Rate Parameters for Reactions of Ground-State Difluorocarbene and Determination of the Absolute Intensity of the $\tilde{A^1}B_1 - \tilde{X^1}A_1$ Absorption Bands

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Received 17th October, 1968

An effective extinction coefficient (to base 10) of 7620 ± 400 l. mole⁻¹ cm⁻¹ at 298°K was derived for the band maximum of CF₂ at 249 nm, by measuring the intensity of the $\tilde{A}({}^{1}B_{1}) - \tilde{X}({}^{1}A_{1})$ system after flash photolysis of NO₂ in mixtures containing C₂F₄ and N₂. The oscillator strength of the transition was 0.028 ± 10 %. The decay of CF₂ was studied in flashed C₂F₄+N₂ and CF₂CFCl+N₂ mixtures and rate parameters for the dimerization were recorded :

 $k_1 = (2.5 \pm 0.5) 10^6 T^{\frac{1}{2}} \exp(-200 \pm 50/T(^{\circ}\text{K})) \text{ l. mole}^{-1} \sec^{-1}$.

An approximate rate constant for reaction of CF₂ with CFCl at 298°K is $6(\pm 5)10^8$ l. mole⁻¹ sec⁻¹. Data for the reaction (2) of CF₂ with C₂F₄ were combined with the value for k_1 , to obtain

 $k_2 = (8.7)10^4 T^{\frac{1}{2}} \exp(-3200 \pm 625/T(^{\circ}\text{K})) \text{ l. mole}^{-1} \text{ sec}^{-1}.$

The dimerization of difluorocarbene

$$CF_2 + CF_2 \rightarrow C_2F_4 \tag{1}$$

is a dominant process for removal of CF_2 throughout the range of gas-phase conditions so far investigated. The kinetics were studied by Dalby ¹ who monitored the absorption spectrum photoelectrically after flash photolysis of C_2F_4 or $CF_3CF:CF_2$. The decay follows a second-order rate equation in the temperature range 298-572°K and was unaffected by addition of ~1 atm Ar. Arrhenius parameters for k_1 were derived from measurements of the rate of decrease of CF_2 intensity in the band at 249 nm, the absolute intensity of this band being estimated from the yield of C_2F_4 in flashed $CF_3CF:CF_2$. The rate constant defined by

$$d[CF_2]/dt = -2k_1[CF_2]^2$$
(A)

was (8.5) 10⁶ l. mole⁻¹ sec⁻¹ (\pm 75 %) at 298°K.

In the liquid phase, CF_2 adds to unsaturated C---C bonds, but only one reaction of this type has been studied quantitatively in the gas phase, namely the addition to C_2F_4 :

$$CF_2 + C_2F_4 \rightarrow cyclo - C_3F_6. \tag{2}$$

Values of $k_2k_1^{-\frac{1}{2}}$ agreeing to a factor of 2 are now available from the steady-state kinetics of systems in which CF₂ was produced by different methods ²⁻⁴ at temperatures from 298-550°K. CF₂ adducts with C₂H₄ and C₄-olefins ⁵ have been reported in systems where free CF₂ was probably present, and CF₂O is formed in flashphotolyzed C₂F₄+O₂ mixtures.^{1, 6} Reactions of singlet CF₂ with olefins or O₂ are slow ¹ in comparison with reaction (1). In order to obtain more accurate values of k_1 required for evaluation of k_2 , and to provide a basis for determination of other rate constants, the dimerization has been re-investigated in flash-photolyzed C₂F₄

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and CF₂CFCl. A new method has been developed for measuring the absolute intensity of the CF₂ band spectrum in flashed $NO_2+C_2F_4+N_2$ mixtures. The result is independent of reaction (1), and the value derived for the oscillator strength of the transition is in good agreement with shock-tube measurements.⁷

In the following text, all optical densities and effective extinction coefficients are decadic, and k_1 is defined by eqn. (A). It was found practical to retain the torr as an experimental unit of concentration: 1 torr = $(1.603)10^{-2}/T(^{\circ}K)$ mole 1.⁻¹.

