An Electron Paramagnetic Resonance Study of Oxygen Fluorides. II. Tetraoxygen Difluoride

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Abstract: An epr study has been made of O_4F_2. The spectrum obtained is probably the isotropic pattern of the radical FOO. This same spectrum has been found in O_2F_2 and ultraviolet light irradiated OF_2.

The existence of a free radical giving an asymmetric spectrum in monochlorotrifluoromethane has been established recently[1] through our epr study of O_2F_2 and O_3F_2. The spectrum was shown to be probably due to FOO·. Since then an epr study of O_4F_2 has been made. While these studies were in progress, Reinhard,[2] Metz and co-workers,[3] and Neumayr and Vanderkooi[4] each observed an epr doublet when OF_2 was irradiated with ultraviolet light. Fessenden and Schuler[5] also observed a doublet when CF_4 was irradiated in presence of O_2. They stated that this doublet was probably due to FOO·. In their infrared studies, Arkell and co-workers[6] reported obtaining the OF radical when OF_2 was irradiated with ultraviolet light at 4°K. Upon warming to 40°K the OF radical recombined with the F atom to give OF_2. Arkell[7] also observed that the photolysis of OF_2–O_2 or F_2–O_2 mixtures at 4°K produced the FOO· radical. Reinhard[2] observed in his epr studies that when ultraviolet light irradiated dilute samples of OF_2 in $CClF_3$ were cooled from 77°K to 20°K, the epr doublet changed to the asymmetric pattern of the FOO· radical reported by Kasai and Kirshenbaum.[1] This prompted us to reinvestigate the solutions of O_2F_2.

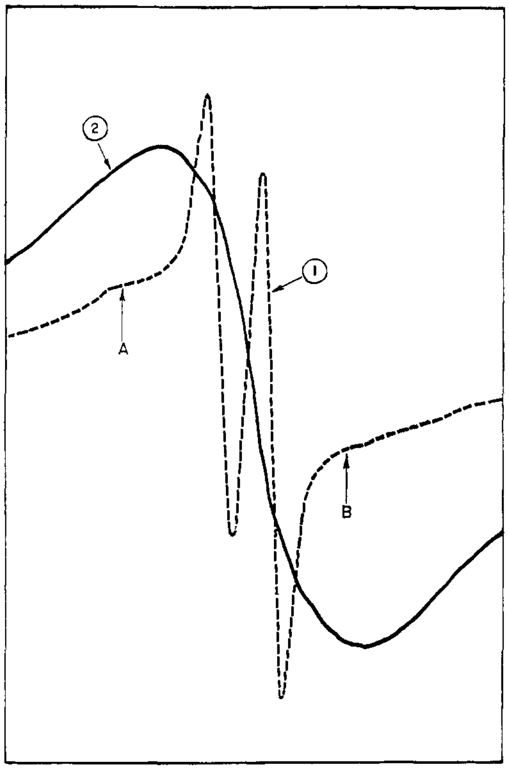

Figure 1. Epr spectra of (1) 0.2% O_4F_2 in CF_4 and (2) solid O_4F_2.

Experimental Section

When undiluted solid O_4F_2 was studied at 77°K, a single broad band signal was obtained having a peak-to-peak line-width value of 52 ± 1 gauss and a *g* value of 2.003_5 (see curve 2 in Figure 1). However, a different epr spectrum was obtained for dilute samples (~0.2 mole %) of O_4F_2 in the diamagnetic solvent carbon tetrafluoride, CF_4, prepared at 90°K and studied at 77°K. This spectrum consisted of a strong, sharp doublet and not completely resolved shoulders on either side of the doublet, as shown by arrows A and B in curve 1 of Figure 1. The hyperfine splitting value of the doublet was 14 ± 1 gauss and its *g* value was 2.005_0. When the samples were kept at 90°K the shoulders disappeared and the doublet lost some of its resolution, as shown in Figure 2.

