PHOTOABSORPTION SPECTRA OF GASEOUS CH_3SO_2Cl, CCl_3SCl, SO_2ClF AND $(CH_3O)_2SO$

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Summary

The UV–visible absorption spectra of CH_3SO_2Cl, CCl_3SCl, SO_2ClF and $(CH_3O)_2SO$ were quantitatively analyzed at 298 K. The threshold wavelengths for photodissociation of these molecules and SO_2F_2 were calculated from thermochemical data and estimates were made of their atmospheric photodissociation rate coefficients.

1. Introduction

Consideration of the photochemical processes that may occur when a molecule absorbs radiation requires quantitative information on the photoabsorption cross section as a function of absorbing wavelength. The photodissociation reaction

$$XY + h\nu \rightarrow X + Y \tag{1}$$
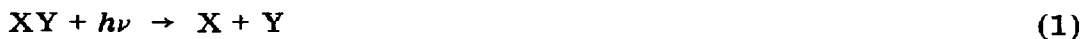
may take place if the photon absorbed by molecule XY is of sufficient energy to overcome the endothermicity associated with the chemical change. If the absorbing wavelength is less than or equal to the wavelength calculated from

$$hc/\lambda = \Delta H_f^\circ(X) + \Delta H_f^\circ(Y) - \Delta H_f^\circ(XY) \tag{2}$$

then process (1) is energetically possible.

The photoabsorption spectra of gaseous $(CH_3O)_2SO$, CH_3SO_2Cl, CCl_3-SCl, SO_2ClF and SO_2F_2 are reported and the energetically favorable photodissociation steps that may result are determined. These molecules may be present in the atmosphere in trace amounts as a result of formation reactions involving free-radical chemistry or because of their release into the atmosphere at the Earth's surface, and therefore atmospheric photodissociation rate coefficients are estimated for them. Previous investigations on the spectra of $SOCl_2$ [1], SO_2Cl_2 [1 - 3] and $HOSO_2Cl$ [2, 3] have been recently reported.

2. Experimental details

The experimental techniques were similar to those described previously [1, 4]. UV–visible measurements were made on quartz cells of path length 2, 5 and 10 cm using Perkin–Elmer 450 and Cary 219 spectrophotometers. The pressure of the gases was measured with mercury and dibutyl phthalate manometers.

Dimethyl sulfite (Eastman Organic), methane sulfonyl chloride (Eastman Organic, purity 98% or above), trichloromethanesulfenyl chloride (Eastman Organic), sulfuryl fluoride (Linde, at least 99% pure) and spectro grade sulfuryl chloride fluoride (Aldrich) were outgassed on a greaseless vacuum line and distilled in order to collect the middle fraction.

UV absorption by $(CH_3O)_2SO$, SO_2F_2 and SO_2ClF showed the sharp bands of SO_2 impurity [5, 6]. Analogous to the purification of SO_2Cl_2 [1], pumping on SO_2ClF held at chloroform slush bath temperature (-63.5 °C) removed the SO_2 impurity. The concentration of SO_2 in the SO_2F_2 samples was reduced but never completely removed by distilling from -98 to -196 °C and all the UV absorption spectra resembled SO_2 absorption. The cross sections that were determined for SO_2F_2 are upper limits to the actual values because no correction was made for SO_2 absorption. The amount of SO_2 in SO_2F_2 was estimated to be about 0.2 mol.% by assuming that all the absorption from 250 to 310 nm was due to SO_2 absorption. The UV spectrum of $(CH_3O)_2SO$ that had been further outgassed at room temperature showed continuous absorption from 190 to 226 nm and only trace amounts of the sharp absorption bands of SO_2 in this region. In calculating the cross sections for $(CH_3O)_2SO$, corrections were made for the absorption due to the presence of trace SO_2.

Vapor phase IR spectra of the purified samples of CH_3SO_2Cl [7], CCl_3SCl [8], SO_2F_2 [9, 10] and SO_2ClF [11], having the product of optical path length and pressure up to 18.6 cm Torr, 51.1 cm Torr, 7600 cm Torr and 5400 cm Torr respectively, agreed with those found in the literature.

