(CH₃)₃Sn : ⁻ 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 $Sn-CH_3$ 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 $Sn-CH_3$ 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)₃SnH 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 substitu-

tion of H for CH₃ in the coupling $Sn-CH_3$ (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 CH₄ or SiH₄,[20] or for the coupling $Sn-CH_3$ upon substitution of Cl for CH₃ in (CH₃)₄Sn.[4] A discussion of possible explanations for these deviations is given by Juan and Gutowsky.[20b]

(20) (a) N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962); (b) *cf.* discussion and references in C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

The Chemical Properties of Dioxygen Difluoride[1]

By A. G. Streng

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 ClF, BrF₃, SF₄, 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,[2a] O₂F₂,[2b] O₃F₂[3] and O₄F₂.[4] It is an orange-yellow solid which melts at 109.7°K. 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°K.

Dioxygen difluoride has been known since 1933, when Ruff and Menzel achieved its preparation.[2b] Since then a number of investigations have been devoted to the methods of preparation of O₂F₂ and to its thermodynamic and physical properties[5–8]; 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.

Reagents Used

Dioxygen difluoride was prepared directly from the elements by the method described elsewhere.[9] It was stored in a Pyrex glass cylinder, frozen at 90°K. Chlorine monofluoride, ClF, nitryl fluoride, NO₂F, phosphorus trifluoride, PF₃, and silicon tetrafluoride, SiF₄, were also prepared by the well known methods.[10–13]

All other reagents were the commercial products of the highest available purity, supplied by Stauffer Chemical Co., General Chemical Division of Allied Chemical Co., Pennsalt Chemicals Corp., E. I. du Pont de Nemours and Co., Matheson Co., Air Reduction Co. and others. Most of these reagents were further purified by fractional distillation.

Experimental Technique

The experiments were carried out either in a closed vacuum system made of Pyrex glass or in one made of Kel-F, fitted with stainless-steel valves and T-pieces. Mercury manometers with a protective layer of Kel-F oil were used for measuring the gas pressure.

The experimental conditions were varied according to the requirements of each combination of reagents. In most cases, O₂F₂ was first frozen on the walls or on the Raschig-ring packing of the reaction vessel. The second reagent was then added in small portions by vacuum distillation and condensed above the O₂F₂. The vessel was then slowly warmed to the temperature of reaction. The solid and liquid products remained in the reaction vessel, and the gaseous products were removed for analysis. The reaction vessel was then cooled again to the original

(1) This paper describes a part of the work sponsored by the Office of Naval Research, under Contract Nonr-3085(01).

(2) (a) P. Lebeau and A. Damiens, *Compt. rend.*, **185**, 652 (1927); (b) O. Ruff and W. Menzel, *Z. anorg. u. allgem. Chem.*, **211**, 204 (1933).

(3) S. Aoyama and S. Sakuraba, *J. Chem. Soc. Japan*, **59**, 1321 (1938).

(4) A. V. Grosse, A. G. Streng and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **83**, 1004 (1961).

(5) O. Ruff and W. Menzel, *Z. anorg. u. allgem. Chem.*, **217**, 85 (1934).

(6) H. J. Schumacher and P. Frisch, *Z. physik. Chem.*, **B37**, 1 (1937).

(7) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

(8) A. D. Kirshenbaum and A. G. Streng, *J. Chem. Phys.*, **35**, 1440 (1961).

(9) A. G. Streng and A. V. Grosse, "Addition and Substitution Compounds of Oxygen Fluorides," Second Annual Progress Report for the Office of Naval Research, Contract Nonr-3085(01), Research Institute of Temple University, Philadelphia 44, Pa., January 19, 1962.

(10) O. Ruff, E. Ascher and F. Laas, *Z. anorg. allgem. Chem.*, **176**, 256 (1928).

(11) Georg Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954.

(12) L. Lebouche, W. Fischer and W. Biltz, *Z. anorg. allgem. Chem.*, **207**, 64 (1932).

(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 O_2F_2 was consumed. The reaction products (gaseous, liquid and solid) were measured and analyzed.

