(CH₃)₄Sn⁻ ion, and, by the trends in coupling constants observed in the neutral stannanes, substitution of a hydrogen for a methyl group in the trimethyltin anion would be expected to increase the SnCH₃ coupling, as observed. Due to rapid solvolytic proton exchange, the tin-bonded hydrogen atom would not be expected to split the tin-methyl resonance into a doublet, nor would it be possible to observe a resonance for this proton as distinct from the solvent protons in such dilute solutions.

Substituent Effects on Sn–H and Sn–CH₃ Coupling.— The effect of substituting CH₃ for H on the coupling Sn–H in SnH₄ and the methylstannanes is not strictly additive, as illustrated in Fig. 1. The coupling for (CH₃)₄Sn strongly deviates from the extrapolated straight line, and is larger than might have been expected if the effects were additive. The first three points are nearly linear, except for a slight alternation in positions which, though small, we nevertheless feel is real. A similar pattern of behavior, including a slight alternation, is observed for the effects of substitution of H for CH₃ in the coupling Sn–CH₃ (starting with (CH₃)₄Sn and extrapolating to the methylstannanes). There have been other observations of non-additivity of substituent effects, such as the increasing positive deviations obtained for C–H or Si–H coupling by substitution of halogens (particularly F) in CH₃ or SiH₄,²⁹ or for the coupling Sn–CH₃ upon substitution of Cl for CH₃ in (CH₃)₃Sn. A discussion of possible explanations for these deviations is given by Juan and Gutowsky.²⁶

Acknowledgment.—The authors wish to thank Professor Daniel E. Kivelson of this Department and Dr. J. R. Holmes of the Allied Chem. Corp., Morris-town, N. J., for valuable discussions; Mr. Richard Gillespie for assistance in obtaining magnetic resonance spectra on the 40 Mc. instrument; and the Ethyl Corporation for a sample of (CH₃)₄Pb.

(20) A. G. Streng

The Chemical Properties of Dioxygen Difluoride

BY A. G. STRENG

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Dioxygen difluoride has a remarkably high oxidizing power, even at very low temperatures. The reactivity of O₂F₂ with Cl₂, Br₂, I₂, P, S, and their lower fluorides, as well as with the fluorides of nitrogen, with HCl, HBr, H₂S and with some other compounds was studied. Formation of intermediate addition products was observed in the reactions with CIF, BFI, SF₆, HCl, and HBr. Most intermediates have only a transitory existence.

Introduction

Dioxygen difluoride, O₂F₂, is the second member of the oxygen-fluoride family, consisting of OF₂,²⁸ O₂F₃,²⁹ O₂F₄, and O₂F₅. It is an orange-yellow solid which melts at 106.7°C to an orange-red liquid. Dioxygen difluoride is sufficiently stable at temperatures below its melting point but decomposes rapidly into O₂ and F₂ at temperatures close to its normal boiling point, 216°C.

Dioxygen difluoride has been known since 1933; when Ruff and Menzel achieved its preparation.²⁴ Since then a number of investigations have been devoted to the methods of preparation of O₂F₂ and to its thermodynamic and physical properties;²⁵ but very little has been published about its chemical properties. Only recently, when this paper was ready for typing, there appeared a very interesting article, by R. T. Holzmann and M. S. Cohen [Inorg. Chem., 1, 972 (1962)], describing the reaction of O₂F₂ with tetrafluoroethylene.

Since dioxygen difluoride is stable only at low temperatures, its chemistry was studied in a temperature region which is substantially below the usual range of chemical studies.

An exploratory study of the behavior and reactivity of dioxygen difluoride with various substances was made in order to obtain information on the basic chemistry of O₂F₂ and its ability to form addition products.

(1) This paper describes a part of the work sponsored by the Office of Naval Research, under Contract Non-3085(01).
(2) (a) P. Lebeau and A. Damiani, Compt. rend., 188, 652 (1929); (b) O. Ruff and W. Menzel, Z. anorg. u. allgem. Chem., 111, 204 (1923).
(13) O. Ruff and E. Ascher, ibid., 196, 413 (1931).
temperature and a new portion of reagent was added. The procedure was repeated until all the O₂F₂ was consumed. The reaction products (gaseous, liquid and solid) were measured and analyzed.

If O₂F₂ was used as liquid, it was condensed in the bottom of the reaction vessel. In some cases reactions were performed with O₂F₂ dissolved in a suitable solvent. Two-limb apparatus was used for some of the reactions between two liquid reagents or their solutions. The reagents were condensed separately in the two limbs and one liquid was added to the other by tilting the apparatus.

