave little or none of the desired t-butyl hypofluorite, whereas t-butyl peroxide was unreactive toward oxygen difluoride under the experimental conditions employed.

D. Experiments designed for the selection of suitable solvent media for oxygen difluoride indicated that Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and Spectro-grade carbon tetrachloride can be used. In particular, no reaction occurred between oxygen difluoride and Spectro-grade carbon tetrachloride during 25 hours at ambient temperature.

E. It was determined that oxygen difluoride can be stored in dry glass vessels at ambient temperature for several weeks without decomposition or without reaction with the container.

F. Calculations show that aluminum hydride in an organic binder, together with a liquid oxidizer, is capable (theoretically) of yielding specific-impulse values of above 290 lbf sec/lbm at a chamber pressure of 1000 psia.

II. TECHNICAL DISCUSSION

A. PREPARATION OF N-F COMPOUNDS

1. Introduction

a. Interest in the use of oxygen difluoride as a fluorinating agent for the present program has stemmed mainly from the work of George Wright, who reported the isolation of dibutyl fluoramine from oxygen difluoride and dibutylamine*, and from the fact that chlorine dioxide (OCl_2) can be used to prepare chloramines so that presumably oxygen difluoride might be similarly used to prepare fluoramines. Of further interest to the present program is the possible use of hypofluorites as fluorinating agents for the preparations of fluoramines, by analogy with the standard method for preparing chloramines, involving the use of a hypochlorite. However, the known hypofluorites (CF_3OF , SF_5OF , $\text{CF}_3\text{CO}_2\text{F}$, etc.) are not readily obtainable, so ~~the~~ attention has been directed rather toward the preparation of unknown hypofluorites (as t-butylhypofluorite) from oxygen difluoride.

b. Although it may be possible to prepare fluoramines by using oxygen difluoride or hypofluorites, several observations have recently come to light which indicate that the synthesis of a fluoramine in this manner may not be realized except in a small number of isolated cases (see paragraphs II,A,2,3). In the first place, there is reason for believing that Wright's material is not dibutylfluoramine. Also, it appears that there may be a fundamental difference in the chemistry of the reactions of oxygen difluoride and the hypofluorites, as compared with that of the other halogen oxides and hypohalites. These matters are discussed more fully in a later part of the report (paragraph II,3,1 and B,3).

c. The use of other types of fluorinating agents (F_2 , HgF_2 , AgF , AgF_2 , ClF_3 , etc.) for the preparation of fluoramines does not appear promising since all such materials presumably react by a free radical mechanism involving fluorination of carbon as well as of nitrogen. From the standpoint of selectivity, oxygen difluoride and the hypofluorites appear to be the most useful.

*In private communication with J.W.B. Mason.

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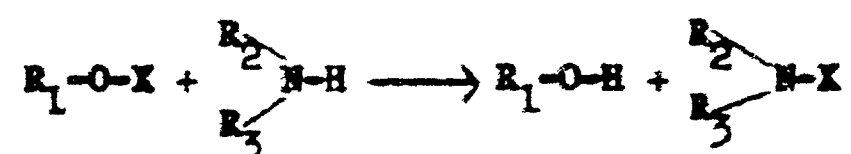
II Technical Discussion, A (cont.)

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d. Another possible method, i.e., the reaction of nitriles with mercuric fluoride, is currently being investigated under Contract AF 49(638)-25, Project No. 37507 (Reference 2).

2. Displacement Reactions Involving Hypohalites

a. Halogen oxides and hypohalites other than hypofluorites are known to react with amines to produce the corresponding N-haloamines by displacement:



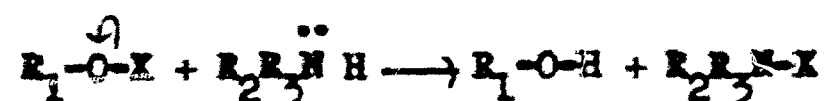
where

R_1 = H, alkali metal, t-butyl, or X

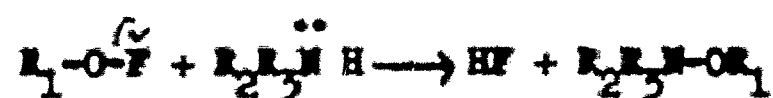
R_2 and R_3 = H, or alkyl group

X = Cl, Br, or I

From Pauling's "Table of Electronegativities" (Reference 3), it may be observed that in all cases under discussion, X is less electronegative than oxygen (Cl, 3.0; Br, 2.8; I, 2.5; O, 3.5) so that the reaction may be logically considered to involve a nucleophilic displacement by the amine or halogen, as shown below.



However, in the case of oxygen difluoride or hypofluorites the reaction may be expected to follow a different course as a result of the fact that fluorine is more electronegative (4.0) than oxygen (3.5). In this case one would expect the nucleophilic displacement to occur on oxygen, as follows:



R_3 = F, CF_3 , SF_5 , CF_3CO

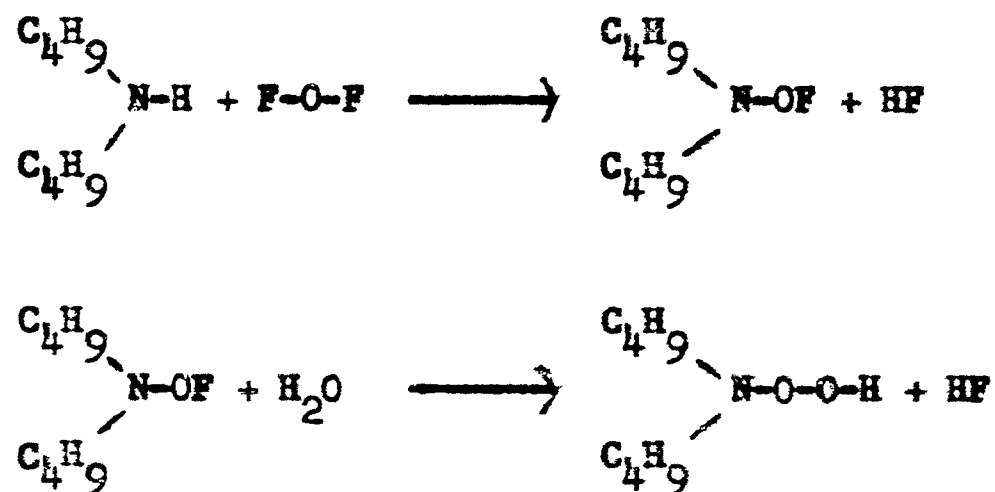
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If this distinction in mechanism is real, it will not be possible to prepare a fluoramine from an amine, and oxygen difluoride, or a hypofluorite. This point is now being investigated.

b. It is of interest that according to the above mechanism, the reaction between oxygen difluoride and an amine would be expected to yield an O-fluorohydroxylamine of the type R_2R_3N-OF , which may be more valuable as a monopropellant than the corresponding fluoramine, R_2R_3N-F .

