The Reaction of Oxygen Atoms with Tetrafluoroethylene[1]

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Oxygen atoms, $O(^3P)$, were prepared from the mercury-photosensitized decomposition of N_2O at 24°. In the presence of C_2F_4, the products are equal amounts of N_2 and CF_2O, and smaller amounts of cyclo-C_3F_6. The mechanism of the reaction is outlined, and several rate constant ratios are established. For some runs, either C_2H_4 or 1-C_4H_8 was added and the competition with C_2F_4 for the oxygen atom was measured. Tetrafluoroethylene and ethylene scavenge the oxygen atoms with equal ease, the rate constant being 0.60×10^9 l./mole sec. In the presence of molecular oxygen $\Phi(CF_2O)$ is enhanced, thus suggesting that O_2 reacts with the triplet CF_2 produced from the $O + C_2F_4$ reaction. The cyclo-C_3F_6 yields are much larger than expected from singlet CF_2 radicals alone. In all likelihood, the majority of the cyclo-C_3F_6 results from triplet CF_2 radical addition to C_2F_4.

Introduction

The reaction of oxygen atoms with olefins has been studied by three different techniques. Avramenko and Kolesnikova[2] generated oxygen atoms in a glow discharge; Cvetanović[3-5] decomposed N_2O by mercury photosensitization to give oxygen atoms; and Sato and Cvetanović[6-9] photolyzed NO_2. The results of these studies have been reviewed recently by Kaufman[10] and by Cvetanović.[11] The most useful of the three techniques is the mercury-photosensitized decomposition of N_2O, which yields $O(^3P)$ atoms exclusively, first studied by Cvetanović.[12] The advantages of this method are discussed in detail in both reviews.[10,11]

The addition of oxygen atoms to ethylene produces a variety of products including CO, H_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, CH_3CHO, and ethylene oxide. Heicklen, Knight, and Greene[13] have investigated the mercury-photosensitized oxidation of tetrafluoroethylene in the presence of molecular oxygen. Their study revealed that CF_2O, cyclo-C_3F_6, and possibly a third compound were the only products. The lack of a large variety of products suggested that the mechanism of oxygen atom attack on olefins could be elucidated further with the help of perfluoroolefins because these reactions seemed to be unhampered by C–F bond cleavage; C–H bond breaking is, of course, manifest in the hydrocarbon system. The purpose of the present study is to investigate the basic nature of the process and, hopefully, to elucidate some of the mechanistic details.

Experimental

Matheson Company research grade nitrous oxide, ethylene, 1-butene, and CO_2 were used after degassing by pumping through a spiral trap at −196°. The oxygen used was Matheson extra dry grade (99.6%), which was not further purified. The preparation and purification of the C_2F_4 have been described previously.[13]

Mixtures were prepared by filling the cell with the lower pressure gas and reading the pressure on an upright mercury manometer. For pressures less than 5 mm., a Consolidated Vacuum Corporation McLeod gauge was used whenever possible. (For some runs there was insufficient C_2F_4 to use the McLeod gauge.) The higher pressure gas was then expanded into the cell by just cracking the valve to prevent back diffusion. The total pressure was then read on the manometer. The working part of the vacuum system was greaseless, employing Teflon stopcocks and greaseless joints with Viton O-rings.

The x-shaped cell was fitted with silica and sodium fluoride windows, held by Apiezon W black wax. The windows were attached so as to leave a negligible surface of wax exposed inside the cell.

The cell and mercury arc lamp were arranged, as shown in Figure 1, in the sample compartment of a Beckman 5A infrared spectrophotometer. By this arrangement, the infrared spectra could be taken during the photolysis. A Hanovia, flat, spiral, low pressure mercury arc was used without collimation. The radiation was always passed through a Corning 9-54 glass, which absorbs radiation below 2200 Å. to ensure that the absorbed radiation was 2537 Å. For some runs, two Corning 9-30 glasses were placed as shown. The 9-30 filters reduce the 2537-Å. radiation to 17.6%.