If O_2F_2 was used as liquid, it was condensed in the bottom of the reaction vessel. In some cases reactions were performed with O_2F_2 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 O_2F_2 (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 O_2F_2 and *vice versa* caused explosions.

The Reactivity of O_2F_2 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 O_2F_2 was added to liquid methane, cooled at 90°K., a white flame was produced instantaneously, which turned green upon further burning. When 0.2 cm.^{3} of liquid O_2F_2 was added to 0.5 cm.^{3} of liquid CH_4 at 90°K., a violent explosion occurred.[14]

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 O_2F_2 in HF reacted violently with a flash with benzene at 195°K.[15]

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 H_2O, at 195°K.: the brown color of the solution disappeared and O_2 gas escaped.

In view of the high reactivity of hydrogen atoms at low temperatures, it was considered of interest to study their reaction with O_2F_2. 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.[15]

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 O_2F_2 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 O_2F_2 at the same conditions, forming a white solid. Several times during the experiment, the H-atom generator was turned off and the O_2F_2 warmed to its melting point to allow it to separate from the layer of reaction products, which covered the O_2F_2 and prevented further reaction. After about two-thirds of the O_2F_2 was consumed, the generator was turned off, the U-tube warmed to the

melting point of O_2F_2 and the excess of O_2F_2 pumped off. Hydrogen fluoride, hydrogen peroxide and water were the reaction products. The amounts of the products indicate that the reaction proceeded in accordance with the summary equation

$$O_2F_2 + 5H\cdot \longrightarrow 2HF + 0.5H_2O_2 + H_2O \qquad (1)$$

Traces of H_2O_4 were also formed. No radical or other intermediate products have been found.

### Reaction with Cl_2, ClF and HCl

A rapid addition of chlorine to dioxygen difluoride cooled to about 140°K. caused a violent explosion. However, when small portions of Cl_2 were added slowly to O_2F_2 cooled to 130°K., a violet intermediate product did form, together with ClF_3.[16] Here, the first step was most probably the fluorination of Cl_2 to ClF

$$O_2F_2 + Cl_2 \longrightarrow O_2 + 2ClF \qquad (2)$$

After ClF was formed, it reacted further with O_2F_2, as described below.

The study of the reaction of O_2F_2 with ClF 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

$$O_2F_2 + ClF \longrightarrow O_2 + ClF_3 + 30.1 \text{ kcal.} \qquad (3)$$
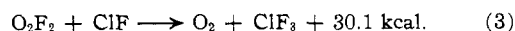
The ClF abstracts the fluorine from O_2F_2, forming ClF_3 and liberating O_2. Simultaneously, due to the heat of reaction 3, a part of the O_2F_2 decomposes to O_2 and F_2.

$$O_2F_2 \longrightarrow O_2 + F_2 + 4.73 \text{ kcal.} \qquad (4)$$
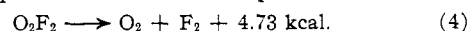
In the reaction products, fluorine was determined by the Moissan method by absorbing it with mercury in a gas buret. Oxygen was determined by absorption in an alkaline solution of pyrogallol. The volume of chlorine trifluoride was measured as liquid and also as gas after vaporization and the compound identified by the melting and boiling points and by infrared spectrum.

When, however, the reaction between O_2F_2 and ClF was carried out at moderate temperatures (119–130°K.) and with a slow addition of ClF, a third reaction took place, *forming an intermediate compound of the elementary composition* $(O_2ClF_3)_n$ in accordance with the scheme

$$nO_2F_2 + nClF \longrightarrow (O_2ClF_3)_n \qquad (5)$$
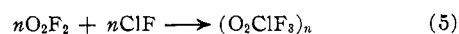
The extent of each of the reactions 3, 4 and 5 depends upon the reaction conditions.

The intermediate compound, dioxygen chlorine trifluoride (referred to simply as O_2ClF_3), has an intense violet color and is a very strong oxidizer. Its properties were described elsewhere.[16]

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 ClF_3, 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 O_2F_2

$$3O_2F_2 + 3ClF \longrightarrow 2O_3 + 3ClF_3 \qquad (6)$$
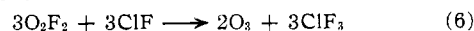
Although ozone is deep blue and the reaction product violet-blue, ozone and liquid O_2F_2 form a violet-blue solution.