If a reaction between liquid O₂F₂ (or its solution) and a gas was studied, the gas, usually diluted with an inert gas, was bubbled through the liquid.

The reagents and the reaction products were measured carefully. In the gaseous and in the liquid phase, they were measured volumetrically; in the solid phase, by weight. The reaction products were identified by chemical methods, by determination of their physical constants and by infrared spectrography.

Liquid nitrogen, liquid oxygen, various Freons and Dry Ice were used as refrigerants. It must be emphasized that inadequate cooling or a fast addition of reagents to O₂F₂ and vice versa caused explosions.

**The Reactivity of O₂F₂ with Organic Compounds**

Being a high energy oxidizer, dioxygen difluoride reacted vigorously with organic compounds, even at temperatures close to its melting point. It reacted instantaneously with solid ethyl alcohol, producing a blue flame and an explosion. When a drop of liquid O₂F₂ was added to liquid methane, cooled at 90°K, a white flame was produced instantaneously, which turned green upon further burning. When 0.2 cm³ of liquid O₂F₂ was added to 0.5 cm³ of liquid CH₄ at 90°K, a violent explosion occurred. When added to Dry Ice, dioxygen difluoride did not react and was only absorbed by the solid. Addition of acetone to this mixture resulted in sparking accompanied by an explosion.

A 2% solution of O₂F₂ in HF reacted violently with a flash with benzene at 195°K.

**Reactivity with Ammonia, Water and Hydrogen**

Liquid dioxygen difluoride reacted vigorously when added to solid anhydrous ammonia at temperatures close to 110°K. It caused explosions when added to ice at 130–140°K and reacted also with traces of water when dissolved in HF containing H₂O at 195°K. The brown color of the solution disappeared and O₂ gas escaped.

In view of the high reactivity of hydrogen atoms at low temperatures, it was considered of interest to study their reaction with O₂F₂. It was hoped that since hydrogen atoms are likely to abstract fluorine, forming HF, intermediate species, either radicals or others, might form under suitable conditions. The H-atom generator used was described elsewhere.

Dioxygen difluoride was condensed in the form of a ring on the walls of a U-tube cooled to 77°K. There was no reaction between O₂F₂ and molecular hydrogen when the gas was pumped through to the U-tube at 77°K, at the rate of 1.25 l/hr. and with P = 1 mm. Atomic hydrogen, however, reacted with O₂F₂ at the same conditions, forming a white solid. Several times during the experiment, the H-atom generator was turned off and the O₂F₂ warmed to its melting point to allow it to separate from the layer of reaction products, which covered the O₂F₂ and prevented further reaction. After about two-thirds of the O₂F₂ was consumed, the generator was turned off, the U-tube warmed to the melting point of O₂F₂ and the excess of O₂F₂ pumped off. Hydrogen fluoride, hydrogen peroxide and water were the reaction products. The amounts of the products indicate that the reaction proceeded in accord with the summary equation

\[
O₂F₂ + 5HF → 2HF + 0.5H₂O₂ + H₂O
\]

(1) Traces of H₂O were also formed. No radical or other intermediate products have been found.

**Reaction with Cl₂, CIF and HCl**

A rapid addition of chlorine to dioxygen difluoride cooled to about 140°K. caused a violent explosion. However, when small portions of Cl₂ were added slowly to O₂F₂ cooled to 130°K., a violet intermediate product did form, together with CIF₂. Here, the first step was most probably the fluorination of Cl₂ to CIF

\[
O₂F₂ + Cl₂ → O₂ + 2ClF
\]

(2) After ClF was formed, it reacted further with O₂F₂ as described below.

The study of the reaction of O₂F₂ with CIF showed that if the reaction is carried out without special precautions at temperatures above 140°K., the two substances react violently with heat evolutions following the equation

\[
O₂F₂ + CIF → O₂ + CIF₃ + 30.1 \text{kcal.}
\]

(3) The CIF abstracts the fluorine from O₂F₂, forming CIF₃ and liberating O₂. Simultaneously, due to the heat of reaction 3, a part of the O₂F₂ decomposes to O₂ and F₂.

\[
O₂F₂ → O₂ + F₂ + 4.75 \text{kcal.}
\]

(4) In the reaction products, fluorine was determined by the Moissan method by absorbing it with mercury in a gas buret. Oxygen was determined by absorption in an alkaline solution of pyrogallol. The volume of chlorine trifluoride was measured as liquid and also as gas after vaporization and the compound identified by the melting and boiling points and by infrared spectrum.