c. There is now indirect evidence which would indicate that Wright's material may have been impure N,N-dibutylaminehydroperoxide, $(C_4H_9)_2NOOH$:



For example, Wright's analysis for fluorine was based on the ability of his material to oxidize acidified potassium iodide, with the liberated iodine then being titrated with standard thiosulfate to the starch endpoint. However, when the work was repeated in this laboratory,* it was found that the oxidizing product contained no fluorine, as determined from a standard volumetric method of analysis. Wright's workup procedure consisted of treating with aqueous acetic acid, a medium which has been shown in this laboratory to result in the destruction of the O-F bond (see below). Finally, t-butylhydroperoxide has been found to liberate iodine from acidified potassium iodide; thus N,N-dibutylaminehydroperoxide might be expected to undergo this reaction. Wright's elemental analysis does not correspond with the fluoramine, the O-fluoro-hydroxylamine, or

*By Dr. James Robinson, under Contract AF 49(638)-25.

the hydroperoxide; therefore, his product was presumably impure. Although there is still some doubt concerning the nature of Wright's reaction product, the fact that no fluorine was found demonstrates that it could not have been the expected dibutylfluoramine.

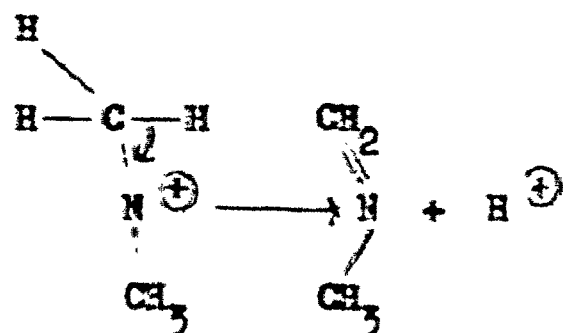
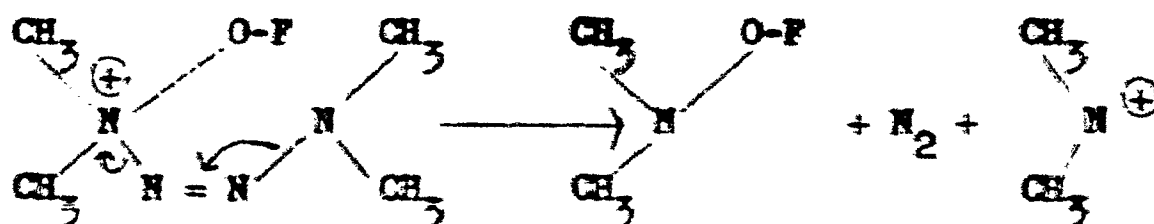
3. Reaction of Oxygen Difluoride with Dimethylamine, Tetramethyltetrazene, and N-Chloroethylethylamine

a. When the reaction of oxygen difluoride with dimethylamine was carried out by Wright's method, the mixture did not oxidize acidified potassium iodide. It is not clear why dibutylamine yielded an oxidizing product whereas dimethylamine did not. The only product isolated from the dimethylamine reaction (in addition to dimethylamine itself) was acetone, in very small yield.

b. Tetramethyltetrazene was considered as a possible precursor to an N-F Type compound, even though the reaction proceeded by a nucleophilic displacement on oxygen:



Alternatively, the reaction might not be intramolecular, in which case it would be unlikely that an N-F compound would form:



When this reaction was carried out on a small scale, slightly more than 1 mole of acid (presumably hydrogen fluoride) was found per mole of oxygen difluoride

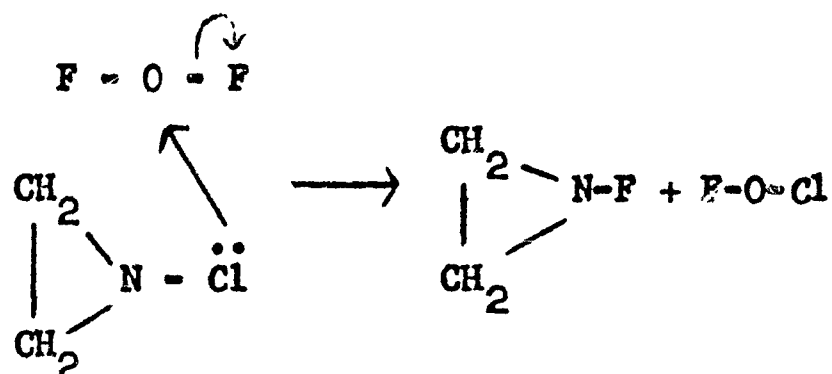
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II Technical Discussion, A (cont.)

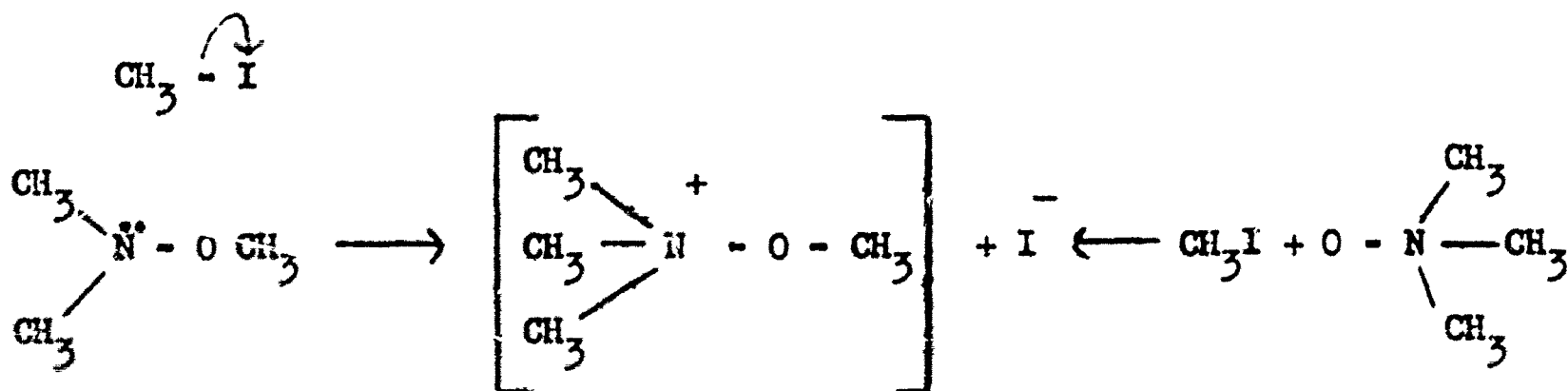
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employed. In mixing the reactants, copious evolution of a gas (probably nitrogen) occurred and the reaction mixture did not oxidize acidified potassium iodide. No attempt was made to isolate the reaction product from this run.

c. Since nitrogen and chlorine are equally electronegative (with values of 3.0 each), there was some question as to which of these elements in, e.g., N-chloroethylenimine, would act as the displacing agent toward oxygen difluoride. If chlorine were the displacing agent, an N-F compound might be formed, as shown below.



