which are based on a value of $+32$ for $\Delta H_f{}^\circ{}_{298}(CH_3(g))$ are all too low. Thus, for example, $DH^\circ{}_{298}(CH_3-CH_3)$ = 88.4 ± 0.7 kcal./mole[19]; $DH^\circ{}_{298}(C_2H_5-CH_3)$ = 84.2 ± 1.3 kcal./mole.[19,20]

In addition, fixing the value of $\Delta H_f{}^\circ{}_{298}(CH_3(g))$ sheds some light on the question of $\Delta H_f{}^\circ{}_{298}(CH_3CO(g))$. Those values which depend on $\Delta H_f{}^\circ{}_{298}(CH_3(g))$[21-23] lead to a value of -2.9 ± 1.5 kcal./mole. A value which is independent of the methyl heat of formation and the extrapolations to high pressure limits, which add uncertainty to the above value, was obtained by studying the kinetics of the reaction between HI and acetyl iodide.[24] This leads to a value of $\Delta H_f{}^\circ{}_{298}$ $(CH_3CO(g))$ = -6.3 ± 2.0 kcal./mole, where the uncertainties are in measuring an activation energy, in taking the activation energy of the reaction between

CH₃CO and I₂ to be zero, and in the value of $\Delta H_f{}^\circ{}_{298}$ $(CH_3COI(g))$. The latter value is probably not off by much more than its standard error of 2 kcal./mole, but the weight of evidence does seem to favor the lower value, so the suggested value is, in agreement with Kerr and Calvert,[22] $\Delta H_f{}^\circ{}_{298}(CH_3CO(g))$ = -4 ($+1$ or -2) kcal./mole.

The absence of CH₂I₂ enables us to set an upper limit on the equilibrium constant for the reaction

$$2CH_3I \underset{6}{\overset{5}{\rightleftharpoons}} CH_4 + CH_2I_2$$
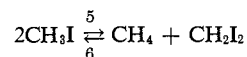
Taking the maximum pressure of CH₂I₂ as 0.03 torr (see Results) it can be calculated that $K_{5,6} \leq 3.6$ at $630^\circ K$. Using the same procedure outlined in the Results section to obtain $\Delta H^\circ{}_{298}$ and taking the data on S° and $C_p{}^\circ$,[2] the following value is obtained: $\Delta H^\circ{}_{298} \geq -2.86$ kcal./mole. In conjunction with $\Delta H_f{}^\circ(CH_4)$,[2a] and the value of $\Delta H_f(CH_3I(g))$ = 3.28 kcal./mole measured in the present work, this leads to $\Delta H_f(CH_2I_2(g)) \geq +21.6$ kcal./mole. This has not previously been measured.

(19) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

(20) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

(21) E. O'Neal and S. W. Benson, *ibid.*, **36**, 2196 (1962).

(22) J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965).

(23) E. Murad and M. G. Inghram, *J. Chem. Phys.*, **41**, 404 (1964).

(24) H. E. O'Neal and S. W. Benson, *ibid.*, **37**, 540 (1962).

Matrix Infrared Studies of OF Compounds. II. The O₂F Radical[1]

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The O₂F radical has been produced during the photolysis of OF₂–O₂ or F₂–O₂ mixtures in O₂, N₂, or argon matrices at 4°K. The radical in argon has infrared absorptions at 584 and 1494 cm.⁻¹ which disappear during thermal cycling of the matrix to the diffusion temperature. The products of diffusion, O₂F₂ and O₄F₂, are formed by combination of O₂F with atomic fluorine and by dimerization of O₂F, respectively. Parallel work using O¹⁸-substituted O₂ gave isotopic infrared absorptions which were in good agreement with calculated values. The stretching force constants derived for O₂F and O₄F₂ indicate relatively short O–O bonds compared to peroxide type compounds and relatively long O–F bonds compared to OF₂. These results are in general agreement with the previously established structure of O₂F₂.

Introduction

During a study of the effects of a radiofrequency glow discharge on OF₂, evidence was obtained for the existence of OF and O₂F radicals. The evidence was based on the formation of new absorptions in the infrared following the matrix (Ar or N₂ at 4°K.) deposition of radiofrequency-discharged OF₂. When the matrix was thermally cycled to its diffusion temperature, the

new infrared absorptions disappeared with the formation of O₂F₂, O₄F₂, and recovered OF₂. It was apparent from the complexity of the spectra that specific assignment of infrared absorptions to radical species would require the selective production of each species for individual study. In this respect the technique of matrix photolysis gave some measure of control not common to other methods of activation. For example, the restricting nature of the matrix allowed only limited migration of atoms during the photolysis step. Thus the choice of a matrix, the photolysis temperature, the range of radiation, and the size of the atom generated during photolysis all had to be considered as factors contributing to successful radical isolation. Ample evidence for the importance of these factors was found in a subsequent study of the matrix photolysis of OF₂ to obtain the OF radical.