Attempts were made to determine the photoabsorption spectra of $CH_3SO_2(OH)$, $ONO(SO_2)OH$ and $ONO(SO_2)Cl$. No absorption was observed on the vapor above liquid methane sulfonic acid (Eastman Organic) and solid nitrosyl sulfuric acid (ICN Pharmaceuticals) that were outgassed at 25 °C. Nitrosyl chlorosulfate was prepared by condensing excess nitrosyl chloride onto chlorosulfonic acid at -196 °C and by warming to 0 °C [12]:

$$ClNO + HO(SO_2)Cl \rightarrow ONO(SO_2)Cl + HCl \qquad (3)$$
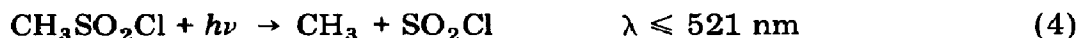
A red solid was formed. IR analysis of the vapors above the solid showed the presence of ClNO, NO and HCl. Outgassing of the solid at 0 and 21 °C resulted in the solid changing color from red to orange to white. UV absorption by the gases above the white solid gave cross sections in agreement with the known ClNO cross sections [13].

3. Results and discussion

The photoabsorption spectra of gaseous CH_3SO_2Cl, CCl_3SCl, SO_2ClF and $(CH_3O)_2SO$ are shown in Figs. 1 - 4. The thermochemical data in Table 1 were used to calculate threshold wavelengths for some energetically possible photodissociation steps.

Gaseous CH_3SO_2Cl absorbs continuously over the wavelength region from 190 to 248 nm with no absorption maxima (Fig. 1). The three lowest energy dissociation steps involve breakage of the C—S, S—Cl and S—O bonds:

$$CH_3SO_2Cl + h\nu \rightarrow CH_3 + SO_2Cl \qquad \lambda \leqslant 521 \text{ nm} \qquad (4)$$

$$CH_3SO_2Cl + h\nu \rightarrow CH_3SO_2 + Cl \qquad \lambda \leqslant 478 \text{ nm} \qquad (5)$$

$$CH_3SO_2Cl + h\nu \rightarrow CH_3SOCl + O \qquad \lambda \leqslant 277 \text{ nm} \qquad (6)$$

The absorption spectrum of CCl_3SCl shows three absorption bands with maxima occurring at 256 ± 2 nm and 298 ± 2 nm (Fig. 2). The two weakest bonds in CCl_3SCl are expected to be the C—S and S—Cl bonds, although no thermochemical data are available to estimate the wavelengths at which photodissociation may take place:
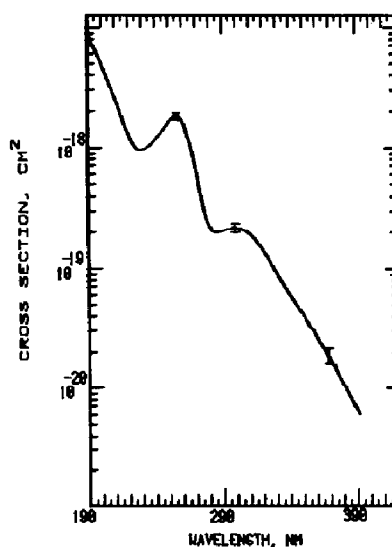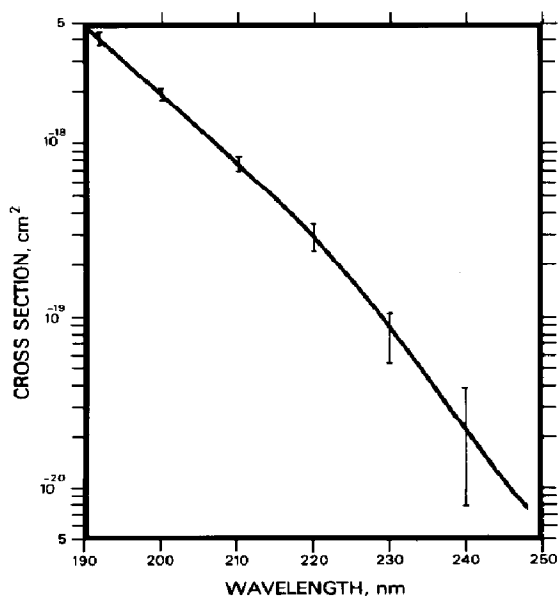
$$CCl_3SCl + h\nu \rightarrow CCl_3 + SCl \qquad (7)$$

