

An Electron Paramagnetic Resonance Study of Oxygen Fluorides. I. Dioxygen Difluoride and Trioxxygen Difluoride

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Electron paramagnetic resonance studies of O_2F_2 and O_3F_2 were performed. Both O_2F_2 and O_3F_2 showed identical e.p.r. spectra which could be attributed to the free radical $F-O-O\cdot$, the concentrations being 0.1 and 5 mole %, respectively. In either system the radical is formed as the result of the respective decomposition process.

Introduction

The oxygen fluorides are an interesting family of compounds. Its four known members, oxygen difluoride (OF_2), dioxygen difluoride (O_2F_2), trioxxygen difluoride or ozone fluoride (O_3F_2), and tetraoxygen difluoride (O_4F_2), are all endothermic compounds with strong oxidizing power. Except for OF_2 and O_2F_2 , very little is known about their molecular structures.^{2a} Electron paramagnetic resonance (e.p.r.) studies on these compounds have been reported by Maguire,^{2b} who stated that O_3F_2 is paramagnetic while O_2F_2 is not. The more extensive e.p.r. study reported here was undertaken in order to gain more information on the structures and the mechanisms of decomposition.³ All the microwave measurements were made at liquid nitrogen temperature, at X-band (9.1 kMc./sec.) or K-band (35.2 kMc./sec.) frequency. The O_2F_2 and O_3F_2 used were prepared in our laboratory by the electric discharge method reported previously.⁴⁻⁶

Results

A. Dioxygen Difluoride, O_2F_2 . Pure O_2F_2 as well as 3 vol. % solutions of O_2F_2 in the diamagnetic solvent $CClF_3$ (Freon 13) were used. In either case, a strong, well-resolved signal was observed near $g = 2.0$. Subjecting the pure sample to 195°K. for various lengths of time (10 min. to 4 hr.) resulted initially in the increase of signal and eventually in the decrease of signal. At any stage, if the sample was quenched back to 77°K. and kept at this temperature, no further change in its intensity was observed. The signal, therefore, is not due to O_2F_2 itself nor to its final decomposition product, O_2 and F_2 , but is most likely due to intermediate radicals

formed in the sequence of decomposition. Depending upon the thermal treatment of the O_2F_2 , the amount of the paramagnetic species observed amounted to 0.05 to 0.5 mole % of the original sample.

The entire powder-pattern spectra at X-band frequency (Figure 1) are consistent with the spin-Hamiltonian

$$\mathcal{H} = g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y) + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

with $S = 1/2$, $I = 1/2$, $g_{\parallel} = 2.0074$, $g_{\perp} = 2.0005$, $A_{\parallel} = 100 \pm 1$ gauss, and $A_{\perp} = 25 \pm 2$ gauss. This implies an unpaired electron experiencing a hyperfine interaction with only one fluorine nucleus. The K-band e.p.r. spectrum of pure O_2F_2 (Figure 2) is also consistent with the Hamiltonian (1), which gives as the positions of the two hyperfine components

$$H = \frac{H_{\parallel}}{\sqrt{1 - \alpha \sin^2 \theta}} \pm \frac{1}{2}A_{\parallel} \frac{\sqrt{1 - \beta \sin^2 \theta}}{1 - \alpha \sin^2 \theta} \quad (2)$$

where

$$H_{\parallel} = \frac{h\nu}{g_{\parallel}\beta}$$
$$\alpha = 1 - \left(\frac{g_{\perp}}{g_{\parallel}}\right)^2 \quad \beta = 1 - \left(\frac{A_{\perp}g_{\perp}}{A_{\parallel}g_{\parallel}}\right)^2$$

and θ is the angle between the applied magnetic field and the axis of symmetry. The angular dependencies of the two lines are shown in Figure 3 along with expected over-all absorption curves, as given by $|d\theta/dH| \sin \theta$ and their derivative patterns. The agreement of the latter with the experimentally observed derivatives is excellent, substantiating our assignment. The weak signals near "X" at $g = 2.003$ in Figures 1 and 3 are surely due to a second, otherwise unidentified free radical; their intensity varied from sample to sample independently of the rest of the pattern.