EXPERIMENTAL

The essential details of the flash photolysis apparatus have been recorded.⁶ When it was desired to photolyze the fluoroethylenes directly, a quartz cell (int. diam. 2.5 cm) was used; for the work with NO₂, the photolytic light was restricted to $\lambda \ge 300$ nm by means of a Pyrex cell (int. diam. 2.0 cm) to avoid photolysis of the fluorethylenes, and to ensure that O(2¹D) was not formed by photolysis of the NO₂. The optical pathlength of each cell and the photolamp (flash energies 1070-1350 J) was 78 cm. The dispersion of the Hilger Quartz Littrow spectrograph was 0.25 nm/mm in the region of 250 nm.

Ilford HP3 plates and Kodak Panchro-Royal film sheets were developed for 3 min in Ilford Contrast FF developer, diluted 1+4, and plate densities were obtained with a Joyce-Loebl recording microdensitometer. The density-logarithmic exposure relationship was determined for individual plates and films by exposure to the output of the spectroscopic flash-lamp through a step-wedge.

In most experiments an excess of N₂, usually 50 torr, was present in the reaction mixture to prevent flash heating. Although the photolysis products in C₂F₄ carry 65 kcal/mole (= 3.5 eV) for $\lambda = 200 \text{ nm}$, and the C₂F₄ formed by dimerization of CF₂ carries 78 kcal/ mole, there was no evidence of temperature rises in the mixtures (e.g., vibrationally excited CF₂ was not observed, although weak "hot" bands in the $v_2'' = 1$ progression appeared in the experiments at 416 and 446°K.)

MATERIALS

The preparation of C_2F_4 and its subsequent purification have been described.⁶ Infrared and gas-chromatographic analysis showed that the product contained about 1 % $CF_3CF:CF_2$, which is insignificant, since it would not be photolyzed in the presence of excess C_2F_4 , and is unlikely to react appreciably with CF_2 under flash photolyis conditions (i.e., high CF_2 concentrations and low C_3F_6 concentrations, which both favour decay of CF_2 by reaction (1)). NO₂ and CF_2CFCl (Matheson) were purified by low-temperature distillation; in prepararing mixtures containing NO₂, a small correction was made for the equilibrium with N_2O_4 . N_2 (B.O.C. " O_2 free "), O_2 (B.O.C.) and He were dried before use by slow passage through a packed trap at 77°K. C_2H_4 (B.O.C., grade X) and $CH_3CH:CH_2$ (Calor Gas Co. Ltd.) were distilled in the vacuum system and used without further treatment.

RESULTS AND DISCUSSION

ABSOLUTE INTENSITY OF THE CF_2 bands

The absorption spectrum of CF_2 near 250 nm has been analyzed by Mathews,⁸ who obtained rotational constants, revised an earlier vibrational numbering scheme and confirmed the theoretical prediction of Simons ⁹ that the upper electronic state has ${}^{1}B_1$ symmetry. At room temperature, the spectrum consists of a progression in the upper state bending vibration, and Mathews showed that the diffuse appearance of bands with $v'_2 > 9$, previously believed to be evidence of predissociation, ¹⁰ actually results from local complexities in the spectrum. Under moderate dispersion, the rotational structure at the band centres is not resolved and the intensity is directly

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proportional to the pathlength.⁶ Thus it is convenient to define an effective extinction coefficient $\varepsilon_{\lambda}^{T}$ for a temperature of $T^{\circ}K$, such that $D_{\max} = \varepsilon_{\lambda}^{T}[CF_{2}]l$, where D_{\max} is the optical density observed for a particular band maximum at λ nm, and l is the optical pathlength. Values of D_{\max} were independent of the slit-width of the spectrograph from 0.025 to 0.2 nm, in experiments where the background intensity was kept roughly constant by means of the step wedge, mounted in front of the spectrograph slit. There was no significant variation of density with pressures of added N₂ between 25 and 250 torr.