However, it appears that nitrogen, with an electronegativity of 3.0, is a better nucleophile than even the more electronegative oxygen (3.5). This is apparent in displacements on hydrogen, since ammonium salts are formed more readily than oxonium salts. It is also true in displacements on carbon, as shown by the formation of N-trimethyl-o-methylhydroxonium iodide from N, N-dimethyl-O-methylhydroxylamine and methyl iodide. That the nitrogen does the displacing was shown by synthesizing the same hydroxonium iodide from trimethylamine oxide and methyl iodide (Reference 4):

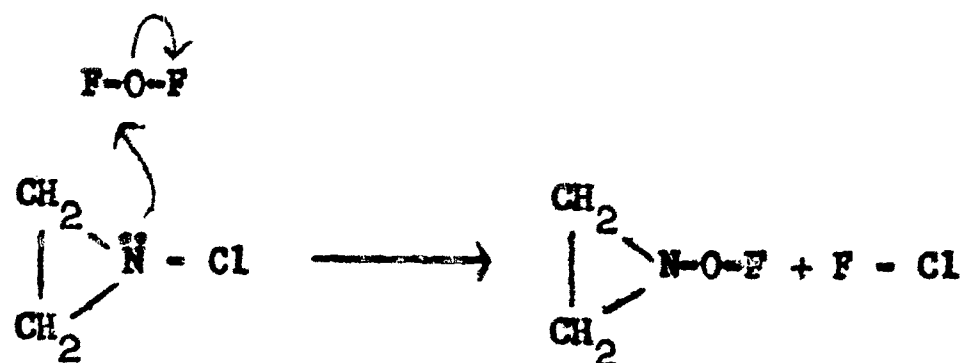


If nucleophilic displacement on oxygen follows the same pattern as that on hydrogen and on carbon, then no N-F compound would be obtained from oxygen difluoride and N-chloroethylenimine:

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II Technical Discussion, A (cont.)

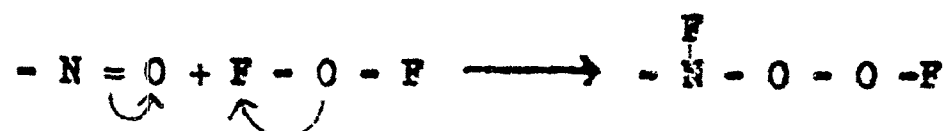
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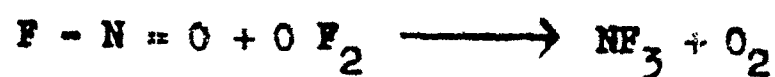
The reaction of N-chloroethylenimine with oxygen difluoride was carried out on a small scale, but unfortunately the reaction medium [Heptane - CaO (sat.) - H₂O] was subsequently shown to rapidly attack the oxygen difluoride (see Section IV). The reaction mixture contained chloride ion to the extent of about 10% of that available in N-chloroethylenimine, but no further analysis of the reaction mixture was attempted. It is intended to repeat this experiment, with the exception that N-chloropiperidine or dibutylchloramine will be used, instead of N-chloroethylenimine, to avoid possible difficulties due to ring opening.

4. Reaction of Oxygen Difluoride with Dimethylnitrosamine

a. Although displacement reactions involving oxygen difluoride may not lead to fluoramines as discussed above, the possibility exists that the addition of oxygen difluoride to an unsaturated nitrogen linkage may result in such a compound. For this purpose, it would appear that the nitrogen should be bound to a more electronegative element (oxygen is the only possibility), so that the fluorine would tend to become attached to nitrogen:



It is of interest that the only reported reaction of oxygen difluoride in which an N-F linkage is formed is one of this type (Reference 5):



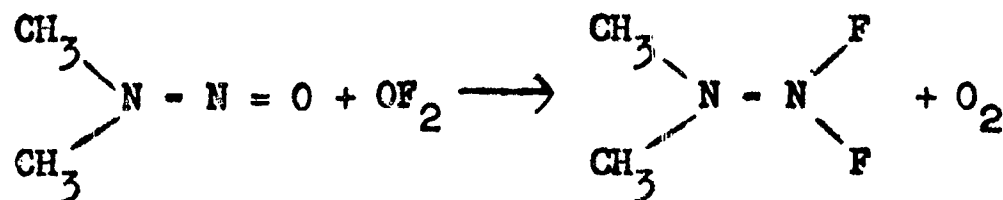
b. Experiments were carried out with dimethylnitrosamine and oxygen difluoride in an effort to determine whether the above reaction could be generalized. If the reaction of oxygen difluoride with the nitrosamine were similar to that with nitrosylfluoride, the product would be N, N-dimethyl-N', N'-difluorohydrazine:

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II Technical Discussion, A (cont.)

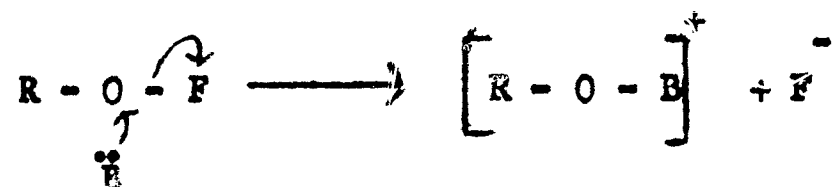
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Although the products of this reaction have not yet been characterized, it has been determined that when carbon tetrachloride is used as a solvent, a product is formed which is capable of oxidizing acidified potassium iodide. When water is used as the solvent, this product is not obtained. Work is now in progress to isolate and identify the oxidizing material.

5. Reaction of Oxygen Difluoride with t-butyl Alcohol and Di-t-butyl Peroxide

a. Some effort has been directed toward the preparation of hypofluorites, since it was originally believed that such compounds might be more valuable than oxygen difluoride as fluorinating agents. In the unknown t-butylhypofluorite, $(\text{CH}_3)_3\text{COF}$, for example, the oxygen atom is in a more reduced state than the oxygen atom in oxygen difluoride, so that side reactions involving oxidation (as opposed to fluorination) might be less likely with the t-butyl compound. In addition, t-butyl-hypofluorite may be a liquid at ambient temperature, and thus more readily handled than oxygen difluoride. If, however, the arguments relative to displacement reactions in hypohalates which were presented in paragraph II,A,2 are valid, hypofluorites cannot be expected to yield the N-F linkage (except possibly in their reactions with tetramethyltetrazene and a few related compounds):



where

$\text{R} = \text{t-C}_4\text{H}_9, \text{CF}_3, \text{SF}_5, \text{CF}_3\text{CO}$ etc