When, however, the reaction between O₂F₂ and CIF was carried out at moderate temperatures (110–130°K.) and with a slow addition of CIF₂, a third reaction took place, forming an intermediate compound of the elementary composition (O₂ClF₃), in accordance with the scheme

\[
O₂F₂ + nCIF → (O₂ClF₃)ₙ
\]

(5) The extent of each of the reactions 3, 4 and 5 depends upon the reaction conditions.

The intermediate compound, dioxygen chlorine trifluoride (referred to simply as O₂CIF₃), has an intense violet color and is a very strong oxidizer. Its properties were described elsewhere.

Since this intermediate product is energy rich, it decomposes rapidly if the reaction proceeds too violently, or even under mild condition, if impurities are present. The product is solid at 195°K. and in the absence of impurities, excepting CIF₃, was kept at this temperature for more than a year without noticeable decomposition.

At first, it was thought that the intense violet color might be due to the formation of ozone mixed with some unreacted O₂F₂

\[
3O₂F₂ + 3CIF → 2O₃ + 3ClF
\]

(6) Although ozone is deep blue and the reaction product violet-blue, ozone and liquid O₂F₂ form a violet-blue solution.

It was found, however, that O₃ does not dissolve in CIF₂ and does not form an addition product with it. In the absence of O₂F₂ and in the presence of CIF₂, ozone, as expected, retains its characteristic deep blue
color. Ozone can be isolated easily from such a mixture either by extraction with liquid O₂, which immediately gives a blue solution, the CIF₃ remaining practically undissolved, or by high-vacuum distillation. At a total pressure of 12 µ and at a temperature of 158⁰K. the violet compound does not distil. Ozone, on the other hand, with a vapor pressure of about 600 mm. at 158⁰K. distils readily.

Following is a typical example of the preparation of the violet product: 1.130 g. of O₂F₂ was distilled under vacuum into a reaction vessel of about 100 cm.³ volume, melted, distributed evenly on the walls of the lower half of the reaction vessel by rotation and frozen at 90⁰K. The stoichiometric amount (1:1 mole) or 0.880 g. of CIF (measured as a gas) was added in portions of about 100 mg. After each addition, the reaction vessel was warmed to 119⁰K. (melting point of CIF) and then slowly to 130⁰K. The violet compound formed rapidly and, simultaneously, white solid CIF also, with some evolution of O₂ and small and varying amounts of F₂. The reaction vessel was then cooled again to 90⁰K., the gases evacuated and collected for analysis, a fresh portion of CIF added and the cycle repeated until all the O₂F₂ was consumed.

Assuming that the heat of formation of O₂CIF₃ is about half—i.e., 15 kcal. per mole—of the total heat of reaction 3, one can readily understand that overheating can lead to the decomposition of the violet compound

\[ \text{O}_2 \text{CIF}_3 \rightarrow \text{O}_2 + \text{CIF}_3 \]  (7)

The relative extents of the reactions 4, 5 and 7 can be determined by analysis of the gases for O₂ and F₂, since only reaction 4 leads to elementary fluorine and reaction 5 proceeds without evolution of O₂ or F₂.

In the example above, only negligible traces of F₂ were found, while the amount of O₂ evolved was 205.8 cm.³ at N.T.P. or 0.294 g. Thus, all the oxygen liberated was due to reaction 7 corresponding to 56.9% by weight of the O₂F₂ used. The remainder, or 43.1% by weight, of O₂F₂ combined, following equation 5, with CIF. Thus, the yield of O₂CIF₃ was 43.1% of theory. After decomposition of O₂CIF₃, the total amount of CIF₃ produced was 1.493 g. as determined by weight. The over-all material balance is given in Table 1.

<table>
<thead>
<tr>
<th>Table I</th>
<th>MATERIAL BALANCE OF THE O₂F₂ + CIF EXPERIMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent used</td>
<td>Products obtained</td>
</tr>
<tr>
<td>O₂F₂</td>
<td>O₂CIF₃</td>
</tr>
<tr>
<td>CIF</td>
<td>O₂</td>
</tr>
<tr>
<td></td>
<td>F₂</td>
</tr>
<tr>
<td></td>
<td>CIF₃</td>
</tr>
<tr>
<td>Total</td>
<td>2.010</td>
</tr>
<tr>
<td></td>
<td>2.010</td>
</tr>
</tbody>
</table>

Much effort was exerted to find the conditions necessary to minimize reactions 3 and 4, i.e., to increase the yield of O₂CIF₃. With C₂F₆ as a diluent, the yield of the violet compound was increased to 81% of theory, but the stability of O₂CIF₃ in the presence of C₂F₆ was found to be low. It was found also that in the presence of traces of water, nitrogen oxides or nitrogen oxyfluorides, the violet compound decomposes quickly or does not form.