$$CCl_3SCl + h\nu \rightarrow CCl_3S + Cl \qquad (8)$$

Fig. 1. Photoabsorption spectrum of gaseous CH_3SO_2Cl at 298 K.
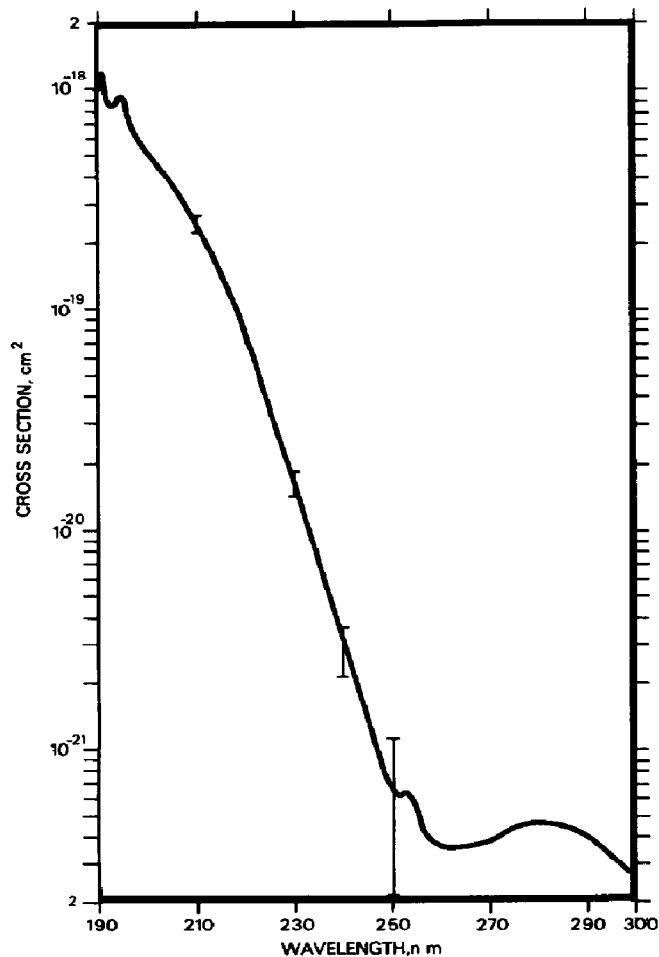
Fig. 2. Photoabsorption spectrum of gaseous CCl_3SCl at 298 K.

Fig. 3. Photoabsorption spectrum of gaseous SO_2ClF at 298 K.