Another weak signal was observed at half magnetic field strength, implying the possible existence of a species in the triplet state. The intensity of this signal remained unchanged when the main signal near $g = 2.0$ increased after a heat treatment, thus showing that its origin is independent of the species giving the main signal at $g \cong 2.0$.

B. Ozone Fluoride, O_3F_2 . Pure O_3F_2 was found to be too strongly paramagnetic to obtain a resolved e.p.r. spectrum. When dilute solutions (0.2–0.4 vol. %) of O_3F_2 in diamagnetic $CClF_3$ (Freon 13) were used, the e.p.r. spectra obtained were identical, except for increased line width, with those observed with O_2F_2 , as can be seen in Figure 1. The concentration of the free radical in pure O_3F_2 is estimated to be 5–10 mole

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(2) (a) A. G. Streng, *Chem. Rev.*, **63**, 607 (1963); (b) R. M. Maguire, "Determination of the Structure of O_3F_2 ," ARL Technical Report 60-287, Armour Research Foundation, May 1960.

(3) A. D. Kirshenbaum and A. V. Grosse, "First Annual Summary Report on Production, Isolation and Identification of the $FO\cdot$, $FO_2\cdot$ and $FO_3\cdot$ Radicals," Research Institute of Temple University, Contract AF 04(611)-9555, Oct. 1964.

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

(5) A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, *ibid.*, **81**, 6398 (1959).

(6) A. V. Grosse, A. G. Streng, and A. D. Kirshenbaum, *ibid.*, **83**, 1004 (1961).

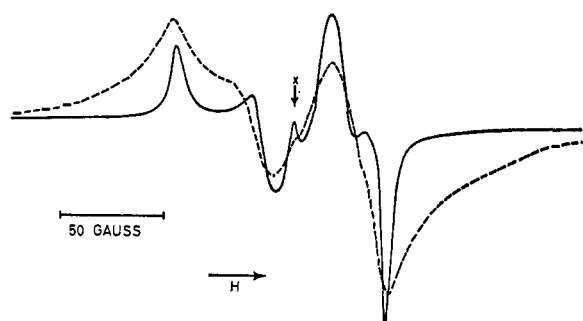


Figure 1. E.p.r. spectra of O_2F_2 (pure, solid line) and O_3F_2 (0.2 vol. % solution in $CClF_3$, dotted line) at 9.10 kMc./sec. The arrow X indicates the position corresponding to $g = 2.003$.

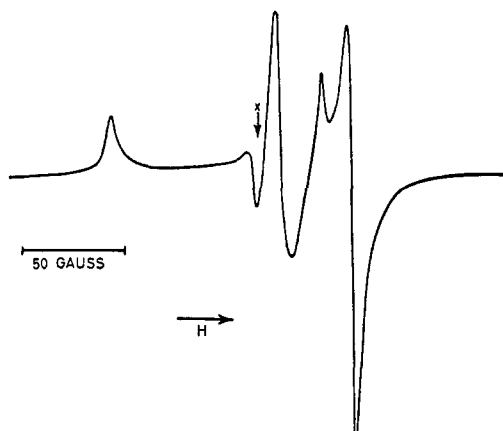
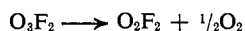


Figure 2. E.p.r. spectrum of O_2F_2 at 35.2 kMc./sec. The arrow X indicates the position corresponding to $g = 2.003$.

$\%$, *i.e.*, 50 to 100 times as great as the radical concentration in pure O_2F_2 .

Since the same signal was obtained from both O_2F_2 and O_3F_2 , the question was raised^{2b} as to whether the O_2F_2 samples were contaminated with small amounts of O_3F_2 . It is known⁴ that O_3F_2 decomposes at 115°K. as



Some of the O_2F_2 samples were therefore kept for several hours at 195°K., and their e.p.r. spectra were re-examined. If the O_2F_2 signal were due to O_3F_2 as a contaminant, it would have decreased in intensity. Instead, it increased. Thus, the possibility that the presence of O_3F_2 as an impurity could have been responsible for the e.p.r. spectrum of O_2F_2 has been ruled out.