The optical density at 249 nm was followed in repeatedly flashed single samples of $NO_2 + C_2F_4 + N_2$ (fig. 1), with a delay time of 584 μ sec, by which time a negligible amount of CF₂ has dimerized. CF₂ is not formed when C₂F₄ is irradiated with light filtered through Pyrex, and atomic oxygen is formed by NO₂ photolysis only in the ground state. The details of the reaction scheme were elucidated by Heicklen and collaborators ^{11, 12} from Hg-photosensitization of N₂O in the presence of C₂F₄, and the processes producing ground state CF₂ were found to be

$$O(2^{3}P) + C_{2}F_{4} \rightarrow CF_{2}^{*} + CF_{2}O$$
(3)

$$CF_2^* + CF_2^* \rightarrow CF_2 + CF_2 \tag{4}$$

$$CF_2^* + M \to CF_2 + M. \tag{5}$$

There is a second primary reaction,

$$O(2^{3}P) + C_{2}F_{4} \rightarrow C_{2}F_{4}O^{*}$$

$$\tag{6}$$

forming an excited epoxide, which is scavenged rapidly by C_2F_4 and does not release CF_2 . At 23°C, $k_3/(k_3+k_6) = 0.85$ and at ~125°C, it is 0.90. In accordance with the spin conservation rule, it was proposed that the CF_2 was formed in a triplet state. The appearance of ground state CF_2 in flash photolysis experiments ⁶ is too rapid to be due to reaction (4), and it therefore must be produced either directly, or by deactivation according to (5). If no process other than (3) or (6) removes $O(2^{3}P)$, and if NO₂ is destroyed only by photolysis, the yield of CF_2 is $k_3/(k_3+k_6)$ times the amount of NO₂ photolyzed. The area under curves such as those in fig. 1, extrapolated to an infinite number of flashes, is therefore the optical density corresponding to a concentration of CF_2 equal to the initial $[NO_2]$ times $k_3/(k_3+k_6)$. In fact, a small correction was necessary because

$$O(2^{3}P) + NO_{2} \rightarrow NO + O_{2} \tag{7}$$

is rapid ¹³ and competes with (3) and (6) even at the highest pressures of C_2F_4 that were used (~40 torr). Rate data for reactions of NO with NO₂ and O₂ collected by Heicklen and Cohen ¹⁴ confirm that these processes are negligible for low partial pressures and for experiments lasting less than 30 min. Although NO bands could be observed after flashing, they were too weak to be photometered as a check on the amount of NO₂ decomposed.

Extinction coefficients were derived from the slopes of the plots shown in fig. 2, in which the CF₂ intensities are corrected for reaction (7), and allowance is made for reaction (6) in the effective NO₂ concentrations. Haszeldine ¹⁵ has described reactions of C₂F₄ with NO₂ at high pressures and ~60°C, which may account for the fall-off in the data obtained at 143°C; mixtures of NO₂ and C₂F₄ bleach overnight even at low total pressures (~50 torr), so that rapid reaction would be expected at higher temperatures. The scatter in the results probably arises mainly in the calibration of plate sensitivity, due to random variations in the output of the spectroscopic flashlamp.

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FIG. 1.—CF₂ intensity in repeatedly flashed NO₂+C₂F₄+N₂ mixtures, 298°K. Flash energies 1070-1350 J. Partial pressures of NO₂ and C₂F₄ respectively: ○, 0.174 and 25; ①, 0.127 and 25; ①, 0.070 and 10. Total pressure made up to 50 torr by addition of N₂.



FIG. 2.—CF₂ intensity against corrected NO₂ concentration. $T(^{\circ}K): \bigcirc, 298; \bullet, 416.$

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Similar results were also obtained for the band at 246 nm (table 1); from the average of several hundred measurements, ε_{246} was found to be 1.03 ε_{249} . Values of the extinction coefficients at 346 and 446°K were extrapolated from all four measured values of ε . A print in Mathew's paper ⁹ shows well that bands of CF₂ with $v_2'' = 1$ contribute no intensity at the centres of the $v_2'' = 0$ bands, and it was

TABLE	1.—Observed	AND EXTRA	POLATED	EFFECTIVE EXT	INCTION	COEFFICIENTS	FOR	CF_2
	<i>T</i> (°K)		ε249 nm	(l. mole ⁻¹ cm ⁻¹)	8246 nm	(l. mole ⁻¹ cm ⁻¹)		
	(±3°)	$\epsilon T_{/\epsilon} 0$	obs	extrap.	obs.	extrap.		
	298	0.956	7600	7620	7900	7850		
	346	0.926		7380		7600		
	416	0.872	6930	6950	7270	7160		
	446	0.846		6740		694 0		

