

**PHOTOCHEMICAL STABILITY OF ATMOSPHERIC CFCl_2NO_2 ,
 CF_2ClNO_2 AND CF_3NO_2** G. B. FAZEKAS and G. A. TAKACS[†]*Department of Chemistry, Rochester Institute of Technology, Rochester, NY 14623 (U.S.A.)*

(Received January 22, 1982; in revised form June 8, 1982)

Summary

CFCl_2NO_2 , CF_2ClNO_2 and CF_3NO_2 were prepared and purified in the laboratory from the oxidation of their corresponding nitrosomethanes with hydrogen peroxide and were characterized by their IR spectra. Quantitative measurements of their UV absorption spectra were made in order to obtain estimates of their atmospheric photochemical stability.

1. Introduction

The absorption of solar radiation by stratospheric chlorofluoromethanes results in C—Cl bond rupture [1, 2] with the formation of halogenated methyl radicals and chlorine atoms that react to deplete the stratospheric ozone concentration [3]. The halogenated methyl radicals may further release their chlorine atoms following chemical reactions involving oxygen and photodecomposition of phosgene-like compounds that are produced in the oxidation mechanism [4, 5].

Trace amounts of halogen-substituted methyl nitrogen oxides may be formed in the stratosphere and, if stable, they may prevent release of the chlorine from the halogenated methyl radicals [6]. Recent papers have provided information on (1) kinetic and IR absorption data for the formation of $\text{CCl}_3\text{O}_2\text{NO}_2$, $\text{CFCl}_2\text{O}_2\text{NO}_2$ and $\text{CF}_2\text{ClO}_2\text{NO}_2$ [7], (2) the thermal stability of $\text{CCl}_3\text{O}_2\text{NO}_2$ [8, 9] and $\text{CFCl}_2\text{O}_2\text{NO}_2$ [10] and (3) the photochemical stability of CCl_3NO [11], CFCl_2NO [12], CF_2ClNO [12], CF_3NO [11], CCl_3NO_2 [11] and $\text{CCl}_3\text{O}_2\text{NO}_2$ [13].

We report here IR and UV absorption spectra for CFCl_2NO_2 , CF_2ClNO_2 and CF_3NO_2 as well as estimates of their atmospheric photochemical stability. These nitromethane molecules may be produced by



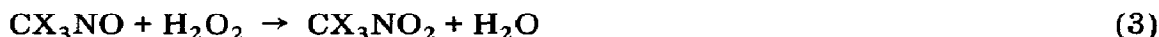
[†]Present address: Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303, U.S.A.

where M is a stabilizing third body. Reaction (1) occurs with CF_3 [14, 15] and CCl_3 [16] radicals, although



may compete with reaction (1) [17]. Reaction (2) takes place at low pressures with CF_3 [18] but is endothermic for CCl_3 radicals at stratospheric temperatures [16].

Early attempts to prepare CF_2ClNO_2 and CF_3NO_2 in the laboratory by the oxidation of the corresponding nitrosomethanes with dimanganese heptoxide, lead dioxide and chromic oxide resulted in low yields because of extensive decomposition [19, 20]. Subsequent work showed that higher yields of CF_3NO_2 were obtained with the milder oxidizing agent H_2O_2 [15, 20] and, in the present study,



was used to synthesize the nitro compounds.

2. Experimental details

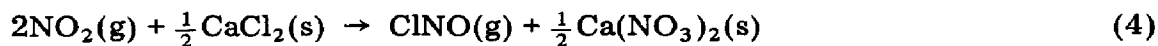
CF_3NO [11], CF_2ClNO [12] and CFCl_2NO [12] at a pressure of 400 Torr were transferred separately on a greaseless vacuum line into 500 ml Pyrex bulbs equipped with a greaseless fitting and stopcock and containing 5 ml of 30% H_2O_2 that had been outgassed at 77 K. The reaction mixtures containing CF_3NO and CF_2ClNO were heated at 323 K for 3 - 4 days while the $\text{CFCl}_2\text{NO}-\text{H}_2\text{O}_2$ samples were kept at 298 K for about 12 h. After reaction, the products were nearly colorless and only a faint trace of the initial blue color remained.