Pure O_3F_2 also showed a broad resonance ($\Delta H_{\text{peak-to-peak}} = 60$ gauss) at half-field, indicating a species in the triplet state. This signal was twice as strong as that observed with pure O_2F_2 but was also found to be independent of the signal in the $g = 2.00$ region.

Discussion

According to Jackson's microwave study,⁷ gaseous O_2F_2 has an H_2O_2 type of structure with a particularly short O-O distance (1.217 Å.) and a rather long O-F distance (1.575 Å.). In fact, the O-O distance in O_2F_2 is practically equal to the distance in the O_2 molecule

(7) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

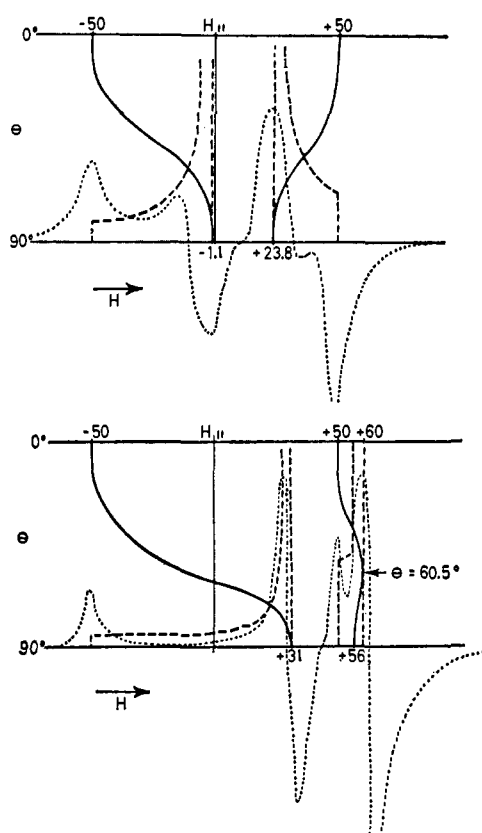
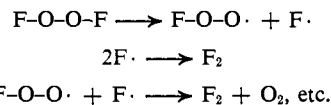
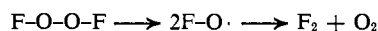


Figure 3. The angular dependencies of the two hyperfine components (solid lines), the expected shapes of the absorption curves (broken lines), and their derivative patterns (dotted lines). The upper figure is for the microwave frequency $\nu = 9.1$ kMc./sec. or $H_{\parallel} = 3250$ gauss and the lower figure is for $\nu = 35.2$ kMc./sec. of $H_{\parallel} = 12,500$ gauss. The positions of the peaks expected in the derivative patterns are given relative to that of H_{\parallel} .

(1.21 Å.).⁸ From the heat of formation data, it has been shown⁵ that the energy required to split the O-F bond (45.7 kcal.) is much less than the 62.1 kcal. required to split the O-O bond. The e.p.r. spectrum observed in O_2F_2 is, therefore, probably due to $F-O-O\cdot$, rather than $F-O\cdot$, and the sequence of the decomposition is likely to be



rather than



Jackson⁷ explained the H_2O_2 -like structure of O_2F_2 by proposing the bonding between one of the antibonding π -orbitals of the oxygen molecule with one fluorine and the other with the second fluorine. If it is assumed that the bonding in $F-O-O\cdot$ is such that the main electronic features of O_2F_2 put forth by Jackson are still maintained, one may assume that one of the antibonding π -orbitals of the O_2 molecule, say $\phi_{\pi y}^*$, forms a bond with the ϕ_{py} orbital of the fluorine, and the electron in the other π -orbital, $\phi_{\pi x}^*$, stays unperturbed and gives rise to paramagnetism. The electronic levels and the wave functions of each orbital in $F-O-O\cdot$ are given schematically in Figure 4, to-