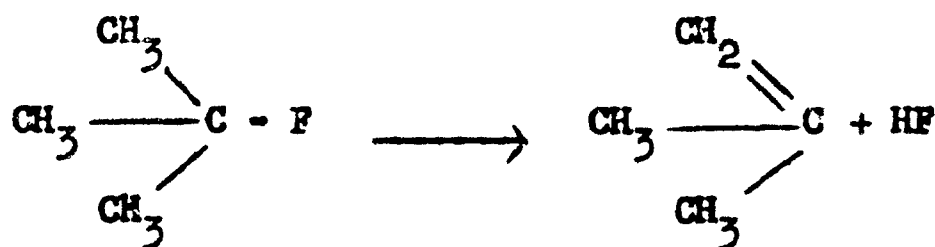
$\text{B} = \text{nucleophile}$

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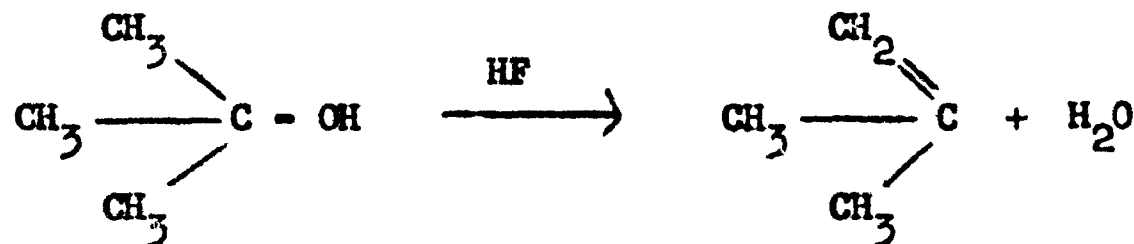
II Technical Discussion, A (cont.)

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b. Attempts were made to prepare t-butylhypofluorite from t-butyl alcohol and oxygen difluoride in the alcohol, as solvent. Isobutylene was isolated from this reaction, and it was also noted that 2 mol of an acid (probably hydrogen fluoride) were formed per mole of oxygen difluoride employed. These results can be interpreted as follows:



Alternatively, the isobutylene may have been formed by the acid catalyzed dehydration of the alcohol:



The reaction mixture was found to contain a product which slowly oxidizes acidified potassium iodide, but the separation of this material from the solvent alcohol was not accomplished. It was suspected that this substance might be di-t-butylperoxide, but it was subsequently found that the latter compound is inert to acidified potassium iodide under the same reaction conditions.

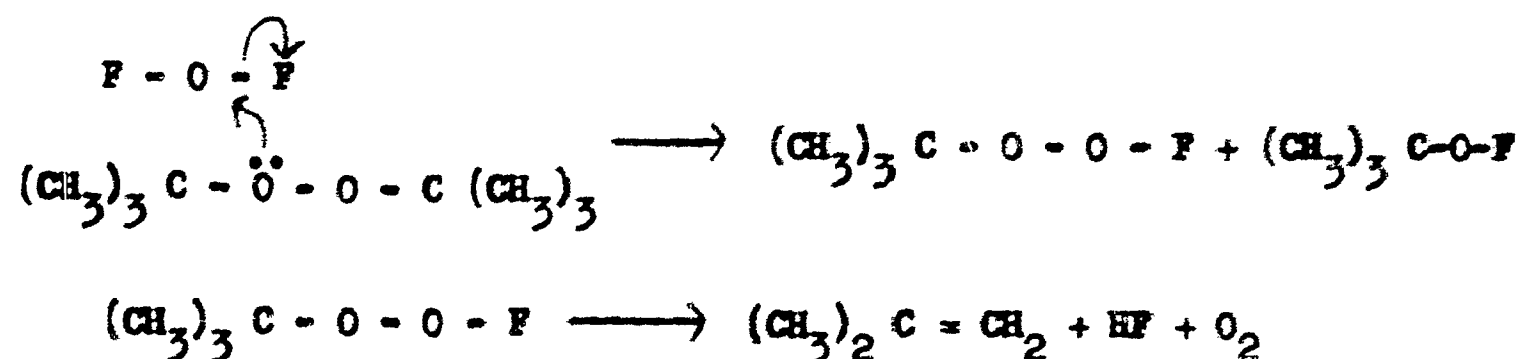
c. No reaction occurred during several weeks, when t-butyl alcohol and oxygen difluoride were mixed in the gas phase at ambient temperature.

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II Technical Discussion, A (cont.)

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d. An attempt was made to prepare t-butylhypofluorite from di-t-butyl peroxide and oxygen difluoride in carbon tetrachloride solution:



However, no appreciable reaction occurred during 25 hours at ambient temperature.

6. The Selection of Suitable Solvent Media for Oxygen Difluoride

The reactivity of oxygen difluoride toward several selected solvent media is shown in Table 1, in which the percent recovery of oxygen difluoride is given for various contact times with the solvents. It appears that oxygen difluoride is reasonably unreactive toward water, but is decomposed by both aqueous acids and bases. The high reactivity of hexane and heptane may be attributed to the presence of isomeric hydrocarbons containing tertiary carbon atoms. Such hydrocarbons may not be completely removed by normal purification procedures involving washing with sulfuric acid, drying over sodium or sodium hydride, and distillation.

7. Storage Stability of Oxygen Difluoride

Oxygen difluoride of 88.4 percent purity was found to undergo no change in composition when stored for 6 weeks in a dry Pyrex bulb, as determined by the reduction of oxygen difluoride with acidified potassium iodide, and by infrared data (quantitative determination).

B. EXPERIMENTAL

1. Apparatus and Manipulations of Materials

a. With the exception of the experiment involving dimethylamine (see below), all experiments were carried out with 0.5 to 3 millimole of oxygen difluoride, in the following manner. Oxygen difluoride was admitted into an evacuated Pyrex bulb (capacity 50-100 ml) equipped with stopcocks at either

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end. The final pressure was always less than 1 atmosphere. The other reactant was then added, either in solution or in an excess of the reactant as solvent, through one of the stopcocks, and the bulb was shaken at ambient temperature for a specified time. At the conclusion of the shaking period, one of two procedures was followed: (1) potassium iodide reagent (see below) was added to the bulb, the bulb again was shaken for 10 min, and the liberated iodine was titrated with standard thiosulfate to the starch endpoint, or (2) the liquid portion of the reaction mixture was withdrawn and the liquid and gas phases were analyzed separately. In this second procedure, the gas was analyzed either by addition of the potassium iodide reagent or from an infrared spectrum of the gas. The liquid portion of the reaction mixture was fractionated under high vacuum, through a series of cold traps; then the contents of each trap was analyzed by infrared and by reduction with acidified potassium iodide.

b. In all instances, the potassium iodide reagent was prepared by (1) adding 2.5 g of analytical-grade potassium iodide to 10 ml of 1-N sulfuric acid and (2) diluting the resulting solution (with water) to 25 ml.

2. Reaction of Oxygen Difluoride with Selected Nitrogen Compounds

a. Dimethylamine

The apparatus for the reaction of oxygen difluoride with dimethylamine was a 300-ml, three-necked, standard-taper, round-bottomed flask fitted with a gas inlet tube, a thermometer, a cold (-80°C) finger, and an efficient trapping system located downstream of the cold finger. The flask was immersed in an ice-water bath, and the contents were stirred magnetically. Dimethylamine and oxygen difluoride were admitted through a calibrated flowmeter, into the reaction mixture in the flask.