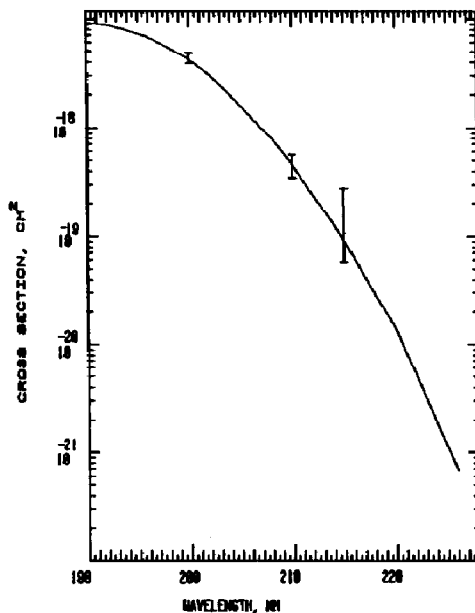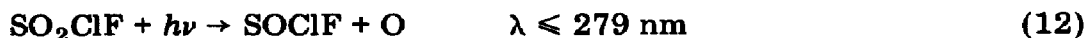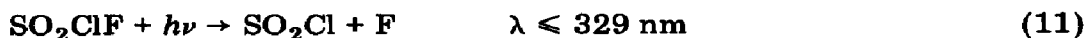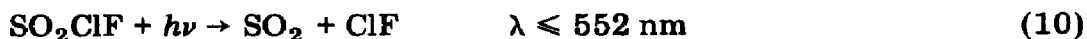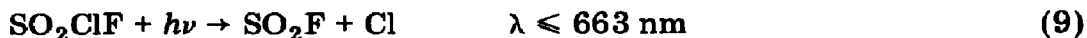Fig. 4. Photoabsorption spectrum of gaseous $(CH_3O)_2SO$ at 298 K.

Gaseous SO_2ClF commences absorption at about 300 nm and this rises rapidly from 254 to 190 nm (Fig. 3). Two weak but definite maxima occur at about 190.5 ± 1 nm and 195 ± 1 nm. Absorption of radiation by SO_2ClF may result in the following four processes:

$$SO_2ClF + h\nu \rightarrow SO_2F + Cl \qquad \lambda \leqslant 663 \text{ nm} \qquad (9)$$

$$SO_2ClF + h\nu \rightarrow SO_2 + ClF \qquad \lambda \leqslant 552 \text{ nm} \qquad (10)$$

$$SO_2ClF + h\nu \rightarrow SO_2Cl + F \qquad \lambda \leqslant 329 \text{ nm} \qquad (11)$$

$$SO_2ClF + h\nu \rightarrow SOClF + O \qquad \lambda \leqslant 279 \text{ nm} \qquad (12)$$

Photodecomposition of gaseous $(CH_3O)_2SO$ by the pathways

$$(CH_3O)_2SO + h\nu \rightarrow CH_3O + CH_3OSO \qquad \lambda \leqslant 437 \text{ nm} \qquad (13)$$

TABLE 1

Heats of formation used in calculating threshold wavelengths

Species (g)	$\Delta H^\circ_{f\,298}$ (kcal mol^{-1})	Reference
Cl	28.992 ± 0.002	[14]
F	18.975 ± 0.072	[14]
O	59.553 ± 0.024	[14]
Cl_2	0	[15]
ClF	−12.14 ± 0.6	[15]
F_2	0	[15]
SO_2	−70.947 ± 0.05	[15]
CH_3	34.82 ± 0.2	[15]
$SOCl_2$	−51	[16]
SOClF	−92	—[a]
SOF_2	−130 ± 25	[17]
SO_2Cl	−67	—[b]
SO_2F	−120.7	—[c]
CH_3O	3.8 ± 0.2	[21]
SO_2Cl_2	−84.8 ± 0.5	[17]
SO_2ClF	−134.8	[22]
SO_2F_2	−184	[22]
CH_3SO_2	−56.3	—[d]
CH_3OSO	−54	—[e]
CH_3SOCl	−44	—[f]
CH_3SO_2Cl	−87	—[g]
$(CH_3)_2SO$	−36.09 ± 0.2	[25]
$(CH_3)_2SO_2$	−89.1 ± 0.8	[25]
$(CH_3O)_2S$	−59 ± 5	[19]
$(CH_3O)_2SO$	−115.5 ± 0.5	[25]

[a]Calculated from the bond dissociation energy of ClFOS=O and the heats of formation for SO_2ClF and O. The bond dissociation energy of ClFOS=O was calculated by averaging the bond dissociation energies of $Cl_2OS=O$ and $F_2OS=O$, which were obtained from the heats of formation of SO_2Cl_2, SO_2F_2, $SOCl_2$, SOF_2 and O.