It was found, however, that O_3 does not dissolve in ClF_3 and does not form an addition product with it. In the absence of O_2F_2 and in the presence of ClF_3, ozone, as expected, retains its characteristic deep blue

(14) A. D. Kirshenbaum, J. G. Aston and A. V. Grosse, Final Report, Contract No. DA-36-034-ORD-2250, Research Institute of Temple University, Philadelphia 44, Pa., November 18, 1958.

(15) A. G. Streng and A. V. Grosse, "Addition and Substitution Compounds of Oxygen Fluorides," First Annual Progress Report for the Office of Naval Research, Contract Nonr-3085(01), Research Institute of Temple University, Philadelphia, Pa., January 3, 1961.

(16) A. G. Streng and A. V. Grosse, *Adv. in Chem. Series*, **36**, 159 (1962).

color. Ozone can be isolated easily from such a mixture either by extraction with liquid O_2, which immediately gives a blue solution, the ClF_3 remaining practically undissolved, or by high-vacuum distillation. At a total pressure of 12 μ and at a temperature of 158°K. *the violet compound does not distil.* Ozone, on the other hand, with a vapor pressure of about 600 mm. at 158°K. distils readily.

Following is a typical example of the preparation of the violet product: 1.130 g. of O_2F_2 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 90°K. The stoichiometric amount (1:1 mole) or 0.880 g. of ClF (measured as a gas) was added in portions of about 100 mg. After each addition, the reaction vessel was warmed to 119°K. (melting point of ClF) and then slowly to 130°K. The violet compound formed rapidly and, simultaneously, white solid ClF_3 also, with some evolution of O_2 and small and varying amounts of F_2. The reaction vessel was then cooled again to 90°K., the gases evacuated and collected for analysis, a fresh portion of ClF added and the cycle repeated until all the O_2F_2 was consumed.

Assuming that the heat of formation of O_2ClF_3 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

$$O_2ClF_3 \longrightarrow O_2 + ClF_3 \qquad (7)$$
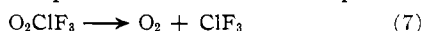
The relative extents of the reactions 4, 5 and 7 can be determined by analysis of the gases for O_2 and F_2, since only reaction 4 leads to elementary fluorine and reaction 5 proceeds without evolution of O_2 or F_2.

In the example above, only negligible traces of F_2 were found, while the amount of O_2 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 O_2F_2 used. The remainder, or 43.1% by weight, of O_2F_2 combined, following equation 5, with ClF. Thus, the yield of O_2ClF_3 was 43.1% of theory. After decomposition of O_2ClF_3, the total amount of ClF_3 produced was 1.493 g. as determined by weight. The over-all material balance is given in Table I.

TABLE I

MATERIAL BALANCE OF THE O_2F_2 + ClF EXPERIMENT

| Reagent used, g.		Products obtained, g.	
O_2F_2	1.130	O_2ClF_3	0.869
ClF	0.880	O_2	.294
		F_2	.000
		ClF_3	.847
Total	2.010		2.010

Much effort was exerted to find the conditions necessary to minimize reactions 3 and 4, *i.e.*, to increase the yield of O_2ClF_3. With C_3F_8 as a diluent, the yield of the violet compound was increased to 81% of theory, but the stability of O_2ClF_3 in the presence of C_3F_8 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, O_2ClF_3, is warmed to about 140°K. in the presence of ClF and ClF_3, 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 ClF at about 125–130°K., 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 O_2ClF_3 in an-