CF_3NO_2 was obtained by outgassing the reaction mixture at 77 K and then collecting the volatile fraction when the mixture was held at the temperature of solid $\text{CO}_2-\text{CH}_3\text{COCH}_3$ slush (187 K). Distillation at the temperature of *n*- C_5H_{12} slush (151 K) was used to remove the more volatile portion including the unreacted blue CF_3NO . The remaining fraction was passed through a column of dried granular LiOH [21] to eliminate trace amounts of CO_2 that have been reported to be produced in the reaction [15]. Final purification was achieved by collecting the more volatile portion at 187 K.

Because blue CF_2ClNO was difficult to separate from the colorless CF_2ClNO_2 , the gas phase of the reaction mixture was further reacted with a fresh supply of 5 ml 30% H_2O_2 at 323 K until no blue color remained (2 - 3 days). CF_2ClNO_2 was isolated from the residual liquids by distilling at the temperature of CHCl_3 slush (210 K) and collecting the volatile fraction. Higher volatile impurities were discarded by distillation at the temperature of CH_3OH slush (175 K).

CFCl_2NO_2 was separated by distilling the product from the liquid phase at the temperature of CCl_4 slush (251 K) and then discarding the more volatile fraction at 187 K. UV-visible and IR absorption scans showed the presence of trace $\text{NO}_2-\text{N}_2\text{O}_4$ in the samples. $\text{NO}_2-\text{N}_2\text{O}_4$ may originate not

only from the oxidation of CFCl_2NO with H_2O_2 but also from the synthesis of CFCl_2NO if the latter system is not kept oxygen free [12]. This impurity was eliminated by passing the material through a short column of dried granular CaCl_2 so as to convert the $\text{NO}_2\text{-N}_2\text{O}_4$ to ClNO by the reaction [22]



Separation of ClNO from CFCl_2NO_2 was accomplished by distillation at 187 K and discarding the more volatile fraction.

The colorless CF_3NO_2 , CF_2ClNO_2 and CFCl_2NO_2 were stored in the dark at 187 K to prevent any possible photodecomposition and thermal decomposition, although none was observed during the course of the experiments.

UV-visible and IR measurements were made using 2 and 10 cm path length cells at 298 K with a Varian Cary 219 spectrophotometer (at and above 185 nm) at a constant spectral bandwidth of 1 nm and 10 cm path length cells with a Perkin-Elmer 621 spectrophotometer ($600 - 4000 \text{ cm}^{-1}$). For the CF_2ClNO_2 and CFCl_2NO_2 experiments the Cary 219 was interfaced to an IMSAI 8080 microcomputer for data handling and storage, while pressures were determined with MKS Baratron gauges and ranged from 0.2 - 86 Torr and 0.2 - 60 Torr respectively for the UV cross section measurements. CF_3NO_2 pressures were determined using mercury and dibutyl phthalate manometers and varied from 0.5 to 78 Torr.

3. Results and discussion

The IR spectrum of the purified CF_3NO_2 was in agreement with that reported in the literature [23]. The IR absorption spectra of CF_2ClNO_2 and CFCl_2NO_2 from 600 to 2000 cm^{-1} are shown in Figs. 1 and 2. Assignments for some of the fundamental vibrational modes of CF_2ClNO_2 and CFCl_2NO_2 were made using the known IR spectra of CF_3NO_2 [23], CCl_3NO_2 [23],

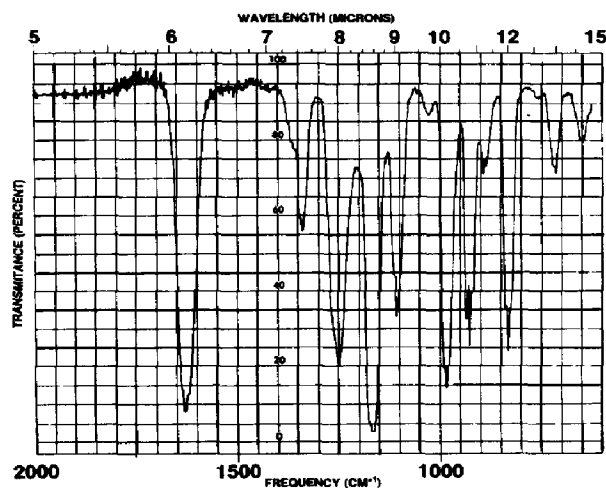


Fig. 1. IR spectrum of gaseous CF_2ClNO_2 at 298 K (pressure, 8 Torr; path length, 10 cm).