Table 2.—Relative intensities and bandwidths in the absorption spectrum of CF_2

λ (nm)	v'2	Irel	Δv (cm ⁻¹)	λ (nm)	v'2	Irel	$\Delta \nu$ (cm ⁻¹)
265.1	1	0.05	150	245.8	7	1.03	290
261.7	2	0.16	210	242.8	8	0.82	290
258.3	3	0.20	210	239.9	9	0.58	210
255.1	4	0.80	250	237.0	10	0.42	210
251.9	5	0.87	260	234.3	11	0.28	200
248.8	6	(1)	270				

assumed in the extrapolation that there was a Boltzmann distribution amongst ground state levels of frequency ¹⁶: 1102 (v_1) , 665 (v_2) , 1222 (v_3) and 1330 $(2v_2)$ cm⁻¹, and that the observed intensity arose only from ground state 0 levels. Thus,

$$\varepsilon^{T} = \varepsilon^{0}[1 - \exp(-665hc/kT) - \exp(-1102hc/kT) - \exp(-1222hc/kT) -$$

 $\exp(-1330hc/kT)$].

There was no evidence for rotational spreading of the bands at 143°C, or of alteration in the relative intensities of the band maxima. Table 1 shows that there was good agreement between extrapolated and observed intensities; the uncertainties in the ε values are estimated to be ± 5 %.

Relative intensities of the bands in the v'_2 progression are listed in table 2; the band with $v'_2 = 12$ could be observed but not measured, because of the low plate sensitivity at 232 nm. By measuring the areas under peaks on microdensitometer traces, and allowing for variation of plate sensitivity with wavelength, the integrated absorption coefficient was 6.57×10^6 l. mole⁻¹. This result is probably slightly low, because the intensities of the ${}^{r}R_{K}$ ($K \gtrsim 6$) subbands and of weak bands with v'_{1} or $v'_{3} \neq 0$ were neglected. The oscillator strength is given by

$$f^{e} = 4.323 \times 10^{-9} \int \varepsilon_{v} \mathrm{d}v$$

for ε in l. mole⁻¹ cm⁻¹ and v in cm⁻¹. The resulting value of the oscillator strength is 0.028 ± 10 %, which can be compared with shock tube estimates ⁷ from C₂F₄ $(f = 0.034, 1804^{\circ}\text{K})$, CF₂Cl₂ $(f = 0.032, 2085^{\circ}\text{K})$ and CF₄ $(f = 0.024, 2878^{\circ}\text{K})$. In theory, these are temperature independent; the average value, 0.030 ± 0.003 , agrees well with the value reported here.

Dalby ¹ derived a value $\varepsilon_{249} = 2000 \pm 800 \,\text{l.}$ mole⁻¹ cm⁻¹ by extrapolating the intensity of this band to zero time in flashed CF₃CF:CF₂ and measuring the yield of C₂F₄. The *f* value was estimated to be 0.01. It will be proposed subsequently

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that excited C_2F_4 molecules are present in flashed C_2F_4 . If the photolysis of CF_3CF : CF_2 also involves excited molecules, the yield of C_2F_4 might not correlate directly with $[CF_2]_0/2$. A further complication is indicated by the faster decay of CF_2 observed in perfluoropropene than in C_2F_4 . The value of ε_{249} could be up to three times too small, if CF_2 were formed by elision from CF_3 —C, or if it were formed together with CF_3CF which rearranged to C_2F_4 . (The analogous reaction of CF_3CH has been reported.¹⁷) Dalby also noted that the CF_2 intensity varied with the slit-width of his spectrograph, which suggests that the bands were not obeying a strict Beer-Lambert relation under low resolution. This may explain the wide variation in his measured values of k_1/ε_{249} , as well as the discrepancy in the two proposals for ε_{249} . The *f*-value reported here and hence the extinction coefficient, are well substantiated by the shock tube experiments.