After the reactants had been admitted to the cell, the lamp was allowed to warm up for 10 to 15 min., during which time the initial infrared spectrum from 2 to 12.5 μ of the mixture was recorded. The sodium fluoride windows (6 mm. thick) absorbed all of the radiation past 12.5 μ. During the photolysis, which was performed at 24°, the infrared spectrum was repeatedly run in the 4.8- to 5.5-μ region at 20-sec. to 2-min. intervals, depending on the exposure time. After the photolysis, the mixture was allowed to equilibrate for 3 to 5 min., and a final full spectrum was recorded. The content of the cell was then expanded through a −196° trap into the McLeod gauge, and the pressure of the noncondensable gases was measured.

The absorption peak at 5.10 μ was plotted against time to ensure that the reaction was kept in the linear

(1) This work was supported by the U. S. Air Force under Contract No. AF 04(695)-469.
(2) L. I. Avramenko and R. V. Kolesnikova, *Vopr. Khim. Kinetiki Kataliza i Reaktsionnoi Sposobnosti, Akad. Nauk SSSR, Otd. Khim. Nauk*, 7 (1955).
(3) (a) R. J. Cvetanović, *J. Chem. Phys.*, 23, 1375 (1955); (b) *ibid.*, 25, 376 (1956).
(4) R. J. Cvetanović, *Can. J. Chem.*, 36, 623 (1958).
(5) R. J. Cvetanović and L. C. Doyle, *ibid.*, 38, 2187 (1960).
(6) S. Sato and R. J. Cvetanović, *ibid.*, 36, 279 (1958).
(7) S. Sato and R. J. Cvetanović, *ibid.*, 36, 970 (1958).
(8) S. Sato and R. J. Cvetanović, *ibid.*, 36, 1668 (1958).
(9) S. Sato and R. J. Cvetanović, *ibid.*, 37, 953 (1959).
(10) F. Kaufman, *Progr. Reaction Kinetics*, 1, 1 (1961).
(11) R. J. Cvetanović, "Advances in Photochemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 115.
(12) R. J. Cvetanović, *J. Chem. Phys.*, 23, 1203 (1955).
(13) J. Heicklen, V. Knight, and S. A. Greene, *ibid.*, 42, 221 (1965).

region. In all instances, no more than 20% of any reactant was exhausted, and in most cases the conversions were less than 10%.

In some cases, the condensables were collected and chromatographed on an F and M Model 720, programmed temperature, dual column gas chromotograph, employing a 0.25-in. × 10-ft. silica gel column and a 5°/min. program traversing from 50 to 150°.

Absolute analysis of the three products was performed in the following manner. The nitrogen pressure in the expanded volume including the McLeod gauge was measured. Then, by use of a suitable expansion factor, the cell pressure before expansion could be computed. The cyclo-C_3F_6 chromatographic peak height was calibrated directly using pure cyclo-C_3F_6 prepared as previously described.[13]

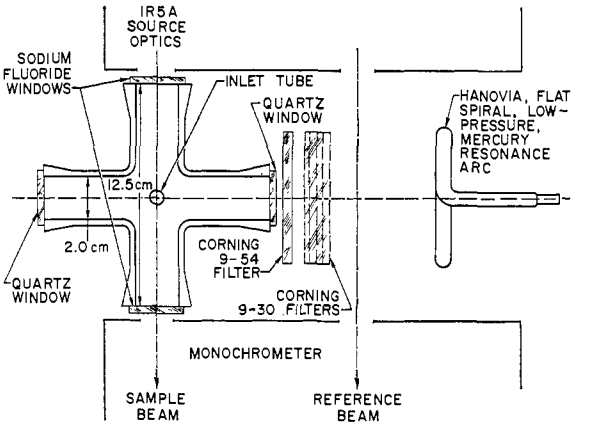

Figure 1. Optical assembly, top view.