The matrix isolation of the OF radical and its identification by infrared spectroscopy[2] was the first direct evidence of a species related to the family of radicals containing only oxygen and fluorine. In contrast to the much discussed OF radical, the other members of this family, namely, O₂F, O₃F, and O₄F, have received relatively little attention. This stems partly from the fact that the initial preparation[3] of two of the parent

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

(3) S. Aoyama and S. Sakuraba, *J. Chem. Soc. Japan*, **59**, 1321 (1938); **62**, 208 (1941).

compounds, O_3F_2 and O_4F_2, was regarded with skepticism until recently,[4] and partly from the notable instability of the higher oxygen fluorides including O_2F_2. This paper describes the production, isolation, and identification of the O_2F radical and confirms that two of the previously observed infrared absorptions from the radiofrequency-discharge work can be assigned to this species.

Kirshenbaum and Grosse[5] have reported the detection of paramagnetic species in O_2F_2 and O_3F_2 samples at 77°K. They have assigned parts of the observed complex spectrum (electron paramagnetic resonance) to the O_2F radical.

Several references[6] have mentioned the ClOO radical as an intermediate in the photolytic reaction of Cl_2 with O_2. There was, however, no evidence for a

$$Cl + O_2 \longrightarrow ClOO \overset{Cl}{\longrightarrow} 2ClO$$
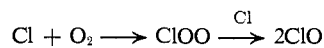
similar reaction between bromine atoms and O_2.[6a]

Recently Milligan and Jacox[7] reported good spectroscopic evidence for the HO_2 radical which was produced by the photolysis of HI and O_2 mixtures in an argon matrix at 4°K. Theoretical calculations by Boyd[8] suggested that HO_2 should have an isosceles triangle configuration. The spectroscopic evidence, however, showed that the two oxygen atoms in HO_2 were nonequivalent and therefore incompatible with the proposed isosceles triangle configuration. This observation was of particular interest because it was expected that a similar isotopic study in the present work would show the nonequivalence of the two oxygens in O_2F.

Experimental

All gas blends were prepared by standard manometric procedure using a matrix to reactant ratio (M/R) of 40. The OF_2 (Allied Chemical Co.), O_2 (Matheson, research grade), N_2 (Airco, prepurified), and argon (Airco) were used without further purification. The preparation of the $O^{18}F_2$ used in one run is described elsewhere.[2] In several runs, oxygen enriched to 30.3% O^{18} and 92.8% O^{18} (Isomet Corp.) was used.

The low-temperature infrared cell and its associated equipment have been described previously.[2] Sample irradiations were made using a high-pressure mercury arc (General Electric BH6). An elliptical spun aluminum reflector was used to focus the light from the arc onto the sample. A water filter (2200–9000 Å.) was used for several runs and an aqueous $NiSO_4$ solution filter (2200–3500 and 4500–5900 Å.) was used for all others. The latter filter (5-cm. quartz cell) contained 100 g. of $NiSO_4 \cdot 6H_2O$/l. of water.

The infrared spectra were recorded on a Beckman IR-9 spectrometer. The estimated resolution and frequency accuracy was ± 1 cm.$^{-1}$ for runs using isotopic substitution and ± 2 cm.$^{-1}$ for all others.

(4) (a) A. D. Kirshenbaum and A. V. Grosse, J. Am. Chem. Soc., 81, 1277 (1959); (b) A. V. Grosse, A. G. Streng, and A. D. Kirshenbaum, ibid., 83, 1004 (1961).

(5) A. D. Kirshenbaum and A. V. Grosse, U. S. Govenment Research Reports, Vol. 39, Office of Technical Services, Department of Commerce, Washington, D. C., June 20, 1964, Div. 4, AD-437465.

(6) (a) G. Porter, Discussions Faraday Soc., 9, 65 (1950); (b) G. Porter and F. J. Wright, ibid., 14, 23 (1953); (c) S. W. Benson and K. H. Anderson, J. Chem. Phys., 31, 1082 (1959).

(7) D. E. Milligan and M. E. Jacox, ibid., 38, 2627 (1963).

(8) M. E. Boyd, ibid., 37, 1317 (1962).

In a typical run the blends or samples from two manifolds were deposited simultaneously at a rate in the range of 120 to 145 μmoles of mixture/min. at 4°K. Depositions required about 30 min., and ultraviolet irradiation periods of up to 22 min. were used. Infrared spectra were recorded before and after deposition of the sample, and after each period of ultraviolet irradiation. At the end of each run the sample was allowed to warm to 40–45°K., depending on which matrix was used, and then cooled to 4°K. This process, termed diffusion, allows the reactive species in the matrix to migrate and react. An infrared spectrum before and after diffusion therefore gives information on new species as well as the products derived from them.

