The Role of Chlorofluorocarbene in the Photolysis and Light-induced Oxidation of Chlorotrifluoroethylene

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A NEW, very weak, band-spectrum has been observed in flash photolysis experiments with chlorotrifluoroethylene vapour, of which the main feature (Table) is a progression of bands with an average spacing of 386 cm.$^{-1}$. Under isothermal conditions (50—100 torr N_2 present) the spectrum persists for *ca.* 1 msec. after the photolytic flash and it is assigned to the free chlorofluorocarbene (CFCl) molecule, since (*a*) the absorption bands of CF_2 also appear, very intensely, and therefore CFCl is expected also to form,† (*b*) the vibrational spacing and electronic excitation energy lie between the values reported for CF_2[1] and CCl_2,[2] and (*c*) the decay of the spectrum is accelerated with addition of small partial pressures of ethylene, propene, or oxygen, which could react with CFCl. The similarities in the spectra suggest that, like CF_2 and CCl_2, CFCl possesses a singlet electronic ground-state. There seems to be no analogue in CFCl above λ 2350 Å of the intense u.v. systems of the iso-electronic molecule, NOCl.

A sudden temporary pressure rise occurred after flashing C_2F_3Cl (5—10 torr) in excess of O_2 (25—100 torr) and transient absorption bands of vibrationally-excited oxygen were observed ($2500 < \lambda < 2800$ Å), decaying in about 75 μsec. Continuous absorption ($\lambda < 2500$ Å) also set in and may be due to hot chlorocarbonyl fluoride, which is an ultimate product and is known to absorb in this region.[3] The lifetime of the CF_2 spectrum was not affected appreciably by the addition of oxygen. Continuous photolysis

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† The i.r. spectra from products of C_2F_3Cl–O_2 and C_2F_3Cl–H_2 mixtures show weak bands of CFClO and H_2CFCl respectively, providing further evidence for generation of free CFCl.

Band centres in CFCl *absorption spectrum*

I*	λ_{air} (Å)	ν_{vac} (cm.$^{-1}$)
4	3736·1	26758
5	3725·2	26837
8	3683·7	27139
4	3662	25300
9	3632·0	27525
4	3595·0	27808
10	3582·7	27904
6	3532·6	28292
5	3499	28571
5	3485	28686
2	3466	28843

* Approximate intensities, from visual examination of a print. Spectra were photographed in a Hilger Large Quartz spectrograph.

(λ 2288 Å) of 20 torr C_2F_3Cl and 80 torr O_2 led to rapid and almost complete conversion to CFClO and CF_2O and no C_2F_4 was formed; a mixture of 250 torr each of C_2F_3Cl and O_2 exploded shortly after commencement of irradiation.

There is evidently a direct reaction of CFCl with oxygen at room temperature, in contrast to CF_2,[4] and the process is probably

$$CFCl + O_2 \rightarrow CFClO + O \qquad (1)$$

CF_2O being formed in subsequent reactions of atomic oxygen with the substrate, since CF_2 apparently is inert in this system. The reaction of C_2F_3Cl with $O(2^3P)$ has been studied directly by long wavelength photolysis of mixtures with NO_2. No CF_2 was observed in flashed C_2F_3Cl–NO_2–N_2 mixtures over a wide range of isothermal conditions; both CF_2O and CFClO were shown not to be formed by i.r. analysis of the products immediately after photolysis. Four intense bands appeared at 1165, 910, 785, and 725 cm.$^{-1}$ and are assigned to trifluorochloroethylene epoxide, by comparison with the spectrum of tetrafluoroethylene epoxide.[5] Absorption bands of the isomer, chlorodifluoroacetyl fluoride were not detected.[6] The spectrum of CF_2 appears *slowly* after flash photolysis of C_2F_4–NO_2 mixtures, and both carbonyl fluoride and tetrafluoroethylene epoxide are formed. Evidently the initial adduct of $O(2^3P)$ with C_2F_3Cl is collisionally stabilised under these conditions, while that of C_2F_4 is not. Experiments are in progress to measure rate constants for the reaction of oxygen atoms with C_2F_4 by photometry of the CF_2 bands.

Reactions (1) and (2)

$$CF_2 + O_2 \rightarrow CF_2O + O \qquad (2)$$

are expected to be about equally exothermic [$\Delta H \sim 50$ kcal./mole, if $O(2^3P)$ is formed] and (2) is usually assumed to be inhibited by a large activation energy. If spin conservation is relaxed in the field of the Cl nucleus, $O(2^1D)$ (excitation energy 45·4 kcal./g. atom) may form in (1) and a thermal explosion would follow if the propagating step (3) is rapid:

$$C_2F_3Cl + O^* \rightarrow CF_2O + CFCl \qquad (3)$$

It is noteworthy that no absorption ($2250 < \lambda < 6000$ Å) in these experiments could be attributed to *triplet* fluorocarbene molecules, which are predicted[7] to form if spin is conserved in:

$$C_2F_4 + O(2^3P) \rightarrow CF_2O + CF_2(\text{triplet}) \qquad (4)$$

The triplet-epoxide transition-complexes therefore must be sufficiently long-lived for relaxation to a single state to occur before fragmentation.

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