Table I. Hg-Sensitized Photolysis of C_2F_4–N_2O Mixtures at 23°

N_2O, mm.	C_2F_4, mm.	Exposure time, min.	$\Phi(N_2)$	Φ (CF_2O)	Φ (cyclo-C_3F_6)	$\Phi(N_2)/\Phi(CF_2O)$
		$I_a = 5.8 \times 10^{13}$ quanta/cc. sec.				
5.70	2.76	2.00	0.76	0.89	...	0.91
4.22	13.8	2.00	0.53	0.74	...	0.73
5.95	33.1	2.00	0.41	0.82	...	0.49
5.70	30.3	6.00	0.40	0.49	...	0.81
5.52	123	2.00	0.18	0.15	0.068	1.19
18.7	3.78	2.00	0.82	0.91	...	0.90
17.2	33.6	5.00	0.76	0.79	...	0.96
17.5	91.0	5.00	0.37	0.46	0.052	0.80
24.0	11.0	5.00	1.01	1.25	...	0.81
49.2	4.11	2.00	1.19	0.97	...	1.22
42.0	10.0	5.00	1.16	1.43	...	0.81
48.0	30.0	6.00	0.90	1.01	...	0.88
55.0	112	8.00	0.48	0.53	0.076	0.91
126	2.90	4.00	1.18	1.37	...	0.86
131	10.0	6.00	1.13	1.06	...	1.06
138	30.5	7.00	1.09	1.09	...	1.00
196	91.5	10.00	0.63	0.81	0.106	0.78
442	2.91	2.00	1.29	1.18	...	1.10
447	10.0	5.00	1.13	0.96	...	1.18
486	32.3	7.00	1.18	1.25	...	0.94
460	100.5	10.00	0.87	0.94	0.26	0.93
		$I_a = 4.8 \times 10^{13}$ quanta/cc. sec.				
454	3.0	2.00	0.93	0.93	0.160	1.00
449	3.0	5.00	0.93	1.01	0.145	0.91
445	11.5	5.00	0.99	1.07	0.128	0.92
441	30	7.00	1.00	1.13	0.163	0.88
520	102	12.00	0.99	1.01	0.35	0.97
6.0	103	3.00	0.23	0.22	0.048	1.07
		$I_a = 1.02 \times 10^{13}$ quanta/cc. sec.				
5.00	40.0	10.00	0.35	0.29	...	1.19
21.0	12.3	20.00	0.99	1.37	...	0.72
18.0	93.0	20.00	0.34	0.31	...	1.09
61	2.79	11.00	0.94	1.12	...	0.84
57.0	30.0	40.00	0.99	0.99	...	1.00
149	11.0	20.00	1.28	1.53	...	0.84
446	3.45	10.00	1.11	1.00	...	1.10

Absolute analysis of the CF_2O was more difficult. In the chromatograph, the CF_2O quantitatively converts to CO_2. Unfortunately, the CO_2 had a retention time identical with N_2O. Thus, the CF_2O had to be calibrated by a circuitous route. The CF_2O was prepared by the mercury-sensitized oxidation of C_2F_4, and the infrared absorption intensities were measured. The CF_2O then was passed into the chromatograph and the resulting CO_2 measured. Separate calibrations for CO_2 then permitted a calculation of the infrared absorption coefficients. All subsequent analyses were by infrared absorption measurements. At 5.10 μ, the absorption coefficient (to base 10) was 0.013 mm.$^{-1}$/cm. of path length. This value was quite reproducible for our system but would undoubtedly be somewhat different in another instrument with a different spectral slit width. Also, our cell was about the same size as the sample beam, thus introducing the possibility of vignetting.

Results

An initial mixture of 21 mm. of C_2F_4 and 18 mm. of N_2O was photolyzed for 30 min. Examination of the final infrared spectra revealed new bands at 5.10, 5.18, 7.94, 8.02, and 8.12 μ, all of which can be attributed to CF_2O. The band at 10.27 μ was just barely visible over the pen noise and background of sodium fluoride. The bands at 12.65 and 12.9 μ were completely obscured by the sodium fluoride. Bands due to perfluorocyclopropane were not observed because of the interference of the C_2F_4 bands. All further runs of the C_2F_4–N_2O mixture gave the same bands unless obscured by a reactant band.

A subsequent run of 3.6 mm. of C_2F_4 and 16 mm. of N_2O was photolyzed for 30 min. and chromatographic analysis performed. The CO_2, C_2F_4, and N_2O had a common peak. Only one other peak, having a retention time exactly equal to that of cyclo-C_3F_6, was observed.

All other photolyses were for short conversions; the results are listed in Tables I–III. Variations in duration of exposure gave no change in quantum yields, thus ensuring that the products did not enter the reaction.