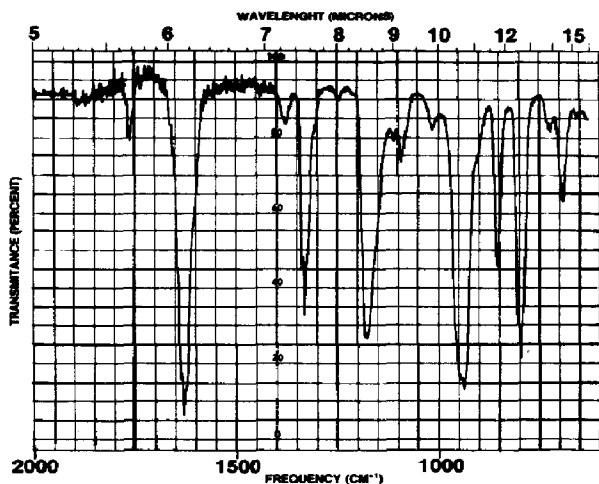


Fig. 2. IR spectrum of gaseous CF_2ClNO_2 at 298 K (pressure, 8 Torr; path length, 10 cm).

CF_2ClNO [24] and CFCl_2NO [24] and are given in Table 1. Complete interpretation of the vibrational spectra of CF_2ClNO_2 and CFCl_2NO_2 is expected to be more complicated than those of CF_3NO_2 and CCl_3NO_2 because of the presence of a greater number of stable rotational conformers in the mixed halogen compounds [25]. The assignments for the C—N symmetric stretch were made so as to be consistent with the CF_3NO_2 and CCl_3NO_2 spectra. The frequencies that have been reported for the C—N symmetric stretches of CF_3NO , CF_2ClNO , CFCl_2NO and CCl_3NO are 810 cm^{-1} [26, 27], 768 cm^{-1} [24], 943 cm^{-1} [24] and 936 cm^{-1} [24] respectively. The C—N symmetric stretch of CF_2ClNO appears to be incorrectly assigned and the correct assignment could possibly be the sharp band at 925 cm^{-1} or the previously [24] unassigned peak at 985 cm^{-1} . The NO_2 deformation frequencies for CF_2ClNO_2 and CFCl_2NO_2 (Table 1) obey the straight-line relationship that has been observed between the deformation frequency and the electronegativity of X in CX_3NO_2 when $X \equiv \text{H, D, Br, Cl}$ and F [23]. The remaining observed peaks that have been left unassigned are located at 654 (w), 882 (w), 983 (s), 1030 (w), 2480 (w), 2650 (w) and 2930 cm^{-1} (w) for CF_2ClNO_2 and 725 (w), 934 (s), 1015 (w), 1090 (w), 1380 (w), 1760 (w), and 2645 cm^{-1} (w) for CFCl_2NO_2 (where w indicates a weak peak and s indicates a strong peak).

The vapor pressure of CF_3NO_2 was taken at six temperatures over the range 141 - 210 K (Table 2) and made to fit the linear equation $\ln p(\text{Torr}) = 18.58 - 2898/T(\text{K})$ using the method of least squares. This is in good agreement with data taken from 238.6 to 242.5 K ($\ln p(\text{Torr}) = 17.37 - 2598/T(\text{K})$) [15] and that reported by Banus ($\ln p(\text{Torr}) = 18.89 - 2936/T(\text{K})$) [20].

The vapor pressures of CF_2ClNO_2 and CFCl_2NO_2 (Table 2) were measured at five temperatures over the range 187 - 273 K and the following respective linear least-squares expressions were obtained:

TABLE 1

Observed frequencies in wavenumbers and tentative band assignments for some halogen-substituted nitromethanes and nitrosomethanes

Vibrational mode	$CF_3NO_2^a$	$CCl_3NO_2^a$	CF_2ClNO^b	$CFCl_2NO^b$	$CF_2ClNO_2^c$	$CFCl_2NO_2^c$
N-O asymmetric stretch	1620	1625	1600.5	1614	1628	1628
N-O symmetric stretch	1310	1311	—	—	1338	1329
C-F symmetric stretch	1151	—	1176	1147.5	1167	1173
			1167.5	1139.5	1107	
			1149	1137		
			1087			
C-N symmetric stretch	860	850	768 ^d	943	832	850
N-O ₂ symmetric deformation	750	677	—	—	713	690
(a') ν (ClCF ₂)	—	—	932	—	934	—
			925		928	
(a'') ν (ClCCl)	—	—	—	829	—	794
				823		
(a') ν (CF ₂ Cl)	—	—	1243.5	—	1250	—

^a Ref. 23.