If the violet compound, O₂CIF₃, is warmed to about 140⁰K., in the presence of CIF and CIF₃, it changes into a greenish-blue compound (or mixture of compounds), which exists only over a very narrow temperature range. The greenish-blue compound dissolves in CIF at about 125-130⁰K., to form a greenish-blue solution, but the color disappears in about three to five minutes. Probably another blue compound was formed while pumping off the oxygen from a violet solution of O₂CIF₃ in anhydrous HF at 190-195⁰K. The solution changed color and became deep blue like that of ozone. The question might well be raised as to whether in the decomposition of O₂CIF₃ the oxygen is liberated as O₂ or a new type of compound is formed which has a color similar to that of ozone. It is of interest to mention here that more than 3.5 wt.% of ozone dissolves in HF at 195⁰K. at pressures less than one atmosphere to form a solution similar in appearance to the one described above.

Freon 12, CCl₂F₂, Freon 13, CCl₃F, perfluoropropane, CCl₃F, perchloryl fluoride, ClO₂F₂, hydrogen fluoride, HF, and oxygen difluoride, OF₂, were tried as diluents. There was no formation of the violet intermediate product when Freon 12 or OF₂ was used as the solvent for O₂F₂ and cooled CIF gas (diluted by He or O₂) was bubbled through the solutions. With Freon 13 or ClO₂F as the solvent, the violet product formed in small amounts and collected on the bottom of the reaction vessel.

Vacuum distillation, in the presence of these compounds was low and O₂CIF₃ decomposed completely at about 195⁰K. With HF, solutions of about 23% of O₂CIF₃ were obtained. A difficulty arises, however, from the fact that the solution of the violet compound in HF is stable at 190-105⁰K. only under an oxygen pressure of two atmospheres. For this reason, the removal of HF and the isolation of the violet compound are complicated. Attempts to lower the melting point of HF by the addition of KF and thereby to increase the stability of the solutions of the violet compound gave no improvement. On the contrary, in the presence of KF the solutions of the violet compound in HF lost their color much faster than normally, most probably owing to the formation of K(CIF₃).

Dioxygen chloride trifluoride, O₃CIF₃, was formed also in the reaction of OF₂ with HCI at 130-140⁰K. The analysis of the reaction products showed that the reaction proceeds in accordance with the equation

\[ 2\text{O}_2\text{F}_2 + \text{HCl} \rightarrow \text{O}_3\text{CIF}_3 + \text{HF} + \text{O}_2 \]  (8)

As an example, 65.0 mg. of O₂F₂ was treated with 17.0 mg. of HCl. The oxygen evolved was determined by absorption in an alkaline pyrogallol solution. The hydrogen fluoride formed was combined with NaF and determined by titration with 0.1 N NaOH after decomposing the violet compound and distilling off the CIF₃. The additional O₂ evolved upon decomposition of O₂CIF₃ was determined separately. The chlorine trifluoride was measured as a gas and identified by the infrared spectrum. The yield of O₂CIF₃, calculated from the amount of O₂ evolved upon decomposition of the violet compound, was about 41%

The suggested reaction steps are

\[ \text{O}_2\text{F}_2 + 2\text{HCl} \rightarrow 2\text{HF} + \text{O}_2 + \text{Cl}_2 \]  (9)
\[ \text{O}_2\text{F}_2 + \text{Cl}_2 \rightarrow 2\text{CIF} + \text{O}_2 \]  (2)
\[ 2\text{O}_2\text{F}_2 + 2\text{CIF} \rightarrow 2\text{O}_2\text{CIF}_3 \]  (5)
\[ 4\text{O}_2\text{F}_2 + 2\text{HCl} \rightarrow 2\text{O}_2\text{CIF}_3 + 2\text{HF} + 2\text{O}_2 \]  (8)

An excess of HCl and a rise of temperature above 140⁰K. caused fast decomposition of O₂CIF₃. At 130 and 140⁰K., HCl is solid (m.p. 158.9⁰K.) but it has a vapor pressure of about 10 mm. at 140⁰K. Thus, the reaction actually takes place between gaseous HCl and gaseous or liquid O₂F₂. The violet compound partly deposited on the walls, but also dissolved in the liquid O₂F₂. Solutions containing up to 8.5% by weight of O₂CIF₃ in O₂F₂ were obtained.

(17) The concentrations of O₂CIF₃ in solutions were determined by measuring O₂ evolved after the decomposition of O₂CIF₃.