Table I is a compilation of results of 34 experiments in which the C_2F_4 was varied from 3 to 120 mm. and the N_2O from 5 to 500 mm. The first set is with full intensity ($I_a = 5.8 \times 10^{13}$ quanta/cc. sec.). An apparent change was noted in the absorbed intensity after cleaning the cell; thus the second set has a lower intensity ($I_a = 4.8 \times 10^{13}$ quanta/cc. sec.). The final set with $I_a = 1.02 \times 10^{13}$ quanta/cc. sec. was made using two Corning 9-30 glasses. The products of the reaction are nitrogen, CF_2O, and cyclo-C_3F_6. Within about 20% scatter, $\Phi(N_2)$ is equal to $\Phi(CF_2O)$, as required by mass balance considerations, and the quantum yields are independent of intensity. As the $(N_2O)/(C_2F_4)$ ratio rises, $\Phi(N_2)$ and $\Phi(CF_2O)$ are

Table II. Hg-Sensitized Photolysis of C_2F_4–N_2O Mixtures in the Presence of Olefins at 23°

N_2O, mm.	C_2F_4, mm.	Olefin, mm.	Exposure time, min.	$\Phi(N_2)$	Φ (CF_2O)
Olefin is C_2H_4; $I_a = 5.8 \times 10^{13}$ quanta/cc. sec.					
544	3.33	5.27	5.00	1.15	0.46
484	3.08	10.0	6.00	1.19	0.29
537	3.40	34.5	6.00	1.19	0.112
478	4.50	125.5	10.00	1.00	...
516	13.5	2.6	5.00	0.88	0.78
475	11.0	13.0	6.00	1.06	0.43
558	12.0	32.5	10.00	1.16	0.29
535	13.0	89.0	10.00	1.24	0.19
520	32.5	3.6	5.00	0.91	0.82
518	31.5	10.5	10.00	1.18	0.87
458	29.0	36.0	12.50	1.24	0.59
450	35.0	88.5	10.00	1.10	0.26
Olefin is 1-C_4H_8; $I_a = 4.8 \times 10^{13}$ quanta/cc. sec.					
508	33	4.0	3.50	0.91	0.57
494	30	10.0	10.00	1.03	0.43
524	73	31.0	10.00	0.90	0.35
518	100	3.0	5.00	1.01	0.76
519	105	10.0	10.00	0.88	0.63

Table III. Hg-Sensitized Photolysis of C_2F_4–N_2O Mixtures in the Presence of Oxygen at 23°

N_2O, mm.	C_2F_4, mm.	O_2, mm.	Exposure time, min.	Φ (CF_2O)	Φ(cyclo-C_3F_6)
$I_a = 4.8 \times 10^{13}$ quanta/cc. sec.					
504	12.0	3.0	2.00	2.50	....
510	12.5	3.5	5.00	2.66	0.044
503.5	11.0	9.0	2.00	2.57	....
513.5	10.0	12.5	5.00	2.57	0.032
510.5	11.5	30.0	2.00	2.35	....
501	10.0	30.0	5.00	2.15	0.022
502	12.0	99.0	2.00	2.10	....
494	11.0	99.0	5.00	1.48	$\leq$0.0090
499.5	30.0	2.5	5.00	1.93	0.130
500	30.0	3.0	5.00	3.06	....
512	30.5	10.0	5.00	2.25	....
515.5	31.0	29.0	5.00	1.97	....
505.5	32.0	98.5	5.00	1.96	....

enhanced and approach the assumed upper limit of one. The cyclo-C_3F_6 yield also increases with an increase in N_2O pressure at C_2F_4 pressures of about 100 mm. However, with 500 mm. of N_2O, the cyclo-C_3F_6 yield is not much affected by a variation of the C_2F_4 pressure. The CF_2O production was monitored continuously throughout the runs. Except when 500 mm. of N_2O was used, the CF_2O bands were enhanced linearly with exposure time. With 500 mm. of N_2O, the CF_2O bands appeared only after an induction period and continued to grow for some time after irradiation was discontinued. In some cases, the half-life of this lag was as long as 40 sec. This effect was attributed to diffusion (which would be slow at the highest pressures) from the reaction arm of the cell to the infrared arm. To substantiate this explanation, a run was done with 19.5 mm. of C_2F_4, 25 mm. of N_2O, and 611 mm. of CO_2. The inhibition and overshoot were found with a half-life of 55 sec. In the absence of CO_2, these effects vanished.