^b Ref. 24.

^c This work.

^d See text for discussion of this assignment.

TABLE 2

Vapor pressure data for CFCl_2NO_2 , CF_2ClNO_2 and CF_3NO_2

Temperature (K)	ln p (Torr)		
	CFCl_2NO_2	CF_2ClNO_2	CF_3NO_2
141.5			-1.61
150.2			-0.92
162.2			0.41
175.2			1.95
187	-2.12	1.22	3.30
209.5	-0.16	2.38	4.77
227.8	1.01	3.38	
250.1	2.73	4.76	
273	4.01	5.70	

$$\ln p \text{ (Torr)} = 16.92 - \frac{3059}{T(\text{K})}$$

$$\ln p \text{ (Torr)} = 17.97 - \frac{3822}{T(\text{K})}$$

Extrapolation of the vapor pressure curves gave 297 K (compared with the previously reported value of 298 K [19]) and 337 K for the boiling points of CF_2ClNO_2 and CFCl_2NO_2 respectively at a pressure of 1 atm. Using the Clausius-Clapeyron equation, the heats of vaporization for CF_2ClNO_2 and CFCl_2NO_2 are calculated to be 6.1 kcal mol⁻¹ and 7.6 kcal mol⁻¹ respectively.

UV absorption by CF_3NO_2 , CF_2ClNO_2 and CFCl_2NO_2 are shown in Figs. 3, 4 and 5 respectively. Analogous to the absorption spectra of CH_3NO_2 [29] and CCl_3NO_2 [11], two absorption bands are prominent: the long wavelength band due to an n,π^* transition of a non-bonding electron on an oxygen atom and the short wavelength band caused by a π,π^* transition [29]. A comparison of the cross sections for CF_3NO_2 , CF_2ClNO_2 , CFCl_2NO_2 and CCl_3NO_2 at the maxima and minima in their UV spectra is given in Table 3. The observed cross sections for CF_3NO_2 are in agreement with previous results [15, 28, 30] at the absorption maximum of the long wavelength band but differ at shorter wavelengths (Fig. 3). The cross sections of CCl_3NO_2 also disagreed with those reported in ref. 28 (see ref. 11, Table 3 and Fig. 3; it should be noted that the cross section axis for ref. 11, Fig. 3, was incorrectly labelled and it should be a factor of 10 larger).

The photodecomposition of chloro- and fluoro-substituted nitromethanes is expected to occur by breakage of the weakest bond, the C-N bond, which is similar to the photodissociation mechanism of CH_3NO_2 [29]:



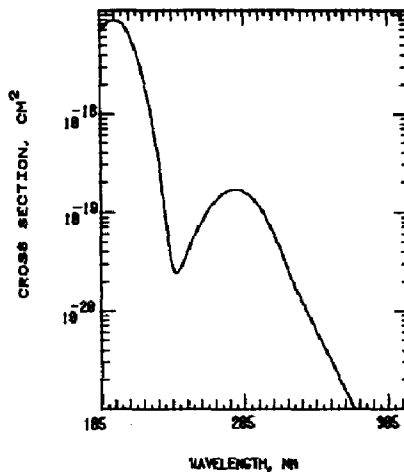
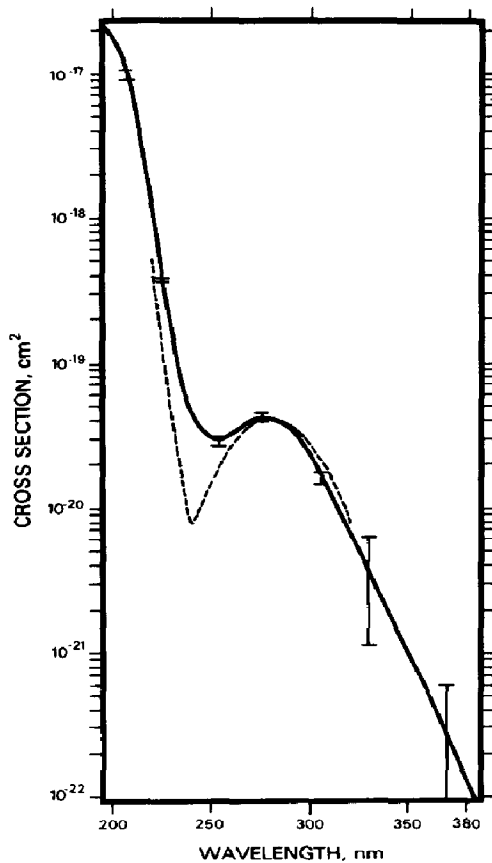