KINETICS OF CF_2 DECAY

Once the absolute intensity of the CF_2 spectrum was determined, rate constants for reaction (1) could be measured. For second-order decay, the slope of a plot of the reciprocal of CF₂ optical density against time equals $2k_1/\epsilon l$. With the total pressure of $C_2F_4 < 1.0$ torr, the CF_2 intensity at short delay times was proportional to the C_2F_4 concentration (~2.5 % decomposition), under which conditions CF_2 must be produced homogeneously. Dalby¹ and Simons and Yarwood¹⁸ both noted that the decay rate of CF₂ is independent of total pressure, i.e., diffusion to surfaces and three-body recombination are unimportant. For an initial CF₂ concentration of 10⁻⁶ mole 1.⁻¹, the maximum rate of removal by diffusion to the cell walls through 50 torr N_2 would correspond to less than 10 % of the observed slope of the second-order decay plots. The decay rate was not altered by changing the diluent from 50 torr N_2 to 280 torr N_2 or 50 torr He, and in subsequent experiments the total pressure of reaction mixtures was made up to 50 torr by addition of N_2 , apart from some experiments with reactive "diluents", described below. The substrates were present in concentrations of 0.2-2.5 torr (C₂F₄) and 1.25-10 torr (CF₂CFCl). In every experiment with C_2F_4 and for CF₂CFCl at long delay times, the decay followed second-order kinetics (fig. 3 and 4); rate data are summarized in table 3. At short delay times, CF₂ decays more rapidly in flashed CF₂CFCl, and this is probably due to the reaction,

$$CF_2 + CFCl \rightarrow CF_2 CFCl. \tag{8}$$

An approximate value of $k_8 = (6\pm 5)10^8$ l. mole⁻¹ sec⁻¹ at 298°K was derived, assuming that CF₂ and CFCl are produced only by direct photolysis, and that they do not react with the substrates under flash photolysis conditions.

The data of table 3 were fitted by least mean squares to the equation :

 $k_1 = (2.5 \pm 0.5) 10^6 T^{\frac{1}{2}} \exp(-200 \pm 50/T(^{\circ}\text{K})) \text{ l. mole}^{-1} \text{ sec}^{-1}.$

It was not possible to follow the reaction through a sufficient temperature range to establish an analytical temperature dependence of the pre-exponential factor; thus the data can be fitted to

$$k_1 = (7.8 \pm 4.0) 10^{10} T^{-1} \exp(-750 \pm 50/T(^{\circ} K)) 1$$
. mole⁻¹ sec⁻¹.

Dalby ¹ assumed a collision diameter of 4×10^{-8} cm for CF₂ and derived an expression for the collision frequency

$$Z = 3.3 \times 10^{10} T^{\frac{1}{2}}$$
 l. mole⁻¹ sec⁻¹.

Accepting the first expression of k_1 , the corresponding steric factor is 7.5×10^{-5} . The activation energy is 400 ± 100 cal/mole = 0.017 ± 0.004 eV (with quoted error







FIG. 4.—Decay with time of optical density of CF_2 (249 nm), in flash-photolyzed mixtures containing 2.5 torr C_2F_4 and 47.5 torr N_2 . For clarity, the curves have been successively displaced upwards by 0.5 units. $T(^{\circ}K); \bigcirc, 446; \bigoplus, 416; \bigoplus, 346$.

limits derived from twice the standard deviations of the experimental points), which is smaller than the value reported by Dalby,¹ of 1.2 kcal/mole. This discrepancy arises mainly from Dalby's neglect of the change of ε with temperature.

Simons ⁹ has convincingly explained the slow recombination of CF_2 by considering the avoided crossing of two ${}^{1}A_{g}$ states of C_2F_4 arising from $2CF_2({}^{1}A_1)$ (repulsive) and $2CF_2({}^{3}B_1)$ (bonding). The experimental activation energy is smaller than would be expected for such a model (i.e., it suggests a very long C—C separation in the transition state), which may indicate that the conventional $T^{\frac{1}{2}}$ dependence of the pre-exponential factor is inadequate. The concept of an avoided crossing may be an oversimplification: the crossing cannot be avoided for all configurations of excited C_2F_4 , as this would preclude the formation of two ground-state CF_2 molecules by photolysis of C_2F_4 .