In order that the rate constants could be related, a series of competitions with ethylene and butene-1 were carried out. The results of these series are compiled in Table II. In addition to the products listed, the carbonyl band at 5.78 μ associated with compounds containing hydrogen was also observed. As the olefin:C_2F_4 ratio rises, $\Phi(CF_2O)$ diminishes.

Finally, a series was run with 500 mm. of N_2O and various mixtures of O_2 and C_2F_4. The results are listed in Table III. The $\Phi(CF_2O)$ is definitely larger than in the absence of oxygen and is about two or greater. The cyclo-C_3F_6 yield drops to zero as the oxygen:C_2F_4 ratio is enlarged.

Discussion

In the mercury-sensitized photolysis of C_2F_4, the reaction mechanism is[13,14]

$$Hg + h\nu \longrightarrow Hg^* \quad (a)$$

$$Hg^* + C_2F_4 \longrightarrow Hg + 2CF_2 \text{ (singlet)} \quad (b)$$

$$2CF_2 \text{ (singlet)} \longrightarrow C_2F_4 \quad (c)$$

$$CF_2 \text{ (singlet)} + C_2F_4 \longrightarrow \text{cyclo-}C_3F_6 \quad (d)$$

where Hg* represents the excited mercury atom. Actually a small amount of an excited C_2F_4 is formed, which does not dissociate at room temperature, and the quantum yield for reaction b must be slightly less than unity.[13] However, this reaction is of negligible significance in this study and can be ignored.

In mixtures of C_2F_4 and N_2O, a competition develops for the excited mercury atom

$$Hg^* + N_2O \longrightarrow Hg + N_2 + O \quad (e)$$

Reaction e originally was thought to occur with a quantum efficiency of 0.78,[15] but recent results favor a quantum yield of unity.[16,17]

The competition gives rise to the expression

$$\frac{1}{\Phi(N_2)} = 1 + \frac{k_b}{k_e}\frac{(C_2F_4)}{(N_2O)} \quad (1)$$

Figure 2 is a plot of $1/\Phi(N_2)$ *vs.* $(C_2F_4)/(N_2O)$. The data are quite scattered, probably owing to the small conversions obtained. However, within the scatter the results are linear with an intercept of unity and a slope of 0.31 corresponding to k_b/k_e. This latter value is listed in Table IV and is somewhat smaller than the value of 0.49 reported by Yarwood, Strausz, and Gunning.[18] There is considerable scatter in our data, so their value is to be preferred. The reciprocal quantum yields for CF_2O formation could also have been plotted on Figure 2. However, their scatter is

Table IV. Rate Constant Ratios

Ratio	Value	Source
k_b/k_e	0.31	Eq. 1, Figure 2
k_h/k_f	0.97	Eq. 2, Figure 4
k_i/k_f	4.3	Eq. 3, Figure 4
k_n/k_j	0.40	Eq. 4, Figure 5

(14) B. Atkinson, *J. Chem. Soc.*, 2684 (1952).
(15) R. J. Cvetanović, *J. Chem. Phys.*, 23, 1208 (1955).
(16) R. J. Cvetanović, W. E. Falconer, and K. R. Jennings, *ibid.*, 35, 1225 (1961).
(17) M. G. Bellas, Y. Rousseau, O.P. Strausz, and H. E. Gunning, *ibid.*, 41, 768 (1964).
(18) A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *ibid.*, 41, 1705 (1964).

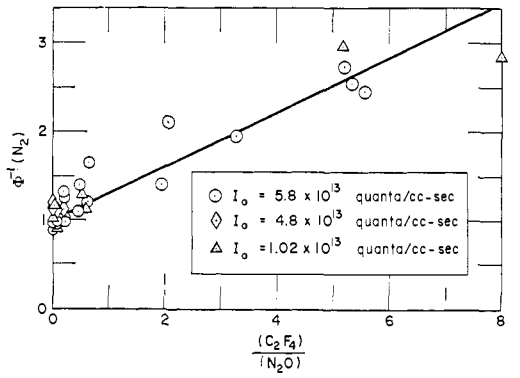

Figure 2. Plot of $\Phi^{-1}(N_2)$ *vs.* $(C_2F_4)/(N_2O)$.

worse owing to the fact that the small conversions produced only small changes in infrared absorption.