hydrous HF at 190–195°K. 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 O_2ClF_3 the oxygen is liberated as O_3 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 195°K. at pressures less than one atmosphere to form a solution similar in appearance to the one described above.
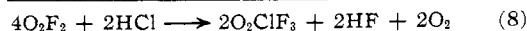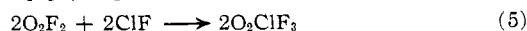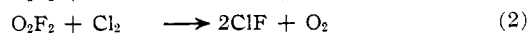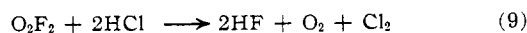
Freon 12, CCl_2F_2, Freon 13, $CClF_3$, perfluoropropane, C_3F_8, perchloryl fluoride, ClO_3F, hydrogen fluoride, HF, and oxygen difluoride, OF_2, were tried as diluents. There was no formation of the violet intermediate product when Freon 12 or OF_2 was used as the solvent for O_2F_2 and cooled ClF gas (diluted by He or O_2) was bubbled through the solutions. With Freon 13 or ClO_3F as the solvent, the violet product formed in small amounts and collected on the bottom of the reaction vessel. Its stability, however, in the presence of these compounds was low and O_2ClF_3 decomposed completely at about 195°K. With HF, solutions of about 23% of O_2ClF_3 were obtained.[17] A difficulty arises, however, from the fact that the solution of the violet compound in HF is stable at 190–195°K. 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[18] 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 $K(ClF_4)$.

Dioxygen chlorine trifluoride, O_2ClF_3, was formed also in the reaction of O_2F_2 with HCl at 130–140°K. The analysis of the reaction products showed that the reaction proceeds in accordance with the equation

$$2O_2F_2 + HCl \longrightarrow O_2ClF_3 + HF + O_2 \qquad (8)$$
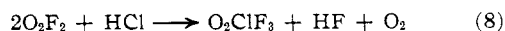
As an example, 65.0 mg. of O_2F_2 was treated with 17.0 mg. of HCl. The oxygen evolved was determined by absorption in an alkaline pyrogallol solution. The hydrogen fluoride formed was combined with NaF and determined by titration with 0.1 N NaOH after decomposing the violet compound and distilling off the ClF_3. The additional O_2 evolved upon decomposition of O_2ClF_3 was determined separately. The chlorine trifluoride was measured as a gas and identified by the infrared spectrum. The yield of O_2ClF_3, calculated from the amount of O_2 evolved upon decomposition of the violet compound, was about 41%.

The suggested reaction steps are

$$O_2F_2 + 2HCl \longrightarrow 2HF + O_2 + Cl_2 \qquad (9)$$
$$O_2F_2 + Cl_2 \longrightarrow 2ClF + O_2 \qquad (2)$$
$$2O_2F_2 + 2ClF \longrightarrow 2O_2ClF_3 \qquad (5)$$
$$\overline{4O_2F_2 + 2HCl \longrightarrow 2O_2ClF_3 + 2HF + 2O_2} \qquad (8)$$

An excess of HCl and a rise of temperature above 140°K. caused fast decomposition of O_2ClF_3.

At 130 and 140°K., HCl is solid (m.p. 158.9°K.) but it has a vapor pressure of about 10 mm. at 140°K. Thus, the reaction actually takes place between gaseous HCl and gaseous or liquid O_2F_2. The violet compound partly deposited on the walls, but also dissolved in the liquid O_2F_2. Solutions containing up to 8.5% by weight of O_2ClF_3 in O_2F_2 were obtained.

(17) The concentrations of O_2ClF_3 in solutions were determined by measuring O_2 evolved after the decomposition of O_2ClF_3.

(18) G. H. Cady, *J. Am. Chem. Soc.*, **56**, 1431 (1934).

Finally, the violet product formed also when pure liquid ClF_3 in a quartz tube under pressure of ~2 atm. O_2 was irradiated with ultraviolet light at 195°K. However, if the O_2 pressure is only 15 mm. or O_3 is used instead of O_2, the violet product does not form.

No reaction was observed between O_2F_2 and ClF_3 in the solid state at 90°K., or in the liquid state at temperatures up to 190°K.

Reaction with Br_2, Bromine Fluorides and HBr

Liquid O_2F_2, at temperatures close to its melting point (109.7°K.), reacted vigorously when added to solid bromine cooled to 90°K.

When liquid BrF_3 cooled to its melting point (282°K.) was dropped onto solid O_2F_2 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

$$O_2F_2 + BrF_3 \longrightarrow BrF_5 + O_2 + 46.1 \text{ kcal.} \quad (10)$$
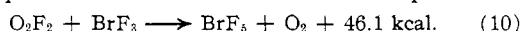
The O_2 was identified by the usual method of gas analysis and the bromine pentafluoride by determination of its melting point (= 211.9°K.), boiling point (= 313.7°K.) and density (= 3.09 g./cm.³ at 212°K.).