Gaseous anhydrous dimethylamine (49.2 mmole) was passed through the gas inlet tube into a stirred mixture of 6 g (100 mmole) of glacial acetic acid in 150 ml of hexane, at 0°C , over a period of 30 min. The hexane had been previously purified by scrubbing with concentrated sulfuric acid, drying overnight over sodium hydride, and finally distilling from sodium hydride.

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II Technical Discussion, B (cont.)

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Upon addition of the amine to the homogeneous hexane-acetic acid mixture, a second layer formed as a heavy oil. Oxygen difluoride of 88.5% purity was now added (25.0 mmole, calculated as pure oxygen difluoride) over a period of 80 min. This was accomplished by evacuating the system sufficiently (76 mm) to permit the oxygen difluoride to flow from the storage bulb. In addition to the -80°C cold finger, three cold traps were used in the experiment. These traps were maintained at -80°C , -160°C , and -196°C during the first part of the experiment.

It was found that the -196°C trap contained 0.623 mmole of oxygen difluoride (2.49% recovery) and 0.166 mmole of carbon tetrafluoride (identified by infrared). Because the original oxygen difluoride contained carbon tetrafluoride (in unknown amount) as an impurity, it is not certain whether any carbon tetrafluoride was produced in the oxygen difluoride-dimethylamine reaction. The -160°C trap contained 0.433 mmole of a gaseous product which was not identified, together with 0.134 mmole of hexane; the -80°C trap contained 0.021 mmole of the same unidentified material and 0.141 mmole of hexane. Subsequent experiments indicated that the material in the -160°C trap was non-oxidizing toward acidified potassium iodide and that it gave no acid reaction with water, as determined by shaking the gas with water and titrating the solution with standard tenth-normal sodium hydroxide to the phenolphthalein endpoint. The material in the -80°C trap was also non-oxidizing.

Distilled water (100 ml) was added dropwise to the two-phase reaction mixture (upper layer, colorless; lower layer, yellow) over a period of 2 hours. During this operation, the pressure in the system was maintained at 76 mm; the three cold traps, at -80° , -112° (ethanol), and -196°C ; and the cold finger, at 70°C .

The -196°C trap contained 0.372 mmole of acetone identified by its infrared spectrum and by conversion to the 2, 4-dinitrophenylhydrazine; the -112°C trap contained 0.145 mmole of acetone and 0.434 mmole of hexane; and the -80°C trap contained 0.488 mmole of pure hexane. The acetone from the -112° trap was also converted to the 2, 4-dinitrophenylhydrazone which, when recrystallized from 50% aqueous methanol, melted at $124-5^{\circ}\text{C}$ (lit. 126°C , Reference 6).

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II Technical Discussion, B (cont.)

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The hexane layer was separated from the aqueous layer, washed with 5% aqueous sulfuric acid, 2% aqueous sodium hydroxide, and water, and ~~was~~ then dried over anhydrous magnesium sulfate. This material did not oxidize acidified potassium iodide and, presumably, contained no dimethylfluoramine. Flash distillation of the hexane left 0.381 g of a yellow residue, which was not identified. An infrared spectrum of this liquid indicated that it may be an amide, such as N, N-dimethylacetamide (from dimethylamine and acetic acid).

The aqueous layer contained 1.372 meq of material capable of oxidizing acidified potassium iodide. Presumably, the oxidizing material was not the desired fluoramine, which would have been expected to appear in the hexane layer. When made strongly basic with 50% aqueous sodium hydroxide, the aqueous layer yielded 18.56 mmole of dimethylamine and no other product. This represents a recovery of 37.8% of the dimethylamine originally used (30.6 mmole of dimethylamine used up) and shows that less than 1.25 mole of the amine reacted per mole of oxygen difluoride used. The actual stoichiometry may be closer to a 1:1 ratio, since not all of the amine could be isolated from the solution.

b. Tetramethyltetrazene

Tetramethyltetrazene was prepared as previously described (Reference 7). A solution of 0.3 ml of the tetrazene, in 6.0 ml of Spectro-grade carbon tetrachloride, was added to 0.574 mmole of oxygen difluoride. A vigorous reaction occurred on shaking, and a gas (probably nitrogen) was steadily evolved. During the reaction, a yellow oil separated as an adherent film on the walls of the reaction vessel. After a shaking period of 10 min, the carbon tetrachloride was withdrawn and water was added to take up the oil. Both the carbon tetrachloride and aqueous solutions were subsequently analyzed.

The residual gas was found to be non-oxidizing, and consequently contained neither unreacted oxygen difluoride nor other gaseous products capable of oxidizing acidified potassium iodide. Both the carbon tetrachloride and aqueous solutions were found to be non-oxidizing. The carbon tetrachloride solution was also non-acidic, but the aqueous solution contained 61% of the 2 mole of acid expected if all of the fluorine in the oxygen difluoride employed had been ~~converted~~ to hydrogen fluoride.

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c. N-Chloroethylenimines

N-chloroethylenimine was prepared as previously described (Reference 8). A blank experiment was conducted in order to test the reactivity of N-chloroethylenimine with the system heptane-water-calcium oxide (sat.). Heptane was employed as part of the solvent system so that both N-chloroethylenimine and any N-fluoroethylenimine formed would be protected, to some extent, from the aqueous base because (1) N-chloramines are known to be unstable in a basic solution, and (2) N-chloramines are miscible with organic solvents, but immiscible with water. Aqueous calcium oxide (i.e., calcium hydroxide) was employed to neutralize any hydrogen fluoride formed, because ethylenimine derivatives, in general, undergo ring opening in acid solution. Calcium oxide (or hydroxide) was preferable to sodium hydroxide, since a saturated solution of the former compound contains only 0.2 percent of the hydroxide (cf. above remark relative to the stability of N-chloramines to aqueous base).

When 3 ml (42.6 mmole) of N-chloroethylenimines in 25 ml of n-hexane (Phillip's A.S.T.M. grade) was added to a suspension of 3.3 g (50 mmole) of calcium oxide in 50 ml of distilled water, and the two-phase system was shaken for 5.5 hours at ambient temperature, 96% of the N-chloroethylenimine was recovered as determined by oxidation of acidified potassium iodide. After acidification, the aqueous layer gave no precipitate of silver chloride with aqueous silver nitrate. The distribution of the N-chloroethylenimine was determined to be 65.5% in the hexane layer, and 35.5% in the aqueous layer.

A suspension of 0.28 g (5.0 mmole) of reagent-grade calcium oxide in 4 ml of water and a solution of 0.30 ml (0.33g = 4.0 mmole) of N-chloroethylenimine in 2 ml of heptane were successively added to 2.19 mmole of oxygen difluoride, and the reaction vessel was shaken for 15 min at ambient temperature until the exothermic reaction ceased. The suspension was withdrawn and centrifuged.