The oxygen atom is quantitatively scavenged by C_2F_4

$$O + C_2F_4 \longrightarrow CF_2O + CF_2 \text{ (triplet)} \qquad (f)$$

where reaction f might proceed *via* a C_2F_4O intermediate molecule. The stable compound $(CF_2)_2O$ has been prepared recently and its infrared spectra, as well as that of CF_3CFO, have been described.[19] No such intermediates were observed in this study. If the spin conservation rules are obeyed, then the CF_2 product should be a triplet, and we believe this to be the case.[20] If the CF_2O were produced solely by the reaction

$$C_2F_4O + C_2F_4 \longrightarrow CF_2O + \text{cyclo-}C_3F_6 \qquad (g)$$

then $\Phi(\text{cyclo-}C_3F_6) \geq \Phi(CF_2O)$, contrary to observation. Thus, reaction f must account for at least part of the CF_2O production, and probably all of it.

The $\Phi(\text{cyclo-}C_3F_6)$ shows an unexpected increase with the $(N_2O)/(C_2F_4)$ ratio. If the cyclo-C_3F_6 were produced solely from singlet CF_2 radicals, then its yield should drop about 30% as the $(N_2O)/(C_2F_4)$ ratio increases from zero to infinity. Figure 3 is a semilog plot showing the variation of $\Phi(\text{cyclo-}C_3F_6)$ with N_2O pressure with 100 mm. of C_2F_4 present. Instead of dropping as the N_2O is enlarged, $\Phi(\text{cyclo-}C_3F_6)$ rises from about 0.06 to 0.35. At 500 mm. of N_2O, the $\Phi(\text{cyclo-}C_3F_6)$ remains unchanged at a value of about 0.15 ± 0.01 for C_2F_4 pressures of 3 to 30 mm., as shown in Table I. It is not easy to explain all of these results in a detailed fashion. However, it seems clear that all the cyclo-C_3F_6 cannot be explained by reaction d. In fact, these results strongly suggest the presence of triplet CF_2 which would add rapidly to C_2F_4, although reaction g cannot be ruled out.

The rate of reaction f was measured by introducing olefins and studying the competition for the oxygen atoms. The presence of C_2H_4 or 1-C_4H_8 introduces the additional reactions

$$O + C_2H_4 \longrightarrow \text{products} \qquad (h)$$

$$O + \text{1-}C_4H_8 \longrightarrow \text{products} \qquad (i)$$

(19) V. Caglioti, M. Lenzi, and A. Mele, *Nature*, 201, 610 (1964).
(20) J. Heicklen, N. Cohen, and D. Saunders, Aerospace Corp., Report No. TDR-469(5250-40)-4 (Dec. 30, 1964); *J. Phys. Chem.*, 69, 1774 (1965).

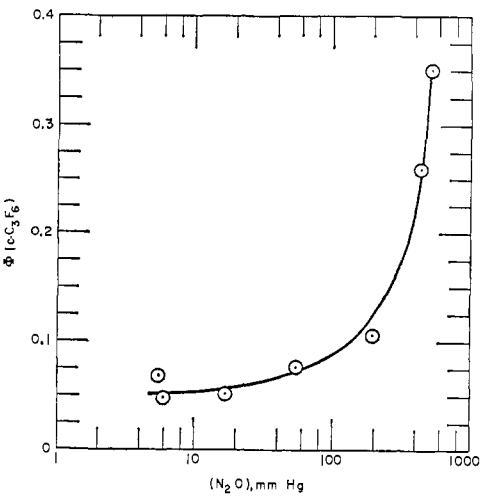

Figure 3. Semilog plot of $\Phi(\text{cyclo-}C_3F_6)$ *vs.* (N_2O) with 100 mm of C_2F_4 present.