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, BrF_3 was condensed on the walls of the reaction vessel at 90°K. A thin layer of O_2F_2 was then condensed on the BrF_3. The bath temperature was raised slowly and at about 130°K. the reaction between BrF_3 and O_2F_2 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). The colorless liquid reaction product was identified as BrF_5. The small amount of F_2 was due to the partial decomposition of O_2F_2. An example of a weight balance of reactants and products is given in Table II.

TABLE II

MATERIAL BALANCE OF THE BF_3 + O_2F_2 EXPERIMENT

Reacted 884 mg. BrF_3 + 452 mg. O_2F_2

Reaction products obtained	Reaction products expected
O_2 evolved during reacn.	
27.0 cm.³ or 38.6 mg.	...
O_2 evolved upon decompn. of the intermediate colored product	
106.0 cm.³ or 151.5 mg.	...
O_2 total	
133.0 cm.³ or 190.1 mg.	144.6 cm.³ or 206.6 mg.
BrF_5 total	
0.37 cm.³ at m.p. or 1143 mg.	1129.4 mg.
F_2 total	
Traces	...
Total	
1333.1 mg.	1336.0 mg.

The violet-brown compound began to decompose at 150°K. and decomposed completely at 170°K. to oxygen and BrF_5.

The formation of the colored intermediate product proceeded analogously to the O_2F_2 + ClF reaction, in accordance with the equation

$$O_2F_2 + BrF_3 \longrightarrow O_2BrF_5 \quad (11)$$
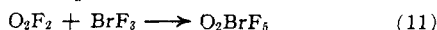
This reaction was always accompanied by some gas evolution due to decomposition of O_2BrF_5 to BrF_5 and O_2 and to partial decomposition of O_2F_2 to O_2 and F_2.

Reaction 11 is more difficult to control than reaction 5.

At approximately the same conditions, dioxygen difluoride reacted with a mixture of Br_2, BrF and BrF_3. Ruff and Menzel[19] and Braida[20] reported that upon mixing Br_2 and BrF_3, an intermediate species, BrF, formed, but pure BrF was not isolated, owing to its dissociation into Br_2 and BrF_3. Fischer and co-workers[21-23] found that in the gas phase the reaction

$$Br_2 + BrF_3 \longrightarrow 3BrF \quad (12)$$
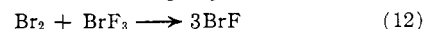
took place to varying extents.

In the experiments with O_2F_2, a product obtained by mixing BrF_3 with 10% of Br_2 was used. This product reacted with O_2F_2 between 90° and 130°K., forming a dark-brown (violet shaded) intermediate, which decomposed to BrF_3 and BrF_5 at temperatures above 130°K. If the reaction was carried out at temperatures above 130°K., it proceeded rapidly and directly to BrF_3, BrF_5 and O_2, without forming any colored intermediates.

The colored intermediate products formed with BrF_3 and Br_2–BrF–BrF_3 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 O_2F_2 and HBr showed that when a small amount of O_2F_2 reacts with an excess of HBr at about 130°K. the reaction proceeds according to the equation

$$O_2F_2 + 2HBr \longrightarrow 2HF + Br_2 + O_2 \quad (13)$$
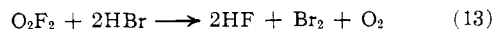
Dioxygen difluoride was condensed on Rashig rings in the reaction vessel. HBr was added at 90°K., allowed to condense above the O_2F_2 and the vessel was then slowly warmed to 130°K. Dioxygen difluoride melted and its vapor reacted with the excess of HBr, liberating Br_2 and O_2. The free bromine, when warmed to 140°K., reacted with O_2F_2 forming colorless BrF_5. No additional colored products were formed. When, however, the HBr layer was condensed lower and contacted with an excess of liquid O_2F_2 at 130°K., a violet compound similar in appearance to O_2BrF_5, formed. The measurements and the analysis of the reaction products indicated that with an excess of O_2F_2 the reaction most probably proceeds in accordance with the equation

$$3O_2F_2 + HBr \longrightarrow O_2BrF_5 + HF + O_2 \quad (14)$$
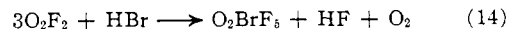
The colored intermediate product decomposed at higher temperatures, forming BrF_5 and liberating gaseous O_2.

