

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

By W. J. R. TYERMAN

(*Department of Physical Chemistry, University of Cambridge*)

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  $386\text{ cm.}^{-1}$ . Under isothermal conditions (50—100 torr  $\text{N}_2$  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  $\text{CF}_2$  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  $\text{CF}_2$ <sup>1</sup> and  $\text{CCl}_2$ ,<sup>2</sup> 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  $\text{CF}_2$  and  $\text{CCl}_2$ , CFCl possesses a singlet electronic ground-state. There seems to be no analogue in CFCl above  $\lambda\ 2350\ \text{\AA}$  of the intense u.v. systems of the iso-electronic molecule, NOCl.

A sudden temporary pressure rise occurred after flashing  $\text{C}_2\text{F}_3\text{Cl}$  (5—10 torr) in excess of  $\text{O}_2$  (25—100 torr) and transient absorption bands of vibrationally-excited oxygen were observed ( $2500 < \lambda < 2800\ \text{\AA}$ ), decaying in about  $75\ \mu\text{sec}$ . Continuous absorption ( $\lambda < 2500\ \text{\AA}$ ) also set in and may be due to hot chlorocarbonyl fluoride, which is an ultimate product and is known to absorb in this region.<sup>3</sup> The lifetime of the  $\text{CF}_2$  spectrum was not affected appreciably by the addition of oxygen. Continuous photolysis

† The i.r. spectra from products of  $\text{C}_2\text{F}_3\text{Cl}-\text{O}_2$  and  $\text{C}_2\text{F}_3\text{Cl}-\text{H}_2$  mixtures show weak bands of  $\text{CFClO}$  and  $\text{H}_2\text{CFCl}$  respectively, providing further evidence for generation of free CFCl.

## Band centres in CFCl absorption spectrum

$I^*$	$\lambda_{\text{air}} (\text{\AA})$	$\nu_{\text{vac}} (\text{cm.}^{-1})$	$I^*$	$\lambda_{\text{air}} (\text{\AA})$	$\nu_{\text{vac}} (\text{cm.}^{-1})$
4	3736.1	26758	10	3582.7	27904
5	3725.2	26837	6	3532.6	28292
8	3683.7	27139	5	3499	28571
4	3662	25300	5	3485	28686
9	3632.0	27525	2	3466	28843
4	3595.0	27808			

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

( $\lambda$  2288 Å) of 20 torr  $\text{C}_2\text{F}_3\text{Cl}$  and 80 torr  $\text{O}_2$  led to rapid and almost complete conversion to CFCIO and  $\text{CF}_2\text{O}$  and no  $\text{C}_2\text{F}_4$  was formed; a mixture of 250 torr each of  $\text{C}_2\text{F}_3\text{Cl}$  and  $\text{O}_2$  exploded shortly after commencement of irradiation.

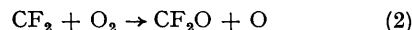
There is evidently a direct reaction of CFCl with oxygen at room temperature, in contrast to  $\text{CF}_2$ ,<sup>4</sup> and the process is probably



$\text{CF}_2\text{O}$  being formed in subsequent reactions of atomic oxygen with the substrate, since  $\text{CF}_2$  apparently is inert in this system. The reaction of  $\text{C}_2\text{F}_3\text{Cl}$  with  $\text{O}(2^3P)$  has been studied directly by long wavelength photolysis of mixtures with  $\text{NO}_2$ . No  $\text{CF}_2$  was observed in flashed  $\text{C}_2\text{F}_3\text{Cl}-\text{NO}_2-\text{N}_2$  mixtures over a wide range of isothermal conditions; both  $\text{CF}_2\text{O}$  and CFCIO 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  $\text{cm.}^{-1}$  and are assigned to trifluorochloroethylene epoxide, by comparison with the spectrum of tetrafluoroethylene epoxide.<sup>5</sup> Absorption bands of the isomer, chlorodifluoroacetyl fluoride were not detected.<sup>6</sup> The spectrum of  $\text{CF}_2$  appears slowly after flash photolysis of  $\text{C}_2\text{F}_4-\text{NO}_2$  mixtures, and both carbonyl fluoride and tetrafluoroethylene epoxide are formed. Evidently the initial adduct of  $\text{O}(2^3P)$  with  $\text{C}_2\text{F}_3\text{Cl}$  is collisionally stabilised

under these conditions, while that of  $\text{C}_2\text{F}_4$  is not. Experiments are in progress to measure rate constants for the reaction of oxygen atoms with  $\text{C}_2\text{F}_4$  by photometry of the  $\text{CF}_2$  bands.

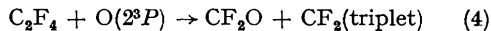
Reactions (1) and (2)



are expected to be about equally exothermic [ $\Delta H \sim 50$  kcal./mole, if  $\text{O}(2^3P)$  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,  $\text{O}(2^1D)$  (excitation energy 45.4 kcal./g. atom) may form in (1) and a thermal explosion would follow if the propagating step (3) is rapid:



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



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

This work was supported by maintenance and equipment grants from the S.R.C.

(Received, February 12th, 1968; Com. 172.)

<sup>1</sup> C. W. Matthews, *Canad. J. Phys.*, 1967, **45**, 2355.

<sup>2</sup> D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1967, **47**, 703.

<sup>3</sup> I. Zanon, G. Giacometti, and D. Picciol, *Spectrochim. Acta*, 1963, **19**, 301.

<sup>4</sup> V. Knight and J. Heicklen, *J. Phys. Chem.*, 1966, **70**, 3901.

<sup>5</sup> V. Caglioti, M. Lenzi, and A. Mele, *Nature*, 1964, **201**, 610.

<sup>6</sup> R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 1959, 1084.

<sup>7</sup> T. Johnston and J. Heicklen, *J. Chem. Phys.*, 1967, **47**, 475.