(8) H. D. Babcock and J. Herzberg, *Astrophys. J.*, 108, 167 (1948).

gether with a diagrammatic representation of the bonding molecular orbitals, where

$$\phi_{OF} = \sin \theta \phi_{\pi y}^*(O_2) - \cos \theta \phi_{p_y}(F) \quad (3)$$

and

$$\phi_{OF}^* = \cos \theta \phi_{\pi y}^*(O_2) + \sin \theta \phi_{p_y}(F)$$

The ground-state wave function for the unpaired electron is primarily $\phi_{\pi x}^*$, and the usual spin-orbit coupling interaction admixes a small amount of ϕ_{σ} , ϕ_{OF} , and ϕ_{OF}^* . The first-order calculations of such an interaction gives as the ground-state Kramer's doublet

$$\begin{aligned} \Phi_+ \cong & \phi_{\pi x}^* \alpha - \frac{\lambda}{2} \left(\frac{\cos^2 \theta}{\delta_1} - \frac{\sin^2 \theta}{\delta_2} \right) \phi_{\pi y}^* \alpha + \\ & \frac{\lambda \cos \theta \sin \theta}{2} \left(\frac{1}{\delta_1} + \frac{1}{\delta_2} \right) \phi_{p_y}(F) \alpha - \frac{\lambda}{2\Delta} \phi_{\sigma} \beta \end{aligned} \quad (4)$$

$$\begin{aligned} \Phi_- \cong & \phi_{\pi x}^* \beta + \frac{\lambda}{2} \left(\frac{\cos^2 \theta}{\delta_1} - \frac{\sin^2 \theta}{\delta_2} \right) \phi_{\pi y}^* \beta - \\ & \frac{\lambda \cos \theta \sin \theta}{2} \left(\frac{1}{\delta_1} + \frac{1}{\delta_2} \right) \phi_{p_y}(F) \beta + \frac{\lambda}{2\Delta} \phi_{\sigma} \alpha \end{aligned}$$

where λ is the spin-orbit coupling constant of the oxygen atom and α and β are the usual spin functions. The calculation of the g value⁹ for this doublet results in

$$\begin{aligned} g_x &= g_e \\ g_y &= g_e + \frac{2\lambda}{\Delta} \\ g_z &= g_e - 2\lambda \left(\frac{\cos^2 \theta}{\delta_1} - \frac{\sin^2 \theta}{\delta_2} \right) \end{aligned} \quad (5)$$

where g_e is the g value of a free electron and is equal to 2.0023. The calculation shows that g_y is greater than g_e , and g_z is less than g_e since it is expected that

$$\frac{\cos^2 \theta}{\delta_1} - \frac{\sin^2 \theta}{\delta_2} > 0$$

The calculated results are consistent with the experimentally observed values if we identify

$$\begin{aligned} g_y &= g_{||} = 2.007 \\ g_x \cong g_z &= g_{\perp} = 2.000 \end{aligned}$$

As can be seen in eq. 5, $\Delta g_y = g_y - g_e$ is rather insensitive to the nature of the O-F bond, and it is expected to be very close to Δg_y of O_2^+ or O_2^- , provided that the degeneracies of the π -orbitals of these species are sufficiently removed by the environment. Although the e.p.r. spectrum of O_2^+ has not been reported, the e.p.r. spectrum of O_2^- has been extensively examined in a molecular sieve system and its g_y has been found to be in the range 2.006–2.009.¹⁰

As is well known, the hyperfine interaction between an unpaired electron and a magnetic nucleus can be expressed as the sum of the isotropic part

$$g_e \beta_e g_n \beta_n \frac{8\pi}{3} |\Phi(0)|^2$$

(9) M. H. L. Pryce, *Proc. Phys. Soc. (London)*, **A63**, 25 (1950).

(10) P. H. Kasai, to be published.