Epr spectra were also obtained at 77°K of dilute solutions of O_4F_2 in CF_4 prepared at temperatures below 85°K. These spectra contained the same single broad-band signal observed with undiluted solid O_4F_2 with only a trace of a doublet. Upon warming these samples to 90°K for 15 min and then recooling to 77°K, the epr spectrum changed from the single broad-band signal to the sharp doublet with partially resolved shoulders. These studies showed that the shoulders and the doublet are due to two species. The shoulders, as shown in Figure 1, are the remains of the single broad signal obtained for O_4F_2 at 77°K before warming, while the sharp doublet is due to a species in the tumbling or averaging state and is a decomposition product of O_4F_2.

Table I. Comparison of the Hyperfine Splitting and *g* Values of the Epr Doublet

Investigator	*g* value	Hyperfine splitting value, gauss	Ref
Kirshenbaum and Streng	2.005_0	14 ± 1	This work
Reinhard	2.004_0	13.6	2
Metz and co-workers	2.003_6	13.5	3
Neumayr and Vanderkooi	2.004_6	13.8	4
Fessenden and Schuler	...	13	5

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(1) P. H. Kasai and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **87**, 3069 (1965).

(2) Private communication.

(3) Quarterly Report No. 2 on "Structural Studies of Inorganic Oxidizers," Contract AF 04(611)-10215, Midwest Research Institute, October 1 to December 31, 1954.

(4) F. Neumayr and N. Vanderkooi, Jr., *Inorg. Chem.*, **4**, 1234 (1965).

(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(6) A. Arkell, R. R. Reinhard, and L. P. Larson, *J. Am. Chem. Soc.*, **87**, 1016 (1965).

(7) A. Arkell, *ibid.*, **87**, 4057 (1965).

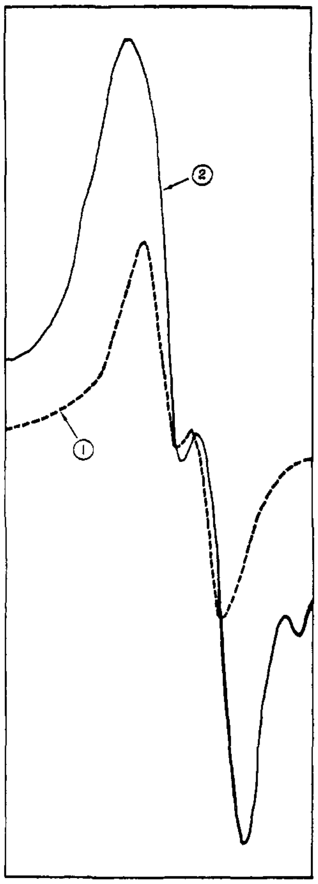

Figure 2. Epr spectra of (1) O_4F_2 in CF_4 at 90°K (liquid) and (2) O_2F_2 in $CClF_4$ (liquid).