Finally, the violet product formed also when pure liquid CIF₃ in a quartz tube under pressure of ~2 atm. O₂ was irradiated with ultraviolet light at 195°K. However, if the O₂ pressure is only 15 mm. or O₂ is used instead of O₂, the violet product does not form.

No reaction was observed between O₂F₂ and CIF₃ in the solid state at 90°K., or in the liquid state at temperatures up to 190°K.

Reaction with Br₂, Bromine Fluorides and HBr

Liquid O₂F₂, at temperatures close to its melting point (109.7°K.), reacted vigorously when added to solid bromine cooled to 90°K.

When liquid BrF₃ cooled to its melting point (282°K.) was dropped onto solid O₂F₂ cooled to 90°K., a spontaneous reaction occurred with evolution of heat and gas. Analysis of the reaction product showed that the reaction proceeded in accordance with the equation

\[ O₂F₂ + BrF₃ \rightarrow BrF₃ + O₂ + 46.1 \text{ kcal.} \] (10)

The O₂ was identified by the usual method of gas analysis and the bromine pentafluoride by determination of its melting point (= 211.3°K.), boiling point (= 37.7°K.) and density (= 3.09 g./cm.³ at 219°K.).

Under milder conditions, in some experiments a brown-violet intermediate product was obtained. The formation of this product was, however, not always reproducible for unknown reasons. In these experiments, BrF₃ was condensed on the walls of the reaction vessel at 90°K. A thin layer of O₂F₂ was then condensed on the BrF₃. The bath temperature was raised slowly and at about 130°K., the reaction between BrF₃ and O₂F₂ began, forming a violet-brown compound, with some gas evolution. Analysis showed that the gas consisted mainly of oxygen (with a small amount of fluorine) and no brown-violet liquid reaction product was identified as BrF₃. The small amount of F₂ was due to the partial decomposition of O₂F₂. An example of a weight balance of reactants and products is given in Table II.

### Table II

<table>
<thead>
<tr>
<th>MATERIAL BALANCE OF THE Br₂ + O₂F₂ EXPERIMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reacted 884 mg. Br₂F₃ + 432 mg. O₂F₂</td>
</tr>
<tr>
<td>Reaction products obtained</td>
</tr>
<tr>
<td>O₂ evolved during reac.</td>
</tr>
<tr>
<td>27.0 cm.³ or 38.6 mg.</td>
</tr>
<tr>
<td>O₂ evolved upon decomp. of the intermediate colored product</td>
</tr>
<tr>
<td>106.0 cm.³ or 151.5 mg.</td>
</tr>
<tr>
<td>O₂ total</td>
</tr>
<tr>
<td>133.0 cm.³ or 190.1 mg.</td>
</tr>
<tr>
<td>144.6 cm.³ or 206.6 mg.</td>
</tr>
<tr>
<td>BrF₃ total</td>
</tr>
<tr>
<td>0.37 cm.³ at m.p. or 1129.4 mg.</td>
</tr>
<tr>
<td>1143 mg.</td>
</tr>
<tr>
<td>F₂ total</td>
</tr>
<tr>
<td>Traces</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>1338.1 mg.</td>
</tr>
</tbody>
</table>

The violet-brown compound began to decompose at 150°K., and decomposed completely at 170°K. to oxygen and BrF₃.

The formation of the colored intermediate product proceeded analogously to the O₂F₂ + CIF₃ reaction, in accordance with the equation

\[ O₂F₂ + BrF₃ \rightarrow O₂BrF₃ \] (11)

This reaction was always accompanied by some gas evolution due to decomposition of O₂BrF₃ to BrF₃ and O₂ and to partial decomposition of O₂F₂ to O₂ and F₂.

Reaction 11 is more difficult to control than reaction 5.

At approximately the same conditions, dioxygen difluoride reacted with a mixture of Br₂, BrF₃ and BrF₄. Ruff and Menzel¹⁹ and Braida²⁰ reported that upon mixing Br₃ and BrF₄, an intermediate species, BrFe, formed, but pure BrF₄ was not isolated, owing to its dissociation into Br₂ and F₂. Fischer and coworkers²¹-²² found that in the gas phase the reaction

\[ Br₁ + BrF₄ \rightarrow 3BrF \] (12)

took place to varying extents.

In the experiments with O₂F₂, a product obtained by mixing BrF₃ with 10% of Br₂ was used. This product reacted with O₂F₂ between 90° and 130°K., forming a dark-brown (violet shaded) intermediate, which decomposed to BrF₃ and BrF₃ at temperatures above 130°K. If the reaction was carried out at temperatures above 130°K., it proceeded rapidly and directly to BrF₃, BrF₃, and O₂, without forming any colored intermediates.