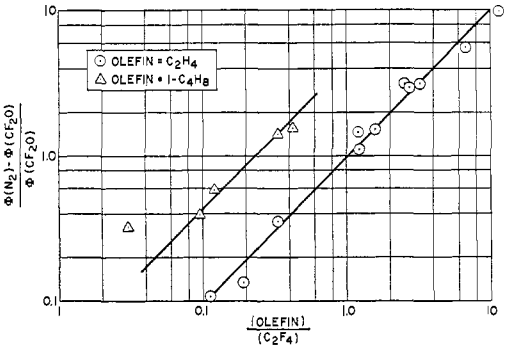

Figure 4. Log–log plot of $[\Phi(N_2) - \Phi(CF_2O)]/\Phi(CF_2O)$ *vs.* olefin : C_2F_4 ratio with 500 mm. of N_2O present.

The competition for oxygen atoms leads to the equations

$$\frac{\Phi(N_2) - \Phi(CF_2O)}{\Phi(CF_2O)} = \frac{k_h}{k_f}\frac{(C_2H_4)}{(C_2F_4)} \qquad (2)$$

or

$$\frac{\Phi(N_2) - \Phi(CF_2O)}{\Phi(CF_2O)} = \frac{k_i}{k_f}\frac{(1\text{-}C_4H_8)}{(C_2F_4)} \qquad (3)$$

The left-hand side of the equations is plotted in Figure 4 *vs.* the olefin : C_2F_4 ratio. The log–log plots are fitted with the best straight line of slope unity. The intercepts yield $k_h/k_f = 0.97$ and $k_i/k_f = 4.3$. The ratio of the latter to the former numbers is about 4.5, which is a reasonable agreement with the accepted value of 5.7 for k_i/k_h.[11] Because of the wider range of the variable available in the C_2F_4–C_2H_4 mixtures, k_h/k_f probably is more reliable than k_i/k_f. The absolute value of k_f is then nearly the same as k_h, *i.e.*, 0.60×10^9 l./mole sec.[11,21]

In the presence of molecular oxygen, $\Phi(CF_2O)$ is markedly enhanced. The details of CF_2O production are not clear from the limited results presented here but are consistent with the C_3F_6 results.[22] The indicated

(21) L. Elias and H. I. Schiff, *Can. J. Chem.*, 38, 1657 (1960).
(22) D. Saunders and J. Heicklen, Aerospace Corp., Report No. TDR-469(5250-40)-8 (Feb. 22, 1965).

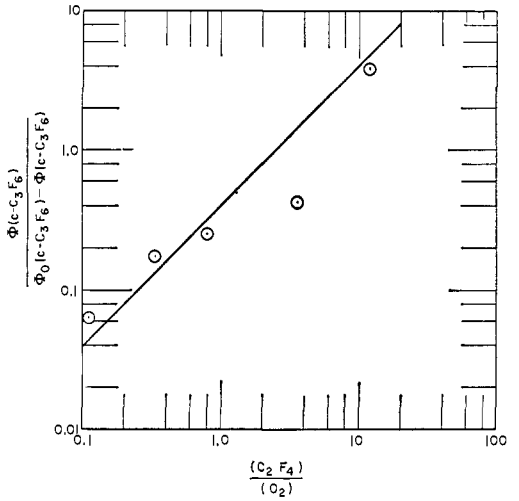

Figure 5. Log–log plot of Φ(cyclo-C_3F_6)/[Φ_0(cyclo-C_3F_6) − Φ(cyclo-C_3F_6)] *vs.* $(C_2F_4)/(O_2)$ with 500 mm. of N_2O present.

mechanism is

$$CF_2 \text{ (triplet)} + O_2 \longrightarrow CF_2O_2 \quad \text{(j)}$$

$$2CF_2O_2 \longrightarrow 2CF_2O + O_2 \quad \text{(k)}$$

$$CF_2O_2 + C_2F_4 \longrightarrow 2CF_2O + CF_2 \text{ (triplet)} \quad \text{(l)}$$

If the intermediate C_2F_4O is present, then it too could be scavenged by O_2 and produced by CF_2O_2 attack on C_2F_4. The ozone-producing reaction has been investigated by many workers.[23-28] The results have been critically analyzed by Leighton[29] and by Kaufman.[10] The generally accepted rate constant is about 10^8 l.^{2}/mole^2 sec. Under our conditions, this reaction would be considerably less important than (f), but could play some role at high $(O_2):(C_2F_4)$ ratios.