Fig. 3. Absorption spectrum of gaseous CF_3NO_2 at 298 K: —, this work; ---, ref. 28. The error bars were obtained from determinate error calculations.

Fig. 4. Absorption spectrum of gaseous CF_2ClNO_2 at 298 K.

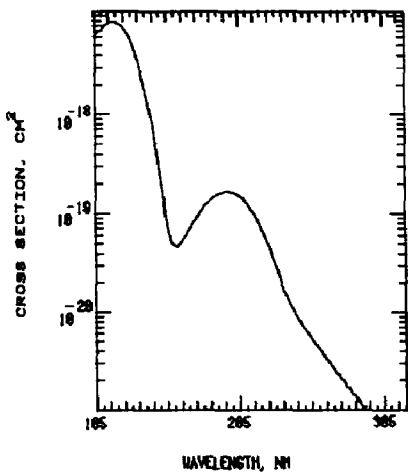


Fig. 5. Absorption spectrum of gaseous CFCl_2NO_2 at 298 K.

TABLE 3

Photoabsorption cross sections at the maxima and minima in the UV absorption spectra of gaseous CF_3NO_2 , CF_2ClNO_2 , CFCl_2NO_2 and CCl_3NO_2

<i>Molecule</i>	λ_{max} (nm)	σ_{max} (cm^2)	λ_{min} (nm)	σ_{min} (cm^2)	<i>Reference</i>
CF_3NO_2	277 ± 2	$(4.3 \pm 0.3) \times 10^{-20}$	250 ± 3	$(3.0 \pm 0.2) \times 10^{-20}$	This work
	277.5	4.3×10^{-20}	239.5	7.6×10^{-21}	[30]
	279	4.2×10^{-20}	239	7.6×10^{-21}	[15, 28]
CF_2ClNO_2	279 ± 3	$(1.7 \pm 0.1) \times 10^{-19}$	238 ± 1	$(2.4 \pm 0.1) \times 10^{-20}$	This work
	195 ± 1	$(9.0 \pm 0.2) \times 10^{-18}$			This work
CFCl_2NO_2	276 ± 3	$(1.7 \pm 0.1) \times 10^{-19}$	241 ± 1	$(4.7 \pm 0.1) \times 10^{-20}$	This work
	198 ± 1	$(8.8 \pm 0.2) \times 10^{-18}$			This work
CCl_3NO_2	272 ± 2	$(1.6 \pm 0.1) \times 10^{-19}$	242 ± 2	$(4.9 \pm 0.2) \times 10^{-20}$	[11] ^a
	275	7.6×10^{-20}	245	2.7×10^{-20}	[28]
	202 ± 1	$(9.7 \pm 0.5) \times 10^{-18}$			[11] ^a

^aThe cross section axis in ref. 11, Fig. 3, is incorrectly labelled and should be a factor of 10 larger.

Smaller quantum yields of decomposition may arise from [29]



and



The energetics of reactions (5) - (7) (Table 4) are such that the absorption of radiation by CF_3NO_2 (Fig. 3), CF_2ClNO_2 (Fig. 4), CFCl_2NO_2 (Fig. 5) and CCl_3NO_2 [11] are of sufficient energy to permit photodissociation by reactions (5) - (7).

The photodissociation rate coefficients J reported in Table 5 are obtained by summing the product of the solar flux intensity I and the photoabsorption cross section σ over all absorbing wavelengths for each altitude h . The quantum yield Φ for the decomposition of CX_3NO_2 was taken to be unity at each of the wavelengths used.

$$J(h) = \int \Phi I \sigma \, d\lambda \quad (8)$$

The integration of eqn. (8) was done using the trapezoidal method for cross section data taken at 1 nm intervals. The solar flux intensities were interpolated so that their wavelengths matched the wavelengths at which the cross sections were calculated. This method of integration is slightly different from our previous calculations [11] which used exact values for solar flux intensities obtained at wavelengths closely corresponding to the cross-sectional wavelengths.