TABLE 3.—RATE DATA FOR DECAY OF CF2

T(°K) (±3°)	$\frac{2k_1/\epsilon_{249}}{(\text{cm sec}^{-1})}$	$2k_1/\epsilon_{246}$ (cm sec ⁻¹)	no. of determinations	$10^{-7} k_1$ (1. mole ⁻¹ sec ⁻¹)
298	5630 ± 400	5570 ± 400	10	$2 \cdot 17 \pm 0 \cdot 2$
346	$7020\pm\!600$	$6750\pm\!300$	4	2.58 ± 0.2
416	$8700\pm\!600$	$8500\pm\!600$	7	3.05 ± 0.2
446	10000 ± 500	9790 ± 500	5	3.38 ± 0.2

Edwards and Small¹⁹ have studied CF₂HCl pyrolysis at 533-750°C, and found $k_1 = 10^{9.94}$ l. mole⁻¹ sec⁻¹, with no energy of activation. Their data leads to a value of the equilibrium constant for C₂F₄ dissociation different from that of Zmbov, Uy and Margrave,²⁰ and so may be incorrect. Zmbov, Uy and Margrave²⁰ also determined $\Delta H = 76.3 \pm 3$ kcal/mole for the heat of dissociation of C₂F₄, and confirmed the value²¹ from shock tube measurements of -39.7 ± 3 kcal/mole for the heat of formation of CF₂.

EXPERIMENTS WITH ADDED O_2

Dalby ¹ found that the decay rate of CF_2 in flashed C_2F_4 was not affected by addition of O_2 , although CF_2O was a product. Oxygen increases the extent of decomposition after flashing C_2F_4 and it was suggested ⁶ that a process such

$$CF_2 + O_2 \rightarrow CF_2O + O \tag{9}$$

might not be detected, since reaction (3) would rapidly return CF_2 to the system. The analogous reactions of CF_2CFCl and CF_2CCl_2 do not form CF_2 , but these substances are not suitable for investigation of reaction (9) because they explode after flashing in the presence of O_2 . When a mixture containing 2.5 torr C_2F_4 , 10 torr O_2 and 37.5 torr N_2 was flashed at 145°C, there was a sudden transient pressure rise of about 15 %, measured by means of a glass spiral gauge connected to the cell. Similar effects were noted in room temperature experiments with the two chlorofluoroethylenes. The rate of decay of CF_2 was not significantly different from the results with N_2 alone, and the "hot" CF_2 bands were not enhanced, suggesting that there was little or no overall temperature rise. As the reaction vessel was separated by ~2 cm of air from the photo-lamp, it is unlikely that appreciable quantities of light were absorbed by O_2 in the cell. It follows that O_2 must react either with CF_2 or with excited C_2F_4 molecules, formed by reaction (1), or directly, by absorption of light. It has also been proposed that metastable C_2F_4 molecules are formed and react with O_2 during continuous photolysis experiments with $C_2F_4+O_2$ mixtures at 185 or 254 nm.²¹ Further evidence for participation of

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excited C_2F_4 is provided by measurements of the extent of decomposition of C_2F_4 + N_2 mixtures, by repeated flashing of a single mixture. The observed values (~2 %) are about 10³ times greater than would be expected from the values of k_1 and k_2 determined here.

Herzberg ¹⁶ discusses the correlation between the first few orbitals of CH_2 and those of C_2H_4 , and his diagram can be adapted for C_2F_4 . The order of the orbitals



FIG. 5.—Predicted low-lying orbitals of C₂F₄, not drawn to scale.



FIG. 6.—Rate data for the reaction $CF_2+C_2F_4 \rightarrow cyclo-C_3F_6$, from references : \bullet , 26, \bigcirc , 2, \triangle , 3 and \oplus , 25.

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is influenced by interaction between orbitals of like symmetry, and as there are many more orbitals to consider in C_2F_4 than in C_2H_4 , the relative order of some of the orbitals as set out in fig. 5 may be inexact. The $6a_1$ orbitals of $2CF_2$ become σ bonding and σ -antibonding in C_2F_4 , and the $2b_1$ orbitals become π -bonding and π -antibonding. According to fig. 5, the ground state is $\dots (2b_{3u})$,² \tilde{X}^1A_g , and the first optical transition is to $\dots (2b_{3u})(2b_{2g})$, \tilde{A}^1B_{1u} . Walsh ²² has shown that the first absorption of C_2Cl_4 has also a ${}^1B_{1u}$ upper state. Two ground-state CF_2 molecules correlate with $C_2F_4 \dots (6b_{1u})$,² 1A_g and formation of two ground state CF_2 molecules in C_2F_4 photolysis must involve this state. For small C—C separations (~1.5 Å) it must therefore lie at energies close to those of the \tilde{A} state. Since $2b_{3u}$ lies below $6b_{1u}$, the state $\dots (2b_{3u})(6b_{1u})$, ${}^1B_{2g}$ must lie below \tilde{A} . Although the ${}^1B_{2g}$ state may weakly interact with the ground state through $v_8(b_{2g})$, it is optically metastable, and may be the metastable state postulated above. It has been suggested that metastable molecules are products of Hg-sensitization of C_2F_4 . These are probably triplets and fig. 5 indicates that they might be the lowest ${}^3B_{2g}$ or ${}^3B_{1u}$ states, the former being spin-orbit coupled to the ground state.