Reactivity with I_2 and IF_5

A spontaneous reaction occurred when liquid O_2F_2 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 O_2F_2 in Freon 13 ($CClF_3$) and iodine at temperatures up to 195°K.

Iodine pentafluoride, IF_5, in contrast to its chlorine and bromine analogs (ClF and BrF_3), did not react with O_2F_2 over the temperature range of 90–195°K. Only a slow decomposition of O_2F_2 to O_2 and F_2 took place. Under more drastic conditions the formation of iodine heptafluoride, IF_7, will probably take place.

Reaction with Phosphorus and PF_3

With red phosphorus, O_2F_2 reacted vigorously when added rapidly at about 110°K.

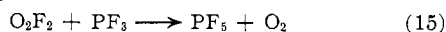(19) O. Ruff and W. Menzel, Z. anorg. allgem. Chem., **202**, 60 (1931).

(20) O. Ruff and A. Braida, ibid., **214**, 87 (1933).

(21) J. Fischer, R. D. Stennenberg and R. C. Vogel, J. Am. Chem. Soc., **76**, 1497 (1954).

(22) J. Fischer, J. Bingle and R. C. Vogel, ibid., **78**, 902 (1956).

(23) R. D. Stennenberg, R. C. Vogel and J. Fischer, ibid., **79**, 1320 (1957).

Phosphorus trifluoride, PF_3, reacted with O_2F_2 at 125°K. forming PF_5 and O_2

$$O_2F_2 + PF_3 \longrightarrow PF_5 + O_2 \qquad (15)$$

At the same time some of the liberated oxygen reacted with PF_3, forming a white solid which was fairly stable at 0°. This compound was the only solid reaction product; it was *not* the well known POF_3, which melts at 233.4°K. and boils at 233.8°K., but rather an interesting polymer of POF_3

$$nO_2F_2 + 3nPF_3 \longrightarrow nPF_5 + 2(POF_3)_n \qquad (16)$$

On standing at 0° or at room temperature, the polymer depolymerized completely to POF_3

$$(POF_3)_n \longrightarrow n(POF_3). \qquad (17)$$
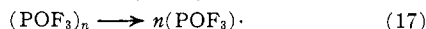
If the amount of PF_3 added in one portion was larger than 50 mg. or if the compounds were warmed quickly, the reaction proceeded with flame.

Reactivity with NO_2F, NF_3 and N_2F_4

Dioxygen difluoride is soluble in nitryl fluoride, NO_2F, at 195°K., forming a very fluid orange solution. A slow decomposition of O_2F_2 takes place at this temperature, but no reaction with NO_2F was observed.

There was no visible reaction between nitrogen trifluoride, NF_3, and O_2F_2 at 130–140°K. Tetrafluorohydrazine, N_2F_4, reacted with O_2F_2 at 170°K., forming NF_3 and O_2, but without the formation of any colored intermediate product.

Our experience with N_2F_4 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 O_2F_2 and ClF. It was made clear however (before using N_2F_4 for the reaction with O_2F_2), that this violet compound is not of the same type as that obtained in the O_2F_2 + ClF reaction. The violet compound formed by N_2F_4 could be distilled, for example, from one vessel into another, together with N_2F_4 without decomposition, whereas O_2ClF_3 is non-volatile.

According to Johnson and Colburn,[24] condensation of cold gaseous N_2F_4 (−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, NF_2NO.[24a]

Reaction with S, SF_4 and H_2S

When added rapidly to sulfur cooled to 90°K., liquid O_2F_2 reacted instantaneously with a flash.