Results

Irradiation of OF_2 in O_2 using a water filter gave new bands at 582 and 1496 cm.$^{-1}$. A parallel run in which $O^{18}F_2$ in O_2 was used showed no shift in the new bands. During the course of a prolonged irradiation the absorption for $O^{16}F_2$ was found to increase as the $O^{18}F_2$ absorption decreased. After diffusion in these runs the bands at 582 and 1496 cm.$^{-1}$ disappeared and two new bands were formed at 590 and 1520 cm.$^{-1}$.

When a mixture of F_2 in O_2 was irradiated using a water filter, the rate of formation of the new bands was clearly much faster than in the run using OF_2. As shown in Figure 1, the absorption at 1496 cm.$^{-1}$ reached a maximum at about 30 min. of irradiation and then decreased to what appeared to be a steady-state concentration. At 30 min. the absorbance levels were 0.712 for the F_2 curve and 0.380 for the OF_2 curve. After the first 15 min. of ultraviolet irradiation, the shape of the 1496-cm.$^{-1}$ band indicated the possible presence of other unresolved absorptions. With improved resolution two other absorptions at about 1503 and 1512 cm.$^{-1}$ appeared as partially resolved side bands on the 1496-cm.$^{-1}$ absorption. Although these bands were unidentified at the time of this work, they have since been assigned to the O_3F and O_4F radicals, respectively.[9] During the course of the irradiation, there was a steady formation of OF_2 and the amount of O_2F_2 formed was greater than in the run using OF_2. The greater O_2F_2 formation emphasized the availability of two fluorine atoms in the same matrix cage. Diffusion in this run produced the bands at 590 and 1520 cm.$^{-1}$ and an increase in the OF_2 and O_2F_2 absorptions.

The use of oxygen as a matrix in the previous work was considered to be unsuitable for further studies using labeled oxygen. A series of runs ($O_2 + F_2 + N_2$) was made to determine the utility of N_2 as a matrix. In general, the interpretation of spectral data was difficult because of multiplet formation. Interpretation became even more difficult when isotopic oxygen was used and, as a result, satisfactory assignments for the infrared fundamental frequencies were not obtained. A test run made with $O_2 + F_2 + Ar$ showed that argon would be more satisfactory than nitrogen as a matrix material because the tendency toward multiplet formation was significantly reduced.

The first run, shown in Figure 2, was made using O^{16}_2 to establish the fundamental frequencies of the normal molecules. A mixture of O_2, F_2, and Ar (2:1:40)
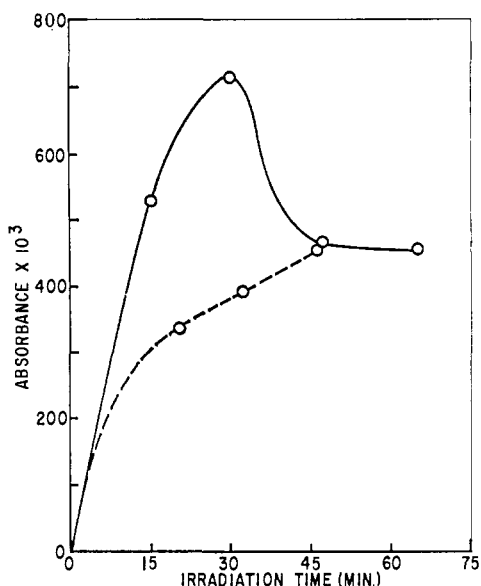
(9) A. Arkell, in preparation.

Figure 1. A comparison of the rate of formation of the absorption at 1496 cm.$^{-1}$ using two sources of fluorine atoms. Ultraviolet irradiation (water filter) of an oxygen matrix containing OF$_2$ (--------) or F$_2$ (————).
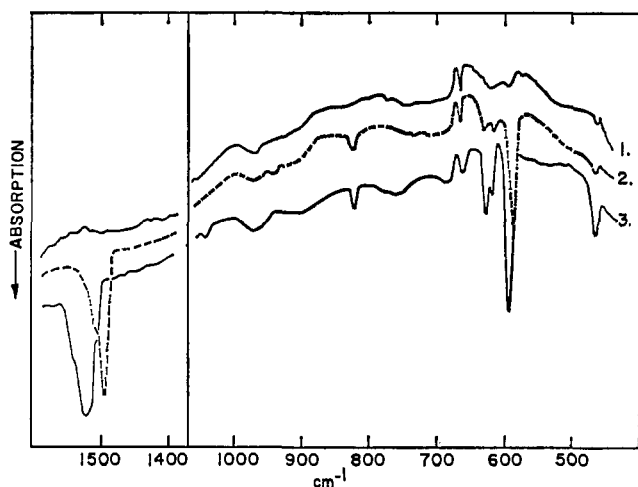

Figure 2. Photolysis and diffusion of a mixture of O$_2$, F$_2$, and Ar (2:1:40): (1) before irradiation, (2) after 20 min. of irradiation using a BH-6 through aqueous NiSO$_4$, (3) after diffusion (4–45–4°K.).