EXPERIMENTS WITH ADDED OLEFINS

Ethylene had no effect on the decay rate of CF_2 in flashed C_2F_4 at 298°K. At 145°C, the rate of disappearance of CF_2 decreased by 10 % when 5 or 12.5 torr C_2H_4 was present. Reaction (1) produces C_2F_4 molecules which initially carry ~78 kcal/mole excess energy, and possibly a reaction such as

$$C_2F_4^* + C_2H_4 \rightarrow C_3H_4F_2 + CF_2$$
 (10)

returns CF₂ to the system, decreasing the net decay rate. The invariance of the effective decay rate when different partial pressures of C_2H_4 were present suggests that there is a parallel deactivation of $C_2F_4^*$, and that $k_{10}/k_{deactivation} \sim 0.25$ at 145°C. This reaction is consistent with the tentative assignment of a $C_3H_4F_2$ product by Atkinson and McKeagan⁴ when CF₂ was generated in the presence of C_2H_4 and also with the work of Fielding and Pritchard,²⁴ who found no evidence at 250°C for reaction of CF₂ with C_2H_4 (under low concentrations, when $C_2F_4^*$ would form slowly, it at all.)

Unexpectedly, the concentration of CF_2 present 584 μ sec after flashing C_2F_3Cl was decreased by addition of C_2H_4 or CH_3CHCH_2 to reaction mixtures. It was expected that CFCl would be scavenged by the olefins, and suppression of reaction (8) would therefore increase the CF_2 yields. As the two olefins were approximately equally effective, the phenomenon cannot result from screening of the CF_2CFCl absorption spectrum by the olefins, indicating that a precursor of the CF_2 is deactivated or chemically destroyed by the olefins.

RATE CONSTANTS FOR THE REACTION OF CF_2 with C_2F_4

Reaction (2) was investigated by Atkinson²⁵ in the Hg-sensitization of C_2F_4 and further rate data were obtained at higher temperatures by Cohen and Heicklen. The reaction has also been followed in the pyrolysis of $C_2F_4O^3$ and cyclo- C_3F_6 ,⁴ which are believed to release free CF_2 . In Hg-sensitized $N_2O+C_2F_4$ mixtures, CF_2 is released by reaction (3),²⁶ but the major source of cyclo- C_3F_6 is

$$C_2F_4O^* + C_2F_4 \rightarrow CF_2O + cyclo - C_3F_6.$$
(11)

In each set of experiments, CF_2 reacts both with itself and with C_2F_4 and steady-state treatment of the kinetics provides values of $k_2k_1^{-\frac{1}{2}}$ which are collected in fig. 6.

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(The datum of Lenzi and Mele³ is corrected for the definition of k_1 adopted here.) Assuming a $T^{\frac{1}{2}}$ dependence, the data are fitted to

$$k_2 k_1^{-\frac{1}{2}} = 55T^{\frac{1}{2}} \exp(-3100 \pm 600/T(^{\circ}\text{K}))$$
 1. mole^{- $\frac{1}{2} sec- $\frac{1}{2}$$} .

Therefore

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$$k_2 = 8.7 \times 10^4 T^{\frac{1}{2}} \exp(-3200 \pm 625/T(^{\circ}K))$$
 1. mole⁻¹ sec⁻¹

The work of Atkinson and McKeagan has been extended ²⁷ and supports this activation energy, but suggests a pre-exponential factor about twice as large. The good agreement of $k_2k_1^{-\frac{1}{2}}$ values in these systems suggests that excited C_2F_4 molecules do not interfere with the results, or that they are deactivated in each case.

This work was supported by Science Research Council maintenance and equipment grants. Helpful correspondence with Dr. B. Atkinson, F. W. Dalby and A. P. Modica is gratefully acknowledged. A referee is thanked for correcting an error in the order of the orbitals in C_2F_4 .

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