An infrared analysis of the gas phase indicated that all of the oxygen difluoride had reacted. When the aqueous, centrifuged layer was acidified with acetic acid and titrated with standard aqueous silver nitrate,

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0.57 mmole of chloride ion was found. It was subsequently shown that both heptane and calcium oxide-water destroy oxygen difluoride rapidly (see Table 1). However, the partial recovery of chlorine as chloride ion in the present experiment showed that reactions of oxygen difluoride with N-chloroethylethylamine had occurred to some extent.

d. Dimethylnitrosamine in Aqueous Solution

Dimethylnitrosamine was prepared from dimethylamine and nitrous acid by standard techniques (Reference 9). A solution of 0.60 ml (8.1 mmole) of the nitroso compound in 10 ml of distilled water was added to 1.39 mmole of oxygen difluoride, and the mixture shaken for one hour at ambient temperature. The reaction was only mildly exothermic. The clear and colorless liquid was withdrawn, and both liquid and gas were subsequently analyzed. Because of the presence of water, infrared spectra could not be taken directly.

The gas phase was fractionated through -80 and -196°C traps. The -196°C trap contained 0.13 mmole of material, and an infrared analysis showed the absence of oxygen difluoride and the presence of an unidentified material absorbing at 4.3, 4.5, and 12.55 microns. This material did not oxidize acidified potassium iodide and contained no hydrogen fluoride as determined by titration of its aqueous solution with standard base. The -80°C trap contained a liquid with a vapor pressure of about 15 mm at 18.5°C ; it was (probably) mostly water. The material in this trap was neither oxidizing nor acidic.

The liquid phase was not further treated when it was found to contain 2.54 mmole of acid (probably hydrogen fluoride), representing 91.4% of the 2 mole of acid expected per mole of oxygen difluoride employed, if all of the fluorine in the oxygen difluoride had been converted to hydrogen fluoride.

e. Dimethylnitrosamine in Carbon Tetrachloride Solution

A solution of 0.60 ml (8.1 mmole) of dimethylnitrosamine in 10 ml of Spectro-grade carbon tetrachloride was added to 1.36 mmole of oxygen

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difluoride, and the mixture was shaken for 3 hours at ambient temperature. During the mildly exothermic reaction, a yellow oil separated in small amount. The liquid (excluding the yellow oil) was withdrawn and both liquid and gas were subsequently analyzed.

An infrared spectrum of the gas phase revealed the absence of oxygen difluoride, as well as the presence of at least two new materials. Apparently, one of these was the same as that obtained in the aqueous reactions (see above) and showed absorption maxima at 4.3 and 4.5 microns; absorption at 12.55 microns was masked by carbon tetrachloride. The other material showed maximum absorption at 5.6 microns. The gas phase was fractionated through the -80 and -196°C trap, and the -196°C trap was found to contain both of the new materials. This fraction was found to be both oxidizing and acidic, and since the material absorbing at 4.3 microns was shown in the experiment (in aqueous solution) to be both non-oxidizing and non-acidic (see above), it may be concluded that the material that was absorbing at 5.5 microns was responsible for these observations. The -80°C trap contained nearly pure carbon tetrachloride, as determined quantitatively from its infrared spectrum. The yellow oil which had separated during the reaction appeared as a semisolid mass having essentially no vapor pressure after the removal, by fractionation, of the gas phase from the reaction vessel. This residue was not examined further.

When the liquid portion of the reaction mixture was fractionated through the -30 , -80 , and -196°C traps, an additional quantity of the oxidizing material appeared in the -196°C trap. The combined yield of the two products which were absorbing at 4.3 and 5.5 microns was about 20 mole %, based on the oxygen difluoride. The -80°C trap contained the bulk of the carbon tetrachloride solvent, the -30°C trap contained unreacted dimethylnitrosamine, and the non-volatile residue (about 0.15 ml) was shown to comprise a solution of Kal-7 grease (which had been used to lubricate the stopcocks of the reaction vessel) in carbon tetrachloride. All of these identifications were based on infrared spectra, with spectra of the pure materials being available for comparison. The total of the acid produced in both the liquid and gas phases, during the run, amounted to 28% of the theoretical 2 mole of hydrogen fluoride

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(cf. preceding experiment). However, since products readily hydrolyzable to hydrogen fluoride may have been formed in this experiment (and, indeed, in all of the other experiments), it is not known to what extent hydrogen fluoride was formed as such during the reaction proper.

3. Reaction of Oxygen Difluoride with Selected Oxygen Compounds

a. Tertiary-butyl Alcohol

In this experiment, t-butyl alcohol was employed both as the reactant and the solvent. To 3.46 mmole of oxygen difluoride was added 7.5 ml of the redistilled alcohol, and the mixture was shaken at ambient temperature of 7-1/2 hours. Previous experiments with this system had indicated the reaction to be relatively slow, and that a reaction time of approximately 7 hours was required for the complete conversion of the oxygen difluoride. The liquid was withdrawn at the conclusion of the run.

An infrared analysis of the gas phase showed only t-butyl alcohol and carbon tetrafluoride, the latter being an impurity in the oxygen difluoride. The gas was non-oxidizing.

The liquid phase was found to contain 90% of the 2 mmole of acid expected if all of the fluorine in the oxygen difluoride had been converted to hydrogen fluoride. The liquid was fractionated through the 0, -40, -80, and -196°C trap, and the subsequent workup of the trap yielded the following results: The -196°C trap contained 1.46 mmole of isobutylene (identified by comparison of the infrared spectrum with that of pure isobutylene), and 0.81 mmole of unidentified material. This fraction was both non-acidic and non-oxidizing. The -80°C trap contained 1.25 mmole of t-butyl alcohol and 1.07 mmole of unidentified material. This non-oxidizing fraction contained 0.04 mmole of acid. The -40°C trap contained the bulk of the alcohol, and an infrared spectrum of the tallings showed only the alcohol. The fraction contained 3.87 mmole of acid and slowly oxidized acidified potassium iodide. That this oxidizing power was not due to di-t-butyl peroxide (which has about the same volatility at low temperatures as the alcohol) was shown when a sample of

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t-butyl peroxide (assay 97%) failed to oxidize under the same conditions. Attempts to separate the oxidizing material from the alcohol were unsuccessful. The 0°C trap contained nothing, and the residue (0.095 g) was not treated further.

When oxygen difluoride (41 mm) and t-butyl alcohol (39 mm) were stored in a 1-liter bulb for 6 weeks, no change was observed in the infrared spectrum. It was also noted that the mole ratio of the two reactants remained constant during the storage period.

b. Di-t-butyl Peroxide

A solution of 0.3 g (2.1 mmole) of di-t-butyl peroxide (assay 97%) in 2 ml of Spectro-grade carbon tetrachloride was added to 0.634 mmole of oxygen difluoride. After a shaking period of 25 hours, approximately 90% of the oxygen difluoride was recovered. Since the peroxide was not completely pure, it is uncertain as to whether the oxygen difluoride reacted with the peroxide to a small extent during the allowed reaction time.