Sulfur tetrafluoride, SF_4, reacted violently with concentrated O_2F_2 at about 130°K., forming SF_6 and O_2

$$O_2F_2 + SF_4 \longrightarrow SF_6 + O_2 + 121.5 \text{ kcal.} \qquad (18)$$
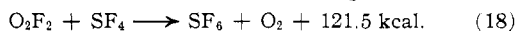
The solutions were used, therefore, to prevent too violent reactions. Sulfur tetrafluoride diluted with ClO_3F (2:3 by volume) was distilled into the reaction tube containing frozen O_2F_2 at 90°K. Traces of an intermediate violet-purple compound formed immediately on the walls of the reaction vessel, even at 90°K. Most of the SF_4 and ClO_3F condensed on the walls above the O_2F_2. The tube was then warmed above 125°K. At about 130°K. the SF_4–ClO_3F mixture began to melt and flow down to the O_2F_2. 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 O_2F_2 remained on the bottom of the shattered reaction tube. The reaction between highly diluted O_2F_2 and SF_4 proceeds without

(24) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

(24a) C. B. Colburn and F. A. Johnson, *Inorg. Chem.*, 1715 (1962).

violence, but the intermediate colored product either forms in very small amounts or does not form at all.

A 12.8% by weight O_2F_2 solution was used, for example. It was frozen at 90°K. and a gaseous SF_4–ClO_3F mixture (1:1) was added in small portions, each containing 20–100 mg. of SF_4. After the addition of each portion, the reaction vessel was warmed to 130°K. Only traces of violet compound formed, which deposited on the walls of the reaction vessel above the O_2F_2–ClO_3F mixture. The formation of the violet compound took place only at temperatures of 90–116°K. At 130°K. a slow visible reaction between O_2F_2 and SF_4 began, with evolution of O_2 gas and formation of SF_6. Further warming to 150–170°K. increased the reaction rate and caused decomposition of the colored compound. Also, decomposition of O_2F_2 to O_2 and F_2 was noted.

The use of a smaller amount of diluent gave a larger quantity of the colored intermediate product, but it could not be preserved. The formation of the colored intermediate product probably proceeds similarly to the formation of the colored products in the O_2F_2 + ClF and O_2F_2 + BrF_3 reactions

$$O_2F_2 + SF_4 \longrightarrow O_2SF_6 \qquad (19)$$

This reaction is even more difficult to control than reaction 11. In most cases it proceeds directly to the formation of SF_6 and O_2 in line with eq. 18 and leads to an explosion. With perchloryl fluoride, ClO_3F, as a solvent, explosions could be avoided in some cases (at temperatures below 116°K.), but the yield and the stability of the intermediate product were very low.

With H_2S, dioxygen difluoride reacted in accord with the equation

$$4O_2F_2 + H_2S \longrightarrow 2HF + 4O_2 + SF_6 + 432.9 \text{ kcal.} \qquad (20)$$
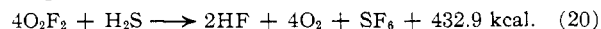
The formation of all these reaction products was established analytically. It was observed that a very slow reaction starts in the gas phase at 130°K. The vapor pressure of O_2F_2 at this temperature is about 1 mm., and of H_2S about 0.5 mm. When the reaction vessel was further warmed slowly to 195°K., the rate of the reaction increased. In contradistinction to the O_2F_2 + HCl and O_2F_2 + HBr reactions, the O_2F_2 + H_2S reaction gave no colored intermediate compound.

Behavior of O_2F_2 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 SiF_4 (m.p. 183°K.) did not react with liquid O_2F_2. Approximately 20% of SiF_4 is soluble in liquid O_2F_2 at 150°K. without noticeable reaction. At about 195°K., O_2F_2 decomposed into O_2 and F_2, while SiF_4 remained unchanged. Similarly, CF_4 did not react with O_2F_2.