The colored intermediate products formed with BrF₃, and BrBrFBrFBrF mixture have only a transitory existence and attempts to stabilize them were not successful. Moreover, these reactions are not always reproducible.

The study of the reaction between O₂F₂ and HBr showed that when a small amount of O₂F₂ reacts with an excess of HBr at about 130°K., the reaction proceeds according to the equation

\[ O₂F₂ + 2HBr \rightarrow 2HF + Br₂ + O₂ \] (13)

Dioxygen difluoride was condensed on Rashig rings in the reaction vessel. HBr was added at 90°K., allowed to condense above the O₂F₂ and the vessel was then slowly warmed to 130°K. Dioxygen difluoride melted and its vapor reacted with the excess of HBr, liberating Br₂ and O₂. The free bromine, when warmed to 140°K., reacted with O₂F₂ forming colorless BrF₃. No additional colored products were formed. When, however, the HBr layer was condensed lower and contacted with an excess of liquid O₂F₂ at 130°K., a violet compound similar in appearance to O₂BrF₃ formed. The measurements and the analysis of the reaction products indicated that with an excess of O₂F₂, the reaction most probably proceeds in accordance with the equation

\[ 3O₂F₂ + HBr \rightarrow O₂BrF₃ + HF + O₂ \] (14)

The colored intermediate product decomposed at higher temperatures, forming BrF₃ and liberating gaseous O₂.

Reactivity with I₁ and IF₃

A spontaneous reaction occurred when liquid O₂F₂ cooled to about 110°K. was added rapidly to iodine crystals cooled to 90°K. There was no visible reaction between 8-50% solutions of O₂F₂ in Freon 13 (CCl₂F₃) and iodine at temperatures up to 195°K.

Iodine pentafluoride, IF₃, in contrast to its chlorine and bromine analogs (CIF and BrF₃), did not react with O₂F₂ over the temperature range of 90-195°K. Only a slow decomposition of O₂F₂ to O₂ and F₂ took place. Under more drastic conditions the formation of iodine heptafluoride, IF₇, will probably take place.

Reaction with Phosphorus and PF₃

With red phosphorus, O₂F₂ reacted vigorously when added rapidly at about 110°K.

(20) O. Ruff and A. Braida, ibid., 214, 87 (1938).
(22) J. Fischer, J. Bingle and R. C. Vogel, ibid., 78, 502 (1956).
Phosphorus trifluoride, PF₃, reacted with O₂F₂ at 125°K, forming PF₃F and O₂

$$O_2F_2 + PF_3 \rightarrow PF_3F + O_2$$  (15)

At the same time some of the liberated oxygen reacted with PF₃, forming a white solid which was fairly stable at 0°. This compound was the only solid reaction product; it was not the well known POPF₃, which melts at 233.4°K and boils at 233.8°K, but rather an interesting polymer of POPF₃,

$$nO_2F_2 + 3nPF_3 \rightarrow nPF_4 + 2n(POF)_{3n}$$  (16)

On standing at 0° or at room temperature, the polymer depolymerized completely to POPF₃

$$(POF)_{3n} \rightarrow n(POF)_3$$  (17)

If the amount of PF₃ added in one portion was larger than 50 mg, or if the compounds were warmed quickly, the reaction proceeded with flame.

Reactivity with NO₂F, NF₃ and N₂F₄

Dioxygen difluoride is soluble in nitryl fluoride, NO₂F, at 195°K, forming a very fluid orange solution. A slow decomposition of O₂F₂ takes place at this temperature, but no reaction with NO₂F was observed.

There was no visible reaction between nitrogen trifluoride, NF₃, and O₂F₂ at 130-140°K. Tetrafluorohydrazine, N₂F₄, reacted with O₂F₂ at 170°K, forming NF₃ and O₂, but without the formation of any colored intermediate product.

Our experience with N₂F₄ showed that upon distillation, either in Pyrex glass or in a Kel-F system, the tetrafluorohydrazine itself formed a dark violet compound which looks like the violet compound formed by the reaction between O₂F₂ and CIF. It was made clear however (before using N₂F₄ for the reaction with O₂F₂), that this violet compound is not of the same type as that obtained in the O₂F₂ + CIF reaction. The violet compound formed by N₂F₄ could be distilled, for example, from one vessel into another, together with NO₂F₂ without decomposition, whereas O₂CIF₃ is non-volatile.

According to Johnson and Colburn, condensation of cold gaseous N₂F₄ (~30°) at relatively high pressures gives a water-white liquid. However, if the gas is condensed at elevated temperatures and low pressures, the liquid obtained has a color varying from light blue to blue-black. The color is said to be due to trace amounts of nitrosodifluoramine, NF₂NO₂F₄.