Figure 3. Photolysis and diffusion of a mixture of O$^{18}_2$–F$_2$–Ar (2:1:40): (1) before irradiation, (2) after 20 min. of irradiation using a BH6 through aqueous NiSO$_4$, (3) after diffusion (4–45–4°K.).

Figure 4. Absorptions produced following the photolysis and diffusion of mixtures of O$_2$, F$_2$, and Ar (1:1:40): (1) before irradiation, (2) after 20–22 min. of irradiation using a BH6 through aqueous NiSO$_4$, (3) after diffusion (4–45–4°K.). O^{18} distribution (%): for O$^{16}_2$, 48.6 (A), 50.3 (B); for O^{16}–O^{18}, 42.2 (A), 6.7 (B); for O$^{18}_2$, 9.2 (A), 43.0 (B).

was used to suppress O$_2$F$_2$ formation during photolysis. The second run, shown in Figure 3, used the same stoichiometry but with predominantly O$^{18}_2$. When labeled oxygen was used, three absorptions were present after photolysis where there had previously been only one in the 1400–1500-cm.$^{-1}$ region. The 550–650-cm.$^{-1}$ region, however, was obscured somewhat by the formation of O$_2$F$_2$ during photolysis. Additional tests using various mixtures showed that O$_2$–F$_2$–Ar (1:1:40) would eliminate O$_2$F$_2$ formation during photolysis. Two more runs were made using this stoichiometry and O$_2$ enriched with O^{18}. The O$_2$ distributions based on O^{18} content and the results of the ultraviolet irradiations and diffusions are shown in Figure 4. With the elimination of O$_2$F$_2$ during photolysis, only two distinct absorptions were found in the 550–650-cm.$^{-1}$ region. The presence of three absorptions in the 1400–1500-cm.$^{-1}$ region compared to only two in the 550–650-cm.$^{-1}$ region and the magnitude of their respective frequency shifts allowed the assignment of these

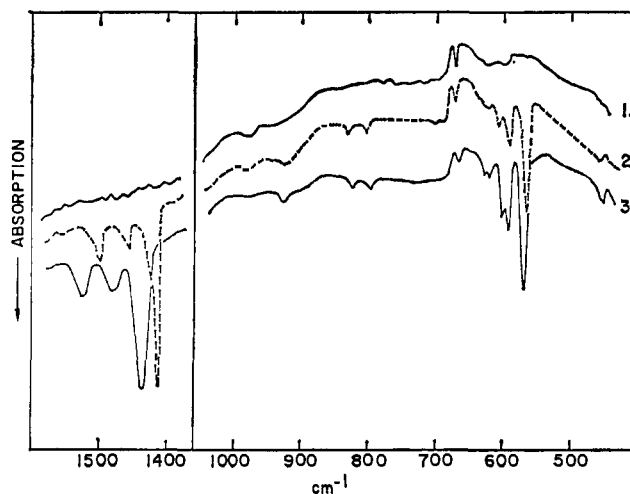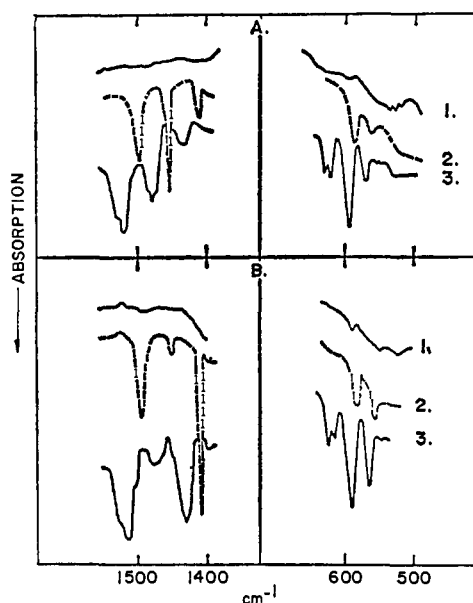two regions to O–O stretching and O–F stretching, respectively. A summary of the absorptions produced during photolysis is given in Table I. As shown, the observed values are in good agreement with the calculated values. It is of interest to note that the absorption at about 822 cm.$^{-1}$ in Figure 2 can be assigned to OF$_2$ as demonstrated by the isotopic shift shown in Figure 3 and Table I. Diffusion (thermal cycling) of the samples in these runs clearly showed the formation of O$_2$F$_2$ by the O^{16}F stretching doublet at 615 and 624 cm.$^{-1}$ in Figures 4A and 4B and by the O^{18}F stretching doublet at 586 and 596 cm.$^{-1}$ in Figure 3. It should be emphasized that there was no OF radical[2] produced in any of these runs during photolysis which indicated that the O$_2$F$_2$ produced after diffusion came from a source other than OF. A summary of the absorptions produced by diffusion of the samples is given