In contact with a Pt sheet covered with PtF_4, 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 ClF, BrF_3 and SF_4, 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 BrF_3 and HBr were more difficult to control than those with ClF and HCl, and

TABLE III

THE HEATS OF FORMATION OF COMPOUNDS INVOLVED AND THE HEATS OF REACTIONS CONSIDERED

Compound	ΔH_{298}, kcal./mole	Reference	Reaction
O_2F_2	$+4.73 \pm 0.3$	25	$O_2F_2 + ClF \rightarrow ClF_3 + O_2 + 30.1$ kcal.
ClF	-13.510 ± 0.11	26	
ClF_3	-38.869 ± 1.0	26	
BrF	-20	27	$2O_2F_2 + BrF \rightarrow BrF_5 + 2O_2 + 95.7$ kcal.
BrF_3	-64.8	28	$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2 + 46.1$ kcal.
BrF_5	-106.2	28	
SF_4	$-171.7 + 2.5$	29	$O_2F_2 + SF_4 \rightarrow SF_6 + O_2 + 121.5$ kcal.
SF_6	-288.5 ± 0.7	26	
H_2S	-4.815	26	$4O_2F_2 + H_2S \rightarrow SF_6 + 2HF + 4O_2 + 432.9$ kcal.
HBr	-8.66 ± 0.05	26	$3O_2F_2 + HBr \rightarrow BrF_5 + HF + 3O_2 + 176.9$ kcal.
HCl	-21.97 ± 0.09	26	$2O_2F_2 + HCl \rightarrow ClF_3 + HF + 2O_2 + 91.5$ kcal.
HF	-65.14 ± 0.03	26	

their intermediate product, O_2BrF_5, has only a transitory existence. Still more difficult to control were the reactions with SF_4 and H_2S, with the result that in most cases the analogous intermediate, O_2SF_6, did not form. These facts are in agreement with the amounts of energy

(25) A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, J. Am. Chem. Soc., 81, 6398 (1959).

(26) JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., 1960.

(27) H. Brodersen and H. J. Schumacher, Z. Naturforschung, 2a, 358 (1947).

(28) L. Stein, J. Phys. Chem., 66, 288 (1962).

(29) DuPont's Information Bulletin: "Sulfur Tetrafluoride Technical."

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 O_2F_2 with ClF and HCl evolve the smallest amounts of energy. In fact, it is much easier to slow down these reactions and obtain the intermediate product O_2ClF_3. 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 O_2SF_6 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 O_2F_2 reacts with ClF 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 O_2F_2 + ClF reaction and of the reaction of O_2F_2 with other reactants at 77° and 90°K. for long periods of time is planned.

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

The Iodine-catalyzed, Positional Isomerization of Olefins. A New Tool for the Precise Measurement of Thermodynamic Data[1]

BY SIDNEY W. BENSON AND A. N. BOSE

It is shown that in the temperature range of 200–300°, small amounts of I_2 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 $\rightleftharpoons$ trans-butene-2 (IV) and cis-butene-2 $\rightleftharpoons$ trans-butene-2 (V) it is found that at 508°K., $K_{IV} = 3.48$ and $K_V = 1.63$. The less accurate values estimated from the API tables are $K_{IV} = 4.58$ and $K_V = 1.74$. Using K_{IV} values at 300° we calculate $\Delta H_{IV} = -3.1 \pm 0.2$ kcal./mole, $\Delta S_{IV} = -3.6 \pm 0.4$ 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 ΔH_V and ΔS_V are in excellent agreement with API values. It is suggested that the I_2 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. The application to keto–enol equilibria and other unsaturates may also be possible.
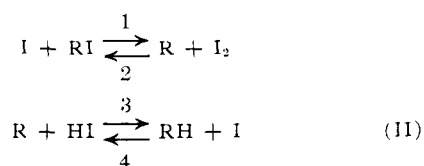
Introduction

The reaction of organic iodides (RI) with HI goes stoichiometrically to yield $RH + I_2$ in the temperature range 250–320°.[2a,b]

$$RI + HI \rightleftharpoons RH + I_2 \qquad (I)$$
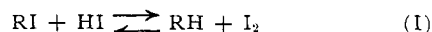
The mechanism of the reaction is atomic, proceeding through an I-atom attack on RI[2]

(2) (a) R. A. Ogg, J. Am. Chem. Soc., 56, 526 (1934); (b) S. W. Benson and H. E. O'Neal, J. Chem. Phys., 34, 514 (1961).

$$I + RI \overset{1}{\underset{2}{\rightleftharpoons}} R + I_2$$

$$R + HI \overset{3}{\underset{4}{\rightleftharpoons}} RH + I \qquad (II)$$

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