The photochemical stability of CX_3NO_2 is such that the fraction 1/e remains after about an hour of photodecomposition by sunlight at 30 km (Table 5).

TABLE 4

Heats of reactions (5), (6) and (7) at 298 K^a

CX_3NO_2	Heat of reaction (kcal mol ⁻¹)			
	Reaction (5)	Reaction (6), producing ClNO	Reaction (6), producing FNO	Reaction (7)
CF ₃ NO ₂	28	—	-36	70
CF ₂ ClNO ₂	28	-56	-34	70
CFCl ₂ NO ₂	28	-47	-25	69
CCl ₃ NO ₂	28	-39	—	69

^aCalculated from the heats of formation of CX₃NO₂, CF₃ [31], CF₂Cl [32], CFCl₂ [32], CCl₃ [31], NO₂ [31], CCl₂O [31], CClFO [31], CF₂O [31], FNO [31], ClNO [33], CX₃NO [12] and O [33, 34]. The heats of formation of CX₃NO₂ were calculated from the bond dissociation energy of X₃C—NO₂ and the heats of formation of CX₃ and NO₂. The bond dissociation energies *D* of F₃C—NO₂ and F₂ClC—NO₂ were estimated using $D(X_3C-NO_2) = D(X_3C-NO) + D(F-NO_2) - D(F-NO)$ while for FCl₂C—NO₂ and Cl₃C—NO₂ the equation $D(X_3C-NO_2) = D(X_3C-NO) + D(Cl-NO_2) - D(Cl-NO)$ was used. The dissociation energies for X₃C—NO were obtained from ref. 12 and those for F—NO₂, Cl—NO₂, F—NO and Cl—NO were calculated from the heats of formation of F [34], Cl [34], NO [31], NO₂ [31], FNO₂ [31] and ClNO₂ [31]. The estimated heats of formation of gaseous CF₃NO₂, CF₂ClNO₂, CFCl₂NO₂ and CCl₃NO₂ at 298 K are -132 kcal mol⁻¹, -84 kcal mol⁻¹, -43 kcal mol⁻¹ and -1 kcal mol⁻¹ respectively.

TABLE 5

Photodissociation rate coefficients *J* and lifetimes 1/*J* for CX₃NO₂^a

Altitude (km)	CF ₃ NO ₂		CF ₂ ClNO ₂		CFCl ₂ NO ₂		CCl ₃ NO ₂	
	<i>J</i> (s ⁻¹)	1/ <i>J</i> (h)	<i>J</i> (s ⁻¹)	1/ <i>J</i> (h)	<i>J</i> (s ⁻¹)	1/ <i>J</i> (h)	<i>J</i> (s ⁻¹)	1/ <i>J</i> (h)
0	6.9 × 10 ⁻⁵	4.0	1.8 × 10 ⁻⁴	1.5	1.6 × 10 ⁻⁴	1.7	1.4 × 10 ⁻⁴	2.0
10	1.0 × 10 ⁻⁴	2.8	2.6 × 10 ⁻⁴	1.1	2.3 × 10 ⁻⁴	1.2	2.1 × 10 ⁻⁴	1.3
20	1.1 × 10 ⁻⁴	2.5	2.8 × 10 ⁻⁴	1.0	2.5 × 10 ⁻⁴	1.1	2.2 × 10 ⁻⁴	1.3
30	1.6 × 10 ⁻⁴	1.7	3.7 × 10 ⁻⁴	0.8	3.2 × 10 ⁻⁴	0.9	2.9 × 10 ⁻⁴	1.0
40	4.4 × 10 ⁻⁴	0.6	7.7 × 10 ⁻⁴	0.4	7.2 × 10 ⁻⁴	0.4	7.3 × 10 ⁻⁴	0.4
50	6.9 × 10 ⁻⁴	0.4	1.2 × 10 ⁻³	0.2	1.3 × 10 ⁻³	0.2	1.3 × 10 ⁻³	0.2

^aSolar flux intensities were taken at a zenith angle of 45°.