4. Solvent Media for Oxygen Difluoride

Various solvent media were examined for reactivity with oxygen difluoride. In each instance, the solvent was added to the oxygen difluoride, the mixture was shaken for an allotted time, and finally potassium iodide reagent was added without the prior removal of the solvent. The results of these experiments are given in Table 1. Essentially, complete recovery was obtained from water, carbon tetrachloride, Freon 113, and the carbon tetrachloride-acetic acid mixture.

C. METHODS PROPOSED FOR PREPARATION OF LIQUID FUELS CONTAINING ALUMINUM HYDRIDE

1. Introduction

The encouraging results obtained by the use of aluminum metal in solid propellants has led to the consideration of compounds of aluminum, or other metals that might be soluble in high-energy fuels for liquid bipropellants,

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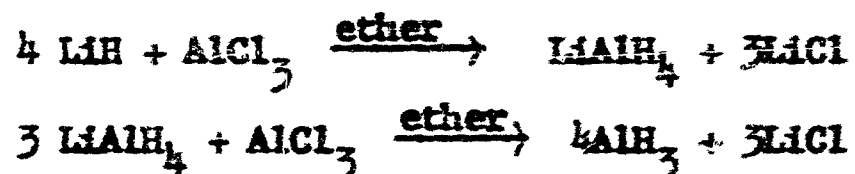
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such as hydrazine or dimethyl hydrazine. In the following sections, theoretical calculations are presented for one possible candidate, aluminum hydride, for possible use in liquid-bipropellant systems or in hybrid rockets.

2. Preparation and Properties of Aluminum Hydride

Aluminum hydride was discovered, by E. Wiberg and O. Stecher in 1942, as a product of the reaction caused by passing an electric current through a mixture of trimethyl aluminum and hydrogen (References 10, 11, and 12). It is formed as a high-molecular-weight polymer of the general composition $(AlH_3)_x$. A more convenient method of preparation is that discovered by A. E. Finholt and co-workers (Reference 13), which consists of adding ethereal aluminum chloride to finely powdered lithium hydride. The soluble lithium aluminum hydride first forms; however, on further addition of aluminum chloride, a solution of monomeric aluminum hydride is obtained:



The latter solution is not stable; it soon deposits a white solid in which the atomic ratio of aluminum to hydrogen still is 3:1, but from which the ether cannot be completely removed without loss of hydrogen. The precipitation of the aluminum hydride as a high-molecular-weight polymer can be prevented or reversed by adding aluminum chloride to the system, or by employing tetrahydrofuran as solvent. Another technique which has been employed recently (Reference 14) for preventing polymerization employs the rapid filtration of the ethereal solution, as prepared by the method of Finholt, into vigorously stirred pentane or ligroin, neither of which is a solvent for aluminum hydride. The product obtained in this manner can be freed from the last traces of hydrocarbon, without decomposition, by vacuum drying.

Depending on the degree of polymerization, the compound $(AlH_3)_x$ is stable in high vacuum to above $100^\circ C$. Above these temperatures, it decomposes rapidly and quantitatively into silvery-white metallic aluminum plus hydrogen:



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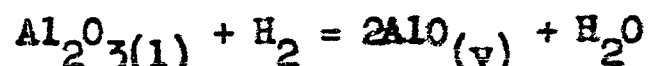
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It reacts vigorously with water, evolving hydrogen:



3. Thermochemical Calculations

In the preceding quarterly report is presented the possibility of utilizing aluminum in liquid fuels. The basis of the utilization of aluminum is that one may formulate propellant systems to obtain the high heat of formation of Al_2O_3 , which is solid or liquid at chamber temperatures, and still produce large amounts of gas for propulsion. This is possible because the equilibrium



is far to the left below 3500°K. This allows formulations to be made in which only the metal and carbon are oxidized (the carbon only to CO), leaving H_2 gas to give overall low-molecular-weight products. A thermodynamic analysis of other metal oxides indicates that only aluminum and beryllium will not react with hydrogen at high temperatures so as to allow this type of formulation. The toxicity and scarcity of beryllium precludes its use; therefore, aluminum is found to be the best metal for use in rocket fuels.

When considering the various formulations, it becomes immediately obvious that aluminum hydride, AlH_3 , will be even better than aluminum metals as a fuel. For 27 g of aluminum, the hydride has only 3 additional grams of hydrogen, but this 3 g produces 1.5 mole of gas. The hydride, although relatively reactive, could probably be protected by incorporating it in a polymer such as polyethylene or rubber. This solid fuel could then be used in a hybrid system in which the solid is cast in the chamber and a liquid oxidizer is introduced as needed.

Table 2 presents the results of calculations made on systems containing AlH_3 monomer, in a polymer, with the oxidizers IRFNA, 90% H_2O_2 , and ClO_3F . All three formulations assumed a solid phase consisting of 80% AlH_3 and 20% polymer and with the fuel-oxidizer ratio such that the only oxides

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formed were CO and Al_2O_3 . The most interesting result of the calculations is that hydrogen peroxide is the best oxidizer. This is due to the more favorable stoichiometry of the system, i.e., to the greater H/O ratio in the oxidizer. The heat of formation of Al_2O_3 is so large that it overshadows any differences in heats of formation of the oxidizers; thus, the best impulse is obtained from the systems that produce the best Al_2O_3 - H_2 ratios regardless of the poor ΔH of formation of the oxidizer. It is also interesting to note that with ClO_3F as oxidizer, the flame temperature is 4024°K vs 3164°K for the 90% peroxide system; yet, the specific impulse is 20 units lower than that of the peroxide system. It is a general characteristic of systems containing large amounts of hydrogen that one obtains lower chamber temperatures for a given specific impulse, because of the very large heat capacity of hydrogen gas. It is somewhat fortunate that H_2O_2 yields the best calculated specific impulse, because this is the oxidizer with which the most experience in hybrid rockets has been gained. An additional calculation, the results of which are also presented in Table 2, was made on the system AlH_3 - 90% H_2O_2 , without hydrocarbon binder, as an example of the limiting case wherein the products are only Al_2O_3 and H_2 .

The calculations shown above were made assuming a chamber pressure of 1000 psia. Generally, one calculates solid-propellant systems at chamber pressures of 1000 psia and liquid propellant systems at 300 psia; where to best operate a hybrid would depend on a complete analysis of the system. Table 3 presents the results of calculations made on one hybrid system at chamber pressures of 300 and 1000 psia. The relative impulse calculated here is general for most systems - that at 300 psia is 0.87 times that at 1000 psia. Other relative values are 0.94 at 500 psia and 0.98 at 750 psia.

Table 4 compares aluminum with AlH_3 in a hydrogen peroxide hybrid system.

The thermodynamic calculations given above say nothing about the physical characteristics of the fuel system - the $(-\text{CH}_2-)_x$ used in the calculations could be a liquid hydrocarbon, as well as a solid polymer of polyethylene or rubber, so that slurry fuels having these high specific impulses

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are

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are possible. In making slurry fuels of reactive materials such as AlH_3 , the biggest problem will be that of obtaining pure hydrocarbons that are free of water and dissolved oxygen. Experience has shown that with slurries of alkali metals prepared during various additive programs, they tend to react with the unsaturated compounds in JP-4 to give colored precipitates which prevent flow into the reaction chamber (Reference 15).