$$M + O + O_2 \longrightarrow O_3 + M \quad \text{(m)}$$

As the $O_2:C_2F_4$ ratio is enhanced, the cyclo-C_3F_6 diminishes. This can be explained by a competition between the O_2 and C_2F_4 for triplet CF_2

$$CF_2 \text{ (triplet)} + C_2F_4 \longrightarrow \text{cyclo-}C_3F_6 \quad \text{(n)}$$

In the presence of excess N_2O, the competition leads to the approximate result

$$\frac{\Phi(\text{cyclo-}C_3F_6)}{\Phi_0(\text{cyclo-}C_3F_6) - \Phi(\text{cyclo-}C_3F_6)} \approx \frac{k_n}{k_j}\frac{(C_2F_4)}{(O_2)} \quad (4)$$

where Φ_0(cyclo-C_3F_6) is the quantum yield of cyclo-C_3F_6 in the absence of O_2. Figure 5 shows a log–log graph of the left-hand side of eq. 4 *vs.* $(C_2F_4)/(O_2)$. The best straight line of slope unity is plotted. The intercept yields a value of 0.40 for k_n/k_j.

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(23) S. W. Benson and A. E. Axworthy, Jr., *J. Chem. Phys.*, **26**, 1718 (1957).
(24) F. Kaufman, *Proc. Roy. Soc.* (London), **A247**, 123 (1958).
(25) F. Kaufman, *J. Chem. Phys.*, **28**, 352 (1958).
(26) L. Elias, E. A. Ogryzlo, and H. I. Schiff, *Can. J. Chem.*, **37**, 1680 (1959).
(27) J. A. Zaslowsky, H. B. Urbach, F. Leighton, R. J. Wnuk, and J. A. Wojtowicz, *J. Am. Chem. Soc.*, **82**, 2682 (1960).
(28) P. G. Dickens, R. D. Gould, J. W. Linnett, and A. Richmond, *Nature*, **187**, 686 (1960).
(29) P. A. Leighton, "Photochemistry of Air Pollution" Academic Press Inc., New York, N. Y., 1961, p. 116.

Electron Paramagnetic Resonance Studies of Irradiated γ-Silica in Static Systems and under Dynamic Flow Conditions

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An electron spin resonance study has been carried out on the interaction of irradiated silica with oxygen, nitric oxide, and a number of gases. The appearance of a doublet characterized the adsorption of the oxygen and nitric oxide, and this was shown to be due to the relaxation of spins on the surface of the irradiated silica. A flow system was developed to study by pulse techniques the interaction of gases with the solid.

Introduction

Electron spin resonance has been used to study the effect of high energy radiations on surfaces[1-6] and also the effect of adsorbed gases in static systems.[7]

The present investigation is a study of the effects of oxygen and nitric oxide and a number of other gases on the electron spin resonance signal of irradiated silica in static systems and under dynamic flow conditions. The latter type of investigation permits the observation of transients that occur when a pulse of a gas passes over a surface.

Experimental

Materials. Silica gel was prepared by hydrolysis of ethyl orthosilicate and was evacuated at 600° and 10^{-5} mm. for 12 hr. The ethyl orthosilicate (Fisher Laboratory chemical) was distilled before the hy-

(1) H. W. Kohn, *Nature*, **184**, 630 (1959).
(2) V. B. Kazansky, G. B. Parisky, and V. V. Voevodsky, *Discussions Faraday Soc.*, **31**, 203 (1961).
(3) P. H. Emmett, R. Livingston, H. Zeldes, and R. J. Kokes, *J. Phys. Chem.*, **66**, 921 (1962).
(4) H. W. Kohn and E. H. Taylor, *Actes Congr. Intern. Catalyse, 2e, Paris*, 2, 1461 (1962).
(5) H. W. Kohn, *J. Phys. Chem.*, **66**, 1185 (1962).
(6) C. Barter and C. D. Wagner, *ibid.*, **68**, 2381 (1964).
(7) F. Nozaki, D. Stamires, and J. Turkevich, *Actes Congr. Intern. Catalyse, Amsterdam*, in press.