Table I. Absorptions[a] Produced during the Photolysis of O_2-F_2-Ar Mixtures at 4°K. Using Several Isotopic Oxygen Compositions

ν_{obsd}	ν_{calcd}[b]	Vibrational assignment
1494		$O^{16}O^{16}$ (O_2F)
1449	$\begin{cases} 1452 \\ 1451 \end{cases}$	$O^{18}O^{16}F$ $O^{16}O^{18}F$
1407	1408	$O^{18}O^{18}$
584		$O^{16}F$ (O_2F)
559	563	$O^{18}F$
822		$O^{16}F$ (OF_2)
796	794	$O^{18}F$

[a] In cm.$^{-1}$. [b] The calculated values were obtained using the force constants derived for O_2F and the mass changes shown above. The value for OF_2 was calculated from $\nu_i{}^2 = [M(M_i + 2m \sin^2 \alpha/2)/M_i(M + 2m \sin^2 \alpha/2)]$, where m = mass of F, M = mass of O, and $\alpha = 103°$.

Table II. Absorptions[a] Produced after the Diffusion Operation (4–45–4 °K.)

ν_{obsd}	ν_{calcd}[b]	Vibrational assignment
1519		$O^{16}O^{16}$ (O_4F_2)
1479	$\begin{cases} 1477 \\ 1476 \end{cases}$	$O^{18}O^{16}F$ $O^{16}O^{18}F$
1432	1432	$O^{18}O^{18}$
588		$O^{16}F$ (O_4F_2)
564	567	$O^{18}F$
624		$O^{16}F$ (O_2F_2, asym. str.)[c]
596	605	$O^{18}F$
615		$O^{16}F$ (sym. str.)
586	596	$O^{18}F$

[a] In cm.$^{-1}$. [b] The calculated values were obtained using the force constants derived for O_4F_2 and the mass changes shown above. The values for O_2F_2 were calculated from $\nu_1{}^2\mu_i = \nu_2\mu$, where μ and μ_i are the reduced masses of $O^{16}F$ and $O^{18}F$, respectively. [c] Assignments for the OF stretch, in O_2F_2 were made by H. Brown, "Free Radical Research Bulletin," National Bureau of Standards, Washington, D. C., June 1959.

in Table II.[10] In order to calculate the force constants and isotopic absorptions for O_4F_2, the molecule was assumed to consist of two equivalent triatomic vibrators. The justification for this assumption came primarily from the closeness of the infrared fundamentals of O_2F and O_4F_2. On this basis, calculated isotopic values were obtained which were within ±3 cm.$^{-1}$ of the observed absorptions. In the case of O_2F_2, agreement was poor because of the less accurate method of calculation used.

Several control runs were made to determine something of the stability of the compound responsible for the infrared bands at 588 and 1519 cm.$^{-1}$. The loss of these infrared bands during warm-up coincided with a loss of material from the infrared cell as followed by system pressure changes. This material, which left the cell in the 96–143°K. range, was trapped at 4°K. and then stored at room temperature. The stored material was 80 to 85% noncondensable at 77°K., and when it was redeposited in the cell at 4°K. it was nonabsorbing in the infrared. Behavior such as this

(10) Under conditions of higher resolution, many of the absorptions shown in Table II became doublets or complex multiplets. For example, the absorption at 1519 cm.$^{-1}$ usually appeared as a doublet at 1514 and 1519 cm.$^{-1}$. However, the 1519-cm.$^{-1}$ absorption was always the more prominent of the two and showed a lesser tendency toward intensity variations between runs than did the 1514-cm.$^{-1}$ band. It was on this basis that all absorption assignments were made.

would be expected from the higher oxygen fluorides since their ultimate decomposition products, O_2 and F_2, are noncondensable (at 77°K. and low pressure) and nonabsorbing in the infrared.