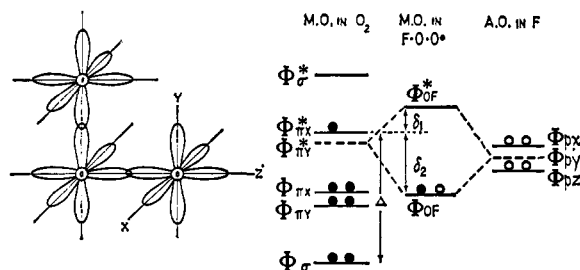


Figure 4. Schematic representation of the structure and the energy levels of the valence electrons in F-O-O.

and the anisotropic part given by

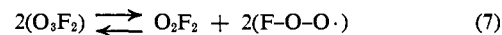
$$g_e \beta_e g_n \beta_n \left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle$$

Here $|\Phi(0)|^2$ indicates the probability of the unpaired electron at the magnetic nucleus, r is the distance between the electron and the nucleus, and θ is the angle between the direction of the applied magnetic field and the line joining the electron and the nucleus. Since the unpaired electron in F-O-O· stays mostly in the antibonding π -orbital, $\phi_{\pi x}^*$, of the O_2 molecule and the fluorine nucleus exists at a relatively long distance away from this orbital, it may be approximated that

$$\begin{aligned} A_x \cong A_z &= g_e \beta_e g_n \beta_n \left[\frac{8\pi}{3} |\Phi(0)|^2 - \frac{1}{R^3} \right] \\ A_y \cong g_e \beta_e g_n \beta_n \left[\frac{8\pi}{3} |\Phi(0)|^2 + \frac{2}{R^3} \right] \end{aligned} \quad (6)$$

where R is the O-F distance. These results are also consistent with the experimentally observed values if we identify $A_y = A_{||} = 100$ gauss and $A_x = A_z = A_{\perp} = 25$ gauss. The experimental results then give $|\Phi(0)|^2 = 0.225 \times 10^{24} \text{ cm.}^{-3}$ and $R = 1.02 \text{ \AA}$. The value of $|\Phi(0)|^2$ should be compared with $74.3 \times 10^{24} \text{ cm.}^{-3}$ obtained for the 2s orbital of the Hartree solution of fluorine atom.¹¹ Thus, a small amount of sp hybridization of the fluorine orbitals would account for the isotropic part of the observed hyperfine interaction. The value of R obtained above is clearly much shorter than the value one might expect from the structural parameters known for O_2F_2 .⁶ However, the anisotropic part of the observed hyperfine interaction must also include the contribution of the $\phi_{\pi y}^*(O_2)$ and $\phi_{p_y}(F)$ orbitals to the extent they are involved in eq. 6, and the inclusion of their contribution should result in a larger value of R than the one obtained above.

It is of particular interest that O_3F_2 contains in a much larger quantity the same radical that O_2F_2 produces in its decomposition process. Since the initial decomposition of O_3F_2 is to O_2F_2 , the free radical in a larger quantity could hardly be due to O_2F_2 which had been produced in O_3F_2 . It is more likely that in O_3F_2 the free radical F-O-O· is present through either a decomposition reaction or a thermal equilibrium in the form of



The intensity of the e.s.r. signal of a Freon 13 solution containing 1 vol. % of O_3F_2 and 1 vol. % of O_2F_2

(11) F. W. Brown, J. H. Bartlett, Jr., and C. G. Dunn, *Phys. Rev.*, **44**, 296 (1933).

was therefore compared with that of a Freon 13 solution containing 1 vol. % of O_3F_2 alone. If the equilibrium reaction is responsible, the intensity of the former should be weaker than that of the latter by a factor of 2-3. Instead it was stronger. Thus, the decomposition

reaction characterized above appears to be responsible for the abundant $FO_2\cdot$ radical in O_3F_2 .

