

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PSOx3

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission.

This data sheet updated: 19