Discussion

O_2F Radical Evidence. Throughout the course of this work evidence was obtained from various sources which allowed the assignment of the 584- and 1494-cm.$^{-1}$ infrared absorptions to the O_2F radical. The following is a summary of these observations which, when taken collectively, confirm the above assignments. (1) Following diffusion the absorptions at 584 and 1494 cm.$^{-1}$ disappeared and the known compound O_2F_2 was formed as shown in Figures 2, 3, and 4 and Table II. The absence of OF radical in these runs indicated that the O_2F_2 probably came from combination of O_2F + F. In addition, the absorptions at 588 and 1519 cm.$^{-1}$ appeared. These absorptions were assigned to O_4F_2 as the other possible product formed by the reaction $2O_2F \rightarrow O_4F_2$. The assignments were supported by the similarities between the observed compound and O_4F_2 with respect to their stabilities and the character of their ultimate decomposition products. (2) During the previous work on the generation of the OF radical,[2] it became evident that an M/R of 40 would effectively isolate this diatomic species, as evidenced by the lack of formation of O_2F_2 during the photolysis step. If it can be assumed that the O_2 molecule, which is of comparable size, will also be effectively isolated, then the formation of new bands during photolysis must be regarded as the reaction of atomic fluorine with the isolated O_2 to give O_2F. (3) As shown in Figure 1 the rate of formation of the band at 1496 cm.$^{-1}$ was nearly doubled by using F_2 instead of OF_2 as the photolytic source of F atoms. Thus, per photon absorbed, F_2 ($h\nu$) $\rightarrow$ 2F, whereas OF_2 ($h\nu$) $\rightarrow$ F + OF. Since it is proposed that atomic F reacts with the isolated O_2, then the doubled rate of formation of O_2F would follow from the greater abundance of atomic F per unit time. (4) The use of O^{18} substitution has shown that both of the new bands were shifted by the mass change, therefore both were produced by oxygen-containing species. The three observed frequencies in the 1400–1500-cm.$^{-1}$ region (curve 2 of Figures 4A and B) and the agreement with calculated values (Table I) confirm assignment to the O–O stretching fundamentals in O_2F. The two observed frequencies in the 500–600-cm.$^{-1}$ region and agreement of the observed and calculated values confirm assignment of these bands to the O–F stretching fundamentals in O_2F.

As shown in Table II the assignments of the 588- and 1519-cm.$^{-1}$ bands to O–F and O–O stretching fundamentals, respectively, in O_4F_2 are additionally supported by the results of the isotopic substitution work.

Structure and Force Constants for O_2F and O_4F_2. The calculation of force constants for a triatomic species can be made using the equations derived by Cross and Van Vleck.[11] A computer program based on these equations was written in Fortran for an IBM 1620. In addition to the calculation of force constants, the program allows for their evaluation by calculation of the fundamental frequencies of the isotopic molecules
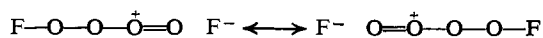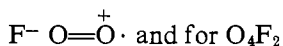
(11) P. C. Cross and J. H. Van Vleck, J. Chem. Phys., 1, 350 (1933).

Table III. Force Constants[a] for O_2F, O_4F_2, and Related Molecules

Molecule	k_{O-F}	k_{O-O}	k_{bend}
O_2		11.8^b	
O_4F_2	1.62^c	10.80	0.54
O_2F	1.59^c	10.45	0.54
HO_2		6.1^b	
OF_2	3.95^d		0.72

[a] In mdynes/Å. for all except k_{bend} which is in mdynes Å. [b] Data from ref. 7. [c] This work, assuming $r_{OF} = 1.63$ Å., $r_{OO} = 1.22$ Å., $\alpha_{OOF} = 100°$, and $\nu_{OOF} = 290$ cm.$^{-1}$. The molecule O_4F_2 was treated as two equivalent triatomics for this calculation. [d] L. Pierce, R. H. Jackson, and N. DiCianni, *J. Chem. Phys.*, **38**, 730 (1963).

for comparison with the observed frequencies. The initial calculation of force constants requires some knowledge of structural parameters as well as the observed fundamental frequencies for the normal molecule. In the case of O_2F and O_4F_2 there has been no prior structural data and it was necessary to assume a model. It was expected that there should be considerable similarity to O_2F_2, for which accurate structural data have been obtained.[12] Thus, as a first approximation the values $r_{OF} = 1.58$ Å., $r_{OO} = 1.22$ Å., and $\alpha_{OOF} = 110°$ were used. The observation of only two fundamental absorptions for O_2F and for O_4F_2 prompted a calculation of their expected bending frequencies. These frequencies were found to be in the region of 300 cm.$^{-1}$, which is outside the range of the IR-9. Each of these four parameters, r_{OF}, r_{OO}, α_{OOF}, and ν_{OOF}, was varied through a range of values. The force constants derived by this procedure were tested for accuracy by calculating isotopic frequencies and comparing them with the observed values. The OOF angle, α_{OOF}, which was tested through the range of angles from 90 to 125°, showed a pronounced sensitivity to change. A minimum deviation between observed and calculated frequencies was obtained at $\alpha_{OOF} = 100°$. A lower sensitivity to change was found for ν_{OOF} in the 270–300-cm.$^{-1}$ range, but a minimum was observed at 290 cm.$^{-1}$. Both r_{OO} and r_{OF} were insensitive to change through a range of interatomic distances. In the case of r_{OO} a Badgers rule calculation showed that the O–O distance of 1.22 Å. in O_2F_2 would be satisfactory. In the case of r_{OF} a similar calculation indicated that the O–F distance should be larger than that found in O_2F_2. A compromise value of 1.63 Å. for r_{OF} was considered most probable. As shown in Table III, the sets of force constants for O_2F and O_4F_2 were obtained using the values just mentioned. Comparison of the O–O stretching force constants shown in Table III indicates that the O–O bonds in O_2F and O_4F_2 have considerable double bond character. These findings, together with the much lower O–F stretching force constants compared to OF_2, lend support to Jackson's[12] explanation of possible contribution from ionic forms. In the case of O_2F the form would be