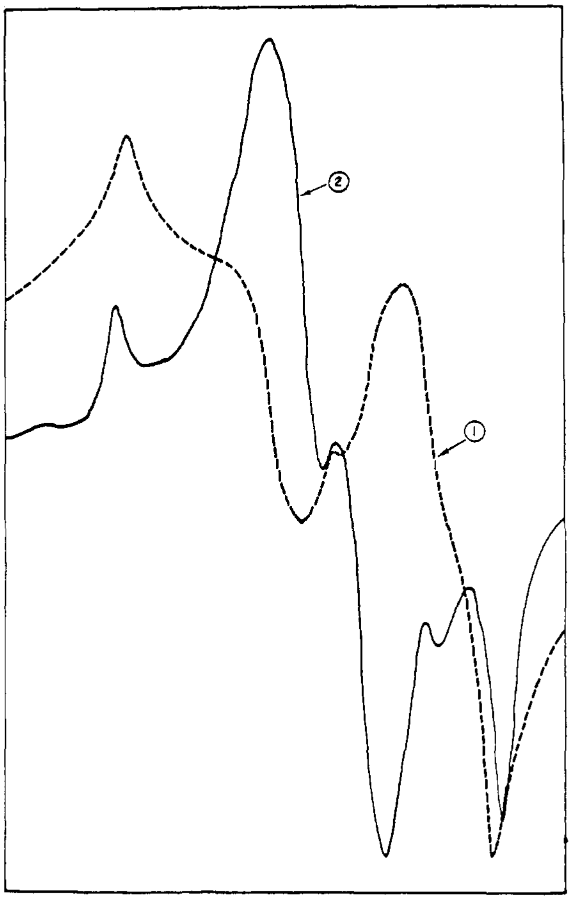

Figure 3. Epr spectra of (1) O_2F_2 in $CClF_3$ (solid) and (2) O_2F_2 in $CClF_3$ (liquid).

A comparison of the hyperfine splitting and g values of the doublet with those reported by the other investigators is given in Table I. A study of these values show that the same free radical must be present in the irradiated OF_2 as in the O_4F_2. Reinhard[2] has since confirmed the doublet obtained with O_4F_2.

In his epr studies, Reinhard observed[2] that when photolyzed dilute samples of OF_2 in $CClF_3$ were cooled from 77°K to 20°K, the epr doublet changed to the FOO· asymmetric pattern. In our epr studies a similar phenomenon was observed. In these studies, some of the solutions of O_2F_2 in $CClF_3$ were slow in solidifying. These samples were saturated solutions of O_2F_2 in $CClF_3$ which had some solid O_2F_2 dispersed in the solutions. The epr spectra obtained for these samples, while still liquid, consisted of the typical asymmetric spectrum for FOO· and a doublet as shown in Figure 3. The doublet was similar to that obtained for O_4F_2 in CF_4 at 90°K as can be seen in Figure 2. However, when the O_2F_2 solutions solidified the epr spectrum changed back to the typical anisotropic FOO· signal as shown in Figure 3.

Discussion of Results

The results of the above experiments indicate that the doublets obtained for the liquid solutions of O_2F_2, the O_4F_2 solutions, and the irradiated OF_2 are due to the same free radical. These doublets are most likely the isotropic epr spectrum of the FOO· radical.

The above can be further seen by comparing the g and A values of the two spectra. It was reported previously[1] that the anisotropic values for FOO· were: $A_{\parallel}$ = 100 gauss, $A_{\perp}$ = 25 gauss, $g_{\parallel}$ = 2.0074, and $g_{\perp}$ = 2.0005. Substituting these values into

$$A_{\text{iso}} = \frac{A_{\parallel} + 2A_{\perp}}{3}$$

and

$$g_{\text{iso}} = \frac{g_{\parallel} + 2g_{\perp}}{3}$$

where $A_{\perp}$ is negative, results in 16.7 gauss and 2.0028 as the calculated isotropic A and g values. The small differences in the calculated and observed A_{iso} and g_{iso} values (14 ± 1 gauss and 2.0050) may be explained in the uncertainty of the $A_{\perp}$ and $g_{\perp}$ values reported.[1] This uncertainty is due to the FOO radical in the solid O_2F_2 not having any actual symmetry. In the calculations it was assumed that two of the three A values and two of the three g values were equal. They were not exactly equal since in the anisotropic patterns of the FOO radical the $A_{\perp}$ line was not as sharp as it should have been. Therefore in the calculations the average of the two A values and 2 g values were used to obtain the $A_{\perp}$ and $g_{\perp}$ values. Thus it would seem that the same free radical FOO· is present in O_4F_2, O_3F_2, O_2F_2, and irradiated OF_2.

Another interpretation, but a less likely one, is that the signals are due to two radicals instead of one. For this case $A_{\perp}$ would be positive and the calculated A_{iso} would be 50 gauss compared to 14 gauss for the doublet.

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