References

- 1 R. K. M. Jayanty, R. Simonaitis and J. Heicklen, *J. Photochem.*, 4 (1975) 381.
- 2 R. E. Rebert and P. J. Ausloos, *J. Photochem.*, 4 (1975) 419.
- 3 M. J. Molina and F. S. Rowland, *Nature (London)*, 249 (1974) 810.
- 4 R. D. Hudson (ed.), *Chlorofluoromethanes and the Stratosphere*, NASA Ref. Publ. 1010, August 1977 (National Aeronautics and Space Administration).
- 5 E. Sanhueza, *J. Photochem.*, 7 (1977) 325.
- 6 T. D. Allston, M. L. Fedyk and G. A. Takacs, *J. Photochem.*, 9 (1978) 116.

- 7 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, *Chem. Phys. Lett.*, **61** (1979) 100.
- 8 R. Simonaitis and J. Heicklen, *Chem. Phys. Lett.*, **62** (1979) 473.
- 9 R. Simonaitis and J. Heicklen, *Chem. Phys. Lett.*, **68** (1979) 245.
- 10 R. Simonaitis, S. Glavas and J. Heicklen, *Geophys. Res. Lett.*, **6** (1979) 385.
- 11 T. D. Allston, M. L. Fedyk and G. A. Takacs, *Chem. Phys. Lett.*, **60** (1978) 97.
- 12 G. B. Fazekas and G. A. Takacs, *J. Photochem.*, **16** (1981) 249.
- 13 O. Morel, R. Simonaitis and J. Heicklen, *Abstracts 178th American Chemical Society Meet., Washington, DC, September 10 - 14, 1979*.
- 14 M. Christie and C. J. Matthews, *J. Chem. Soc., Faraday Trans. I*, **72** (1976) 1652.
- 15 J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, (1954) 912.
- 16 J. B. Cumming, R. Cooper, W. A. Mulac and S. Gordon, *Radiat. Phys. Chem.*, **16** (1980) 207.
- 17 P. Gray, *Trans. Faraday Soc.*, **51** (1955) 1367.
- 18 M. J. Rossi, J. R. Barker and D. M. Golden, *J. Chem. Phys.*, **71** (1979) 3722.
- 19 R. N. Haszeldine, *J. Chem. Soc.*, (1953) 2075.
- 20 J. Banus, *J. Chem. Soc.*, (1953) 3755.
- 21 K. A. Rahn, R. D. Borys and R. A. Duce, *Science*, **192** (1976) 549.
- 22 M. J. McClements and G. A. Takacs, unpublished data, 1978.
- 23 A. Castelli, A. Palm and C. Alexander, Jr., *J. Chem. Phys.*, **44** (1966) 1577.
- 24 N. P. Ernsting and J. Pfab, *Spectrochim. Acta, Part A*, **36** (1980) 75.
- 25 M. I. Dakhis, A. A. Levin and V. A. Shlyapochnikov, *J. Mol. Struct.*, **14** (1972) 321.
M. I. Dakhis and V. A. Shlyapochnikov, *J. Mol. Struct.*, **21** (1974) 305.
- 26 H. F. Shurvell, S. C. Dass and R. D. Gordon, *Can. J. Chem.*, **52** (1974) 3149.
- 27 R. Demuth, H. Burger, G. Pawelke and H. Willner, *Spectrochim. Acta, Part A*, **34** (1978) 113.
- 28 J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, (1954) 919.
- 29 W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski and G. A. Takacs, *Int. J. Chem. Kinet.*, **12** (1980) 231.
- 30 J. Mason, *J. Chem. Soc.*, (1957) 3904.
- 31 D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd edn., in *NBS Natl. Stand. Ref. Data Ser. 37*, 1971 (National Bureau of Standards, U.S. Department of Commerce).
- 32 J. A. Kerr and A. F. Trotman-Dickenson, Strengths of chemical bonds, *Handbook of Chemistry and Physics*, Chemical Rubber Company, Boca Raton, FL, 60th edn., 1979 - 1980.
- 33 M. W. Chase, J. L. Curnutt, H. Prophet, R. A. McDonald and A. N. Syverud, *JANAF Thermochemical Tables, 1975 Suppl.*, in *J. Phys. Chem. Ref. Data*, **4** (1975) 1.
- 34 CODATA recommended key values for thermodynamics, 1977, *J. Chem. Thermodyn.*, **10** (1978) 903.