$$F^- \overset{+}{O}=\overset{}{O}\cdot \text{ and for } O_4F_2$$

$$F{-}O{-}O{-}\overset{+}{O}{=}O \quad F^- \longleftrightarrow F^- \quad O{=}\overset{+}{O}{-}O{-}O{-}F$$

It is of interest to note that the ionic forms of O_4F_2 show two distinctly different types of O–O bonds. Those adjacent to fluorine are equivalent and are nearly double bond in character. In contrast, the central O–O bond may be even weaker than the in-

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

dicated single bond because of the presence of a partial positive charge on the adjacent oxygens.

A comparison of the fundamental infrared absorptions of O_2F and O_4F_2 suggests that the dimerization of O_2F is not accompanied by gross physical change in the O_2F moiety. The unusual closeness of their respective absorptions indicates that the structural character of O_2F is maintained in the O_4F_2 molecule. In this respect the system appears to be a close parallel to the O_2–O_4 system discussed by Pauling.[13] In the case of O_4 he states that it does not have the square, single-bonded structure, "but consists instead of two O_2 molecules, with nearly the same configuration and structure as when free, held together by bonds much weaker than ordinary covalent bonds." A similar description of the O_2F–O_4F_2 system suggests, as previously indicated, that O_4F_2 consists of two O_2F radicals held together by a weak O–O bond. It is quite probable, therefore, that the unusually low thermal stability of O_4F_2 can be attributed to the presence of this weak bond. On this basis, another close parallel can be found between the O_4F_2–O_2F system and the isoelectronic N_2F_4–NF_2 system. In the absence of a restricting matrix, the O_4F_2 may tend to dissociate thermally to O_2F by analogy with the facile thermal dissociation of N_2F_4 to NF_2.[14]

As mentioned earlier, it was expected that the non-equivalence of the two oxygens in O_2F could be demonstrated by the observation of a double absorption in the O^{16}–O^{18} region. However, only a single absorption was found at 1449 cm.$^{-1}$. Although this suggested the possibility of a symmetrical structure for O_2F, the intensity of this infrared fundamental ruled against symmetry. It became apparent after the calculation of the O–O stretching frequencies for the two isotopic forms $O^{18}O^{16}F$ and $O^{16}O^{18}F$ that a theoretical separation of only 1 cm.$^{-1}$ (Table I) would be unresolved.

Observations in an Oxygen Matrix. The formation of the O_4F radical during the photolysis of fluorine in an oxygen matrix may have occurred by either of two reactions

$$F + O_2 \longrightarrow O_2F \overset{O_2}{\longrightarrow} O_4F$$

or

$$F + O_4 \longrightarrow O_4F$$
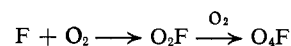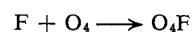
In the first case the presence of excess oxygen allowed for dissipation of residual energy in O_2F by reaction with a second molecule of O_2. In the second case the observed presence (absorption at 1549 cm.$^{-1}$)[15] of O_4 could also account for the O_4F formation. The formation of O_3F during photolysis is believed to occur by O_4F $(h\nu) \to O_3F + O$.

Two other observations were of interest during the matrix oxygen work: the formation of OF_2 during the photolysis of F_2 in O_2 and the formation of $O^{16}F_2$ during the photolysis of $O^{18}F_2$ in O^{16}_2. In the former system the formation of OF_2 could have occurred by assuming a transient intermediate such as
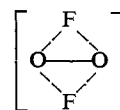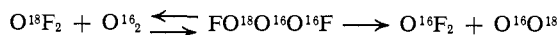
(13) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, New York, N. Y., 1960, pp. 87, 88, 353, 354.
(14) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, 33, 1869 (1960).
(15) R. V. St. Louis and B. Crawford, Jr., *ibid.*, 37, 2156 (1962).

Because of the restricting nature of the matrix, this intermediate could rearrange in only two ways giving either O_2F_2 or $OF_2 + O$.

In the latter system the steady production of $O^{16}F_2$ during the photolysis of $O^{18}F_2$ in $O^{16}{}_2$ suggests an exchange mechanism involving O_3F_2.

$$O^{18}F_2 + O^{16}{}_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{0pt}{1.2em}}} FO^{18}O^{16}O^{16}F \longrightarrow O^{16}F_2 + O^{16}O^{18}$$

Although this may be an oversimplification of the actual mechanism, the end result would be the loss of O^{18} to molecular oxygen where its presence would go undetected.