Reactivity with S, SF₃, and H₂S

When added rapidly to sulfur cooled to 90°K, liquid O₂F₂ reacted instantaneously with a flash.

Sulfur tetrafluoride, SF₄, reacted violently with concentrated O₂F₂ at about 130°K, forming SF₅ and O₂

$$O_2F_2 + SF_4 \rightarrow SF_5 + O_2 + 121.5 \text{ kcal}.$$  (18)

The solutions were used, therefore, to prevent too violent reactions. Sulfur tetrafluoride diluted with ClO₂F (2:3 by volume) was distilled into the reaction tube containing frozen O₂F₂ at 98°K. Traces of an intermediate violet-purple compound formed immediately on the walls of the reaction vessel, even at 90°K. Most of the SF₅ and ClO₂F condensed on the walls above the O₂F₂. The tube was then warmed above 125°K. At about 131°K, the SF₅ClO₂F mixture began to melt and flow down to the O₂F₂. More purple-violet compound formed and the reaction went out of control with an explosively violent evolution of gas and heat. The excess of unreacted O₂F₂ remained on the bottom of the shattered reaction tube. The reaction between highly diluted O₂F₂ and SF₄ proceeded without

$$4O_2F_2 + H_2S \rightarrow 2HF + 4O_2F_2 + 432.9 \text{ kcal}.$$  (20)

The formation of all these reaction products was established analytically. It was observed that a very slow reaction starts in the gas phase at 130°K. The vapor pressure of O₂F₂ at this temperature is about 1 mm., and of H₂S about 0.5 mm. When the reaction vessel was further warmed slowly to 195°K, the rate of the reaction increased. In contradistinction to the O₂F₂ + HCl and O₂F₂ + HBr reactions, the O₂F₂ + H₂S reaction gave no colored intermediate compound.

Behavior of O₂F₂ with Some Other Substances

Liquid dioxygen difluoride at temperatures close to its melting point reacted vigorously when added to charcoal cooled to 90°K. It did not appear to react, however, with beryllium powder, quartz fiber and chromium trioxide, even upon warming to room temperature.

Solid SiF₄ (m.p. 183°K) did not react with liquid O₂F₂. Approximately 20% of SiF₄ is soluble in liquid O₂F₂ at 150°K, without noticeable reaction. At about 185°K, O₂F₂ decomposed into O₂ and F₂, while SiF₄ remained unchanged. Similarly, CF₄ did not react with O₂F₂.

In contact with a Pt sheet covered with PtF₄, dioxygen difluoride exploded at 160°K.

Explanatory Remarks

Experiments showed that dioxygen difluoride has a remarkably high oxidizing power. With most of the substances tested, it reacted at cryogenic conditions. The reactions tend naturally to proceed to completion, i.e., to form the most stable reaction products. With CIF, BrF₃ and SF₄, however, as well as with HCl and HBr, highly colored intermediate products were formed when the reactions were carried out with the necessary precautions. Reactions with BrF₃ and HBr were more difficult to control than those with CIF and HCl, and
The Heats of Formation of Compounds Involved and the Heats of Reactions Considered

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH\text{m.} (kcal./mole)</th>
<th>Reference</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂F₂</td>
<td>+4.73 ± 0.3</td>
<td>25</td>
<td>O₂F₂ + CIF ↔ CIF₂ + O₂ + 30.1 kcal.</td>
</tr>
<tr>
<td>CIF</td>
<td>-13.510 ± 0.11</td>
<td>26</td>
<td>CIF₂ + BrF → BrF₂ + + 0.7 kcal.</td>
</tr>
<tr>
<td>BrF</td>
<td>-20</td>
<td>27</td>
<td>2O₂F₂ + BrF → BrF₂ + + 95.7 kcal.</td>
</tr>
<tr>
<td>BrF₂</td>
<td>-64.8</td>
<td>28</td>
<td>O₂F₂ + BrF₂ → BrF₂ + O₂ + + 40.1 kcal.</td>
</tr>
<tr>
<td>BrF₃</td>
<td>-106.2</td>
<td>29</td>
<td>O₂F₂ + SF₃ → SF₄ + O₂ + + 121.5 kcal.</td>
</tr>
<tr>
<td>SF₃</td>
<td>-288.5 ± 0.7</td>
<td>26</td>
<td>4O₂F₂ + H₂S → SF₃ + + 4HF + 4O₂ + + 432.9 kcal.</td>
</tr>
<tr>
<td>H₂S</td>
<td>-4.815</td>
<td>30</td>
<td>3O₂F₂ + HBr → BrF₂ + + HF + O₂ + + 176.9 kcal.</td>
</tr>
<tr>
<td>HBr</td>
<td>-8.66 ± 0.05</td>
<td>26</td>
<td>2O₂F₂ + HCl → CIF₂ + + HF + 2O₂ + + 91.5 kcal.</td>
</tr>
<tr>
<td>HCl</td>
<td>-21.97 ± 0.09</td>
<td>26</td>
<td>2O₂F₂ + BrF₂ → CIF₂ + + BrF₂ + + 0.7 kcal.</td>
</tr>
<tr>
<td>HF</td>
<td>-65.14 ± 0.03</td>
<td>26</td>
<td>CIF₂ + BrF₂ → BrF₂ + O₂ + + 40.1 kcal.</td>
</tr>
</tbody>
</table>