The enthalpy of formation of $\text{AlH}_3(\text{c})$ was estimated to be -2.6 kcal/mole,* by simply subtracting the enthalpy of formation of $\text{LiH}(\text{c})$, -21.6 kcal/mole, from that of $\text{LiAlH}_4(\text{c})$, -24.2 kcal/mole. This calculation is equivalent to assuming that the heat of reaction of LiH with AlH_3 to form LiAlH_4 is zero. Generally, the heat of formation of the propellant markedly affects the calculated impulse so that accuracy of data is quite important; however, in the systems calculated here, the heats of reactions are quite high, 2.0 or more kcal/g, and the heats of formation are overshadowed by the large heat of formation of Al_2O_3 . Before much work is done with propellant formulations, an accurate value for the heat of formation of AlH_3 must, of course, be determined experimentally.

Occasionally, an application calls for a chemical system that will produce large amounts of gas at moderate temperatures, say in the range of 1000-1500°K. A system that appears to have a good potential here is AlH_3 and aqueous ammonia solutions. With formulations in which only the Al is oxidized to produce Al_2O_3 , H_2 , and N_2 , it is possible to produce 7.0 mole of gas per 100 g of materials in the system at temperatures in the desired range. The liquid could be dripped onto a bed of the hydride and the system so designed that the solid Al_2O_3 would remain in the generator. Excess AlH_3 in the generator would ensure that the reaction produced the desired products. The gases would also have a reasonable heat of combustion with air; thus, additional energy could be obtained this way. In fact, the system might be used as a combustible gas-generator system. One calculation is presented in Table 5.

* A negative value means that heat is evolved from the system.

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III. FUTURE WORK

A. In the immediate future, an attempt will be made to isolate and characterize the oxidizing product formed in the reaction of oxygen difluoride with dimethylnitrosamine. Attention will also be directed to a further investigation of the oxygen difluoride-dimethylamine reaction, without the use of an aqueous workup procedure, in an attempt to isolate $(CH_3)_2NOF$ or other products.

B. Thermochemical calculations of possible high-performance systems will be continued.

C. Elbow-motor tests will be initiated on representative high fuels with perchloryl fluoride.

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TABLE 1

SOLVENT MEDIA FOR OXYGEN DIFLUORIDE

<u>Solvent</u>	<u>Oxygen Difluoride % Recovered</u>	<u>Time, hr</u>
n-Heptane (Phillip's ASTM)	3	0.5
n-Hexane (Purified)	1	0.5
Carbon tetrachloride (Spectro Grade)	99	1
Carbon tetrachloride (Spectro Grade)	99	5
Carbon tetrachloride (Spectro Grade)	98	25
Freon - 113, $\text{CCl}_2\text{F} - \text{C ClF}_2$	100	1
Water	99	1
Saturated calcium hydroxide (0.2% CaO)	1	1
Water/acetic acid (5:1)	79	1
Carbon tetrachloride/acetic acid (5:1)	99	1

Table 1

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TABLE 2

COMPARISON OF VARIOUS OXIDIZERS IN A HYBRID SYSTEM USING AlH_3 AS SOLID FUEL

<u>Oxidizer</u>		<u>IRFNA</u>	<u>ClO₃F</u>	<u>90% H₂O₂</u>	
<u>Propellant Composition</u>					
AlH ₃ , wt %		37.3	28.0	41.5	53.9
Binder, wt %		9.3	7.0	10.4	0.0
Oxidizer, wt %		53.4	65.0	48.1	46.
<u>Specific Impulse, lbf-sec/lbm</u>					
(1000/14.7 psia)		299	289	309	312
<u>Chamber Temperature, °K</u>		3481	4024	3164	3533
<u>Exhaust Temperature, °K</u>		2387	2819	2026	2562
<u>Chamber Composition</u>					
mole/100 g	Al ₂ O ₃ (l)	0.479	0.000	0.646	0.596
	Al ₂ O ₃ (v)*	0.142	0.467	0.046	0.302
	H ₂	2.861	1.120	4.281	4.007
	H	0.199	0.413	0.146	0.334
	CO	0.664	0.499	0.740	
	HCl		0.511		
	Cl		0.124		
	HF		0.634		
	N ₂	0.433			
Total mole of gas/100 g		4.299	3.768	5.213	4.643

* Recently published data show that Al_2O_3 does not exist as a vapor, but dissociates to AlO and Al_2O . These data are being evaluated and will be used, if necessary, to correct the calculated impulse values. Preliminary calculations with these new data indicate an increased theoretical value because of the greater number of moles of gas that are formed in the dissociation process than are formed in the vaporization process.

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Table 2

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TABLE 3

EFFECT OF CHAMBER PRESSURE ON THE CALCULATED
SPECIFIC IMPULSE OF THE SYSTEM: AlH_3 , ClO_2F , $(CH_2)_x$

<u>Propellant Composition, wt %</u>			
	AlH_3	28.0	
	Binder	7.0	
	Oxidizer	65.0	
Chamber pressure, psia		1000	300
Chamber temperature, °K		4024	3831
Exhaust temperature, °K		2819	2905
Specific impulse, lbf-sec/lbm		289	250
Chamber composition			
mole/100g	$Al_2O_3(v)$	0.467	0.467
	H_2	1.120	1.079
	H	0.413	0.527
	CO	0.499	0.499
	HCl	0.511	0.479
	Cl	0.124	0.155
	HF	0.634	0.634
		-----	-----
	Total gas	3.768	3.840

Table 3

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TABLE 4

COMPARISON OF AL AND AlH_3 AS SOLID FUELS IN HYBRID SYSTEMS USING H_2O_2 AS OXIDIZER

Solid fuel	<u>Al</u>	<u>AlH_3</u>
Wt % solid fuel*	28.0	41.5
Wt % binder, $(CH_2)_x$	20.5	10.4
Wt % oxidizer, 90% H_2O_2	51.5	48.1
Specific impulse, lbf-sec/lbm (1000/14.7 psia)	280	309
Chamber temperature, °K	2966	3164
Exhaust temperature, °K	1650	2026
Chamber composition		
moles/100g $Al_2O_3(s)$	0.508	0.646
$Al_2O_3(v)$	0.012	0.046
H_2	3.120	4.281
H	0.000	0.146
CO	1.460	0.740
Total moles of gas	4.592	5.213

* Neither composition was optimized for the particular components, but both are estimated to be near optimum.

Table 4

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TABLE 5

PROPERTIES OF A 104-TEMPERATURE GAS-GENERATOR SYSTEM

System 0.354 AlH_3
0.636 $\text{NH}_4\text{OH}(\text{aq})$

Gas generator Temperature, °K	1340
Combustion Products	
moles/100g $\text{Al}_2\text{O}_3(\text{s})$	0.607
H_2	6.36
N_2	0.91
Total gas	7.27
Heat of Combustion	
with air, Btu/lb	8,000

Table 5

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