The Reaction of Oxygen Atoms with Perfluoropropene

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Contribution from the Aerospace Corporation, El Segundo, California. Received February 27, 1965

Oxygen atoms, $O(^3P)$, were generated by the mercury-sensitized decomposition of N_2O at 24°. In the presence of C_3F_6, the products are N_2, CF_2O, CF_3CFO, and a C_5F_{10} compound. C_2F_4 also may be formed, but our analytical scheme was incapable of measuring its presence. The sum of CF_2O and CF_3CFO was approximately equal to the N_2 formed, but CF_2O accounts for about 85% of the sum. In the presence of molecular oxygen, $\Phi(CF_2O)$ is equal to $\Phi(CF_3CFO)$ and varies from 0 to 20 depending on the conditions. The mechanism of the oxidation is outlined in both the presence and the absence of molecular oxygen. Several rate constant ratios are established and tabulated. The C_3F_6 is 0.27 times as efficient as N_2O in quenching the excited mercury atoms. The absolute rate of the reaction of atomic oxygen with C_3F_6 was measured by competition with C_2H_4. The rate constant for C_3F_6 is 2.1×10^7 l./mole sec.

I. Introduction

As a continuation of our studies on the vapor phase oxidation of perfluorocarbons, we have studied the reactions of oxygen atoms with perfluoropropene. The oxygen atoms were generated from the mercury-sensitized decomposition of nitrous oxide. This method of generating oxygen atoms has been studied extensively by Cvetanović[1-6] and recently applied by us to the study of oxygen atom reactions with C_2F_4.[7] The method was recently reviewed by Cvetanović.[8] The advantages of the method are that the only oxygen species produced is $O(^3P)$ and that N_2O is nonreactive with this species and most radicals. In his initial work,[2] Cvetanović believed the quantum yield of oxygen atom production to be 0.78, but more recent studies have shown that the quantum yield is unity.[9,10]

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(2) R. J. Cvetanović, *ibid.*, **23**, 1208 (1955).
(3) R. J. Cvetanović, *ibid.*, **23**, 1375 (1955).
(4) R. J. Cvetanović, *ibid.*, **25**, 376 (1956).
(5) R. J. Cvetanović, *Can. J. Chem.*, **36**, 623 (1958).
(6) R. J. Cvetanović and L. C. Doyle, *ibid.*, **38**, 2187 (1960).
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(9) R. J. Cvetanović, W. E. Falconer, and K. R. Jennings, *J. Chem. Phys.*, **35**, 1225 (1961).
(10) M. G. Bellas, Y. Rousseau, O. P. Strausz, and H. E. Gunning, *ibid.*, **41**, 768 (1964).

II. Experimental

Matheson Company research grade nitrous oxide and ethylene and Peninsular Chemical Research Company hexafluoropropene were used after degassing by pumping through a spiral trap at −196°. Gas chromatograms of these compounds showed no extraneous peaks. Matheson extra-dry grade oxygen (99.6%) was used without further purification.

The vacuum system, optical system, analytical system, and procedures have been described previously.[7] During photolysis, infrared absorption peaks at 5.12 and 5.30 μ were monitored intermittently. The final full scan was made 3 to 5 min. after irradiation was discontinued.

Calibrations for cyclo-C_3F_6 and CF_2O have been described previously.[7] CF_3CFO was calibrated from the mercury-sensitized photolysis of mixtures of C_3F_6 and O_2. Because equal quantities of CF_2O and CF_3CFO should be produced by this method, the latter product was calibrated *via* the former by taking the ratio of absorbances. The absorption coefficient of CF_3CFO at 5.30 μ (to base 10) is 0.056 mm.$^{-1}$/cm. of path length. It must be cautioned that this value may be somewhat different in another instrument. As a check that indeed equal amounts of CF_2O and CF_3CFO were produced in the mercury-sensitized oxidation of C_3F_6, the reacted mixture was fractionated at −160° and the two fractions were passed through a gas chromatograph. Approximately equal amounts of CO_2 were found in each fraction (the fluorocarbonyl compounds quantitatively convert to CO_2 in our system), and the total amount of CO_2 was twice that expected from the CF_2O alone.

Attempts to calibrate the cell pressure of the C_5F_{10} compound from its chromatographic peak area failed due to an apparent decomposition of the compound. The previously obtained calibration factor for cyclo-C_3F_6 in our system was 5 in.[2] of area per millimeter of pressure. Considering the trend of higher molecular weight compounds to have larger calibration factors, we assumed the reasonable value of 8 in.^{2}/mm.

III. Results

Initially, a mixture of 5 mm. of C_3F_6 and 6 mm. of N_2O was photolyzed for 30 min. The final infrared