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Exchange Reactions of Gallium Bromide with Hydrogen Bromide and with Methyl Bromide in 1,2,4-Trichlorobenzene and in Nitrobenzene¹

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The solubilities of HBr and CH_3Br in 1,2,4-trichlorobenzene and in nitrobenzene have been determined with and without gallium bromide in solution. They all obey Henry's law over the limits tested except for the $C_6H_5NO_2$ - $GaBr_3$ -HBr system where there is evidence for a 1:1 $GaBr_3$ -HBr complex. Values for the Henry's law constants are given. The experimental rate laws for exchange of bromine with $GaBr_3$ are $R = k[HBr]^2$ for HBr and $R = k[CH_3Br][GaBr_3]^2$ for CH_3Br , seemingly independent of the complexing. Temperature coefficients have been determined. The observed exchange is much faster for HBr than for CH_3Br . Exchange is faster in 1,2,4-trichlorobenzene than in nitrobenzene, the difference between solvents being much greater for CH_3Br than for HBr.

Introduction

Gallium bromide catalyzes the alkylation of aromatic compounds by alkyl bromides, the kinetics of the reaction being dependent on the solvent. In pure benzene or toluene the rate is proportional to the square of the gallium bromide concentration and independent of the alkyl bromide^{2,3} concentration, whereas in 1,2,4-trichlorobenzene the reactions are first order with respect to each reactant: the aromatic, the alkyl bromide, and the catalyst.⁴

To investigate the interaction of an alkyl bromide with gallium bromide in the absence of an aromatic reactant, we have determined the kinetics of the exchange of bromine between methyl bromide and gallium bromide in 1,2,4-trichlorobenzene and in nitrobenzene. For comparison, and because HBr is a product of alkylations catalyzed by gallium bromide, we have studied the exchange reactions between gallium bromide and HBr in the same solvents. Gallium bromide forms homogeneous solutions, making it possible to determine quantitatively the dependence of exchange

rates on its concentration, in contrast to the exchange studies which have been made with a number of other metal halide catalysts.⁵ In order to know the concentrations of CH_3Br and HBr in the exchange experiments and whether they are appreciably complexed with gallium bromide, we have determined their Henry's law solubility constants in 1,2,4-trichlorobenzene and in nitrobenzene in the absence and presence of gallium bromide.

Experimental

Materials. Gallium bromide, prepared by the direct combination of metallic gallium with bromine,⁶ was sealed in small ampoules with fragile tips after several resublimations *in vacuo*. Nitrobenzene (Baker Chemical Co., purified) and 1,2,4-trichlorobenzene (Eastman Organic Chemicals, practical) were fractionated in a Todd column and stored over Drierite until used. Hydrogen bromide (Matheson Co.) and methyl bromide (Matheson Co.) were introduced from the cylinders into the vacuum line through a phosphorus pentoxide column.

Procedures for the Exchange Studies. The gallium bromide for each exchange run was sublimed into the reaction vessel in the vacuum system by heating after breaking the tip of an ampoule with a magnetic hammer. Dry Ice was used to aid in condensing the sublimate at the desired place. Following the sublimation, the tube containing the gallium bromide ampoule was sealed off from the vacuum system, and the weight of gallium bromide which had been introduced to the reaction vessel was determined by the difference in weight of the ampoule and its fragments before and after the transfer. The solvent was distilled through a phosphorus pentoxide column onto the gallium bromide. Figure 1 shows the reaction system as it appeared after sealing off the tubes used for introduction of gallium bromide and solvent. A known quantity of $HBr(Br^{82})$ or $CH_3Br(Br^{82})$ was frozen into the system GFB from the calibrated bulb E. With the aid of the

(1) (a) This work was supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-32; (b) presented at the XVIIth International Congress of Pure and Applied Chemistry, Munich, Germany, 1959.

(2) C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245 (1956).

(3) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

(4) S. U. Choi and H. C. Brown, *ibid.*, **85**, 2596 (1963).

(5) (a) C. H. Wallace and J. E. Willard, *ibid.*, **72**, 5275 (1950); (b) W. T. Carnall, M. Blau, and J. E. Willard, *ibid.*, **74**, 5762 (1952); (c) M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951); **75**, 3330 (1953).

(6) W. C. Johnson and J. B. Parsons, *J. Phys. Chem.*, **34**, 1210 (1930).