their intermediate product, O₂BrF₄ has only a transient existence. Still more difficult to control were the reactions with SF₃ and H₂S, with the result that in most cases the analogous intermediate, O₂SF₄, did not form. These facts are in agreement with the amounts of energy evolved: the more energy liberated, the more difficult it is to quench the reaction and to freeze and stabilize the intermediate compound.

The heats of formation of the compounds involved and the heats of reactions to be considered are given in Table III.

It can be seen that the reactions of O₂F₂ with CIF and HCl evolve the smallest amounts of energy. In fact, it is much easier to slow down these reactions and obtain the intermediate product O₂CIF₄. More energy is evolved in the reactions with bromine fluorides and HBr and they are more difficult to control. Still higher amounts of energy are liberated in the reactions with sulfur compounds and attempts to obtain the intermediate O₂SF₄ failed in most cases.

Performing these reactions at lower temperatures for longer times may give better results.

In the experiments described in this paper, the reactions were carried out for only a few hours at temperatures up to 130-140°K. Since the ΔH's of most of the expected reactions are high, much could be gained if the reactions were carried out at lower temperatures over periods of days or weeks. A series of such reactions has been started. It is found that O₂F₂ reacts with CIF even at 90°K., although the reaction proceeds very slowly. The formation of the violet compound was noticed only after 3 days. The amount of the colored intermediate product seems to increase with time. A further study of the O₂F₂ + CIF reaction and of the reaction of O₂F₄ with other reactants at 77° and 90°K. for long periods of time is planned.

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The Iodine-catalyzed, Positional Isomerization of Olefins. A New Tool for the Precise Measurement of Thermodynamic Data

By Sidney W. Benson and A. N. Bose

Received December 20, 1962

It is shown that in the temperature range of 200-300°, small amounts of I₂ will bring about relatively rapid positional as well as geometrical isomerization of olefins in a homogeneous gas phase reaction. There is no other chemical reaction in the system. Applied to butene-1 and -2 this permits very precise measurements of the equilibrium constants and hence the free energy differences. For the reactions butene-1 ↔ trans-butene-2 (IV) and cis-butene-2 ↔ trans-butene-2 (V) it is found that at 308°K., ΔH₂ = 3.48 and ΔS₂ = 1.63. The less accurate values estimated from the API tables are ΔH₂ = 4.88 and ΔS₂ = 1.74. Using ΔH₂ values at 300° we calculate ΔH₂ = -3.1 ± 0.2 kcal./mole, ΔS₂ = -3.6 ± 0.4 e.u. These are appreciably different from the API values of -2.7 kcal./mole and -2.2 e.u. It is proposed that the API values of the entropy of butene-1 be raised by 1.4 e.u. The values of ΔH₂ and ΔS₂ are in excellent agreement with API values. It is suggested that the I₂ catalysis in addition to providing a valuable tool for olefin synthesis may also be used to obtain in a relatively simple manner very precise values of the differences in thermodynamic properties of olefins and their parent hydrocarbons.

Introduction

The reaction of organic iodides (RI) with HI goes stoichiometrically to yield RH + I₂ in the temperature range 250-320°. ²

\[ \text{RI} + \text{HI} \rightarrow \text{RH} + \text{I}_2 \] ²

The mechanism of the reaction is atomic, proceeding through an I-atom attack on RI²

\[ \text{I} + \text{RI} \rightarrow \text{R} + \text{I}_2 \] ³

\[ \text{R} + \text{HI} \rightarrow \text{RH} + \text{I} \] ⁴

For the saturated hydrocarbons, step 4 is very slow in the above temperature range so that reaction I goes to essential completion (> 99%). For the unsaturated hydrocarbons with α-H atoms, the allylic resonance interaction reduces the α(C-H) bond energy by

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]