[b]Estimated using the heats of formation of Cl, Cl_2 and SO_2Cl_2 and the heat of reaction $\Delta H^\circ = -11.5 \pm 2.5$ kcal mol^{-1} at 300 °C for Cl + $SO_2Cl_2 \rightarrow Cl_2$ + SO_2Cl [18]. Benson [19] estimated the bond dissociation energy of O_2ClS—Cl to be 63 kcal mol^{-1} which together with the heats of formation for Cl and SO_2Cl_2 gives −51 kcal mol^{-1} as the heat of formation of SO_2Cl.

[c]Calculated using a bond dissociation energy of 81 ± 2 kcal mol^{-1} for O_2FS—F [20] and the heats of formation of F and SO_2F_2.

[d]The average of the heats of formation calculated from the bond dissociation energies of CH_3—SO_2 and CH_3SO_2—CH_3 (68 kcal mol^{-1}) [19] and the heats of formation of CH_3, SO_2 and $(CH_3)_2SO_2$. The value used for the bond dissociation energy of CH_3—SO_2 was taken as the average of 23.3 ± 1.8, 19.3 ± 3.9 and 20.4 ± 4.9 kcal mol^{-1} [23] and 20.9 ± 1.1 and 18.6 ± 1.6 kcal mol^{-1} [24].

[e]Calculated using the heats of formation of CH_3O and $(CH_3O)_2SO$ and the bond dissociation energy of 65 kcal mol^{-1} for CH_3O—$SO(OCH_3)$ [19].

[f]Calculated from the heats of formation of O and CH_3SO_2Cl and the bond dissociation energy of $CH_3SOCl=O$ (103 kcal mol^{-1}) which was obtained from the mean of the bond dissociation energies of $Cl_2SO=O$ and $(CH_3)_2SO=O$. The bond dissociation energies were calculated from the heats of formation of O, $SOCl_2$, SO_2Cl_2, $(CH_3)_2SO$ and $(CH_3)_2SO_2$.

[g]Mean of the heats of formation of SO_2Cl_2 and $(CH_3)_2SO_2$.

$$(CH_3O)_2SO + h\nu \rightarrow (CH_3O)_2S + O \qquad \lambda \leqslant 246 \text{ nm} \qquad (14)$$

may take place in the region of continuous absorption from 226 to 190 nm (Fig. 4).

The three lowest energy photodissociation steps of gaseous SO_2F_2 are listed below with their respective threshold wavelengths:

$$SO_2F_2 + h\nu \rightarrow SO_2F + F \qquad \lambda \leqslant 347 \text{ nm} \qquad (15)$$

$$SO_2F_2 + h\nu \rightarrow SO_2 + F_2 \qquad \lambda \leqslant 252 \text{ nm} \qquad (16)$$

$$SO_2F_2 + h\nu \rightarrow SOF_2 + O \qquad \lambda \leqslant 251 \text{ nm} \qquad (17)$$
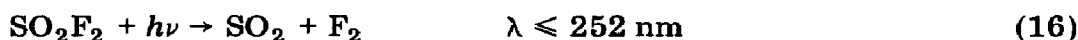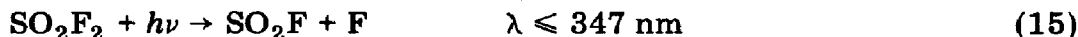
Atmospheric photodissociation rate coefficients J for CH_3SO_2Cl, CCl_3-SCl, SO_2ClF, $(CH_3O)_2SO$ and SO_2F_2 were estimated (Table 2), as described in ref. 4, from the sum over the absorbing wavelengths of the product of the cross sections, the solar flux intensities and a unit quantum yield for photodissociation.

TABLE 2

Atmospheric photodissociation rate coefficients J

Altitude (km)	J (s^{-1}) for the following species				
	CH_3SO_2Cl	CCl_3SCl	SO_2ClF	$(CH_3O)_2SO$	SO_2F_2[a]
0	4.2×10^{-35}	2.0×10^{-3}	1.8×10^{-9}	3.8×10^{-36}	1.1×10^{-8}
10	1.7×10^{-15}	2.9×10^{-3}	3.8×10^{-9}	1.1×10^{-15}	2.0×10^{-8}
20	1.8×10^{-8}	3.0×10^{-3}	1.1×10^{-8}	3.1×10^{-8}	2.6×10^{-8}
30	2.7×10^{-6}	3.3×10^{-3}	8.6×10^{-7}	3.2×10^{-6}	9.6×10^{-8}
40	3.1×10^{-5}	4.1×10^{-3}	9.4×10^{-6}	2.0×10^{-5}	4.6×10^{-7}
50	6.4×10^{-5}	5.6×10^{-3}	1.8×10^{-5}	3.2×10^{-5}	8.2×10^{-7}

[a]The coefficients for SO_2F_2 are upper limits; see text for explanation. Approximately 1000 (ton SO_2F_2) year^{-1} are released by industry into the environment [26].

Acknowledgment

References

1 A. P. Uthman, P. J. Demlein, T. D. Allston, M. C. Withiam, M. J. McClements and G. A. Takacs, *J. Phys. Chem.*, 82 (1978) 2252.
2 M. Kaufman, personal communication, Chemical Manufacturers Association Meeting, Boulder, CO, March 14, 1978.

3 L. W. Strattan, R. E. Eibling and M. Kaufman, *Atmos. Environ.*, *13* (1979) 175.

4 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.

5 B. A. Thompson, P. Harteck and R. R. Reeves, Jr., *J. Geophys. Res.*, *68* (1963) 6431.

6 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.

7 C. J. Pouchert, *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Company, Milwaukee, WI, 2nd edn., 1970, p. 479G.

8 J. A. A. Ketelaar and W. Vedder, *Recl. Trav. Chim. Pays-Bas*, *74* (1955) 1482.

9 W. D. Perkins and M. K. Wilson, *J. Chem. Phys.*, *20* (1952) 1791.

10 R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, *39* (1961) 2171.

11 T. Birchall and R. J. Gillespie, *Spectrochim. Acta, Part A*, *22* (1966) 681.

12 M. Wartel, S. Noel and J. Heubel, *Rev. Chim. Miner.*, *4* (1967) 181.

13 A. J. Illies and G. A. Takacs, *J. Photochem.*, *6* (1976) 35.

14 CODATA recommended key values for thermodynamics, *J. Chem. Thermodyn.*, *10* (1978) 903.

15 D. R. Stull and H. Prophet (eds.), *JANAF Thermochemical Tables, NBS Ref. Data Ser.*, *37* (2nd edn., 1971).

16 D. D. Wagman, W. H. Evans, V. B. Parker, I. Harlow, S. M. Bailey and R. H. Schumm, *NBS Tech. Note 270-3*, 1968 (U.S. National Bureau of Standards).

17 M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud and L. C. Walker, *JANAF Thermochemical Tables, 1974 Suppl.*, in *J. Phys. Chem. Ref. Data*, *3* (1974) 311.

18 Z. G. Szabo, *Advances in Homogeneous Chemical Reactions*, Methuen, London, 1964, p. 150.

19 S. W. Benson, *Chem. Rev.*, *78* (1978) 24.

20 K. Wray and E. V. Feldman, *J. Chem. Phys.*, *54* (1971) 3445.

21 L. Batt and R. D. McCulloch, *Int. J. Chem. Kinet.*, *8* (1976) 911.

22 M. Cartwright and A. A. Woolf, *J. Chem. Soc., Dalton Trans.*, (1980) 817.

23 W. H. Busfield, K. J. Ivin, H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.*, *57* (1961) 1064.

24 J. A. Good and J. C. Thynne, *Trans. Faraday Soc.*, *63* (1967) 2708.

25 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970.

26 J. Plonka and J. Lodge, personal communication to P. J. Crutzen, reported in *Geophys. Res. Lett.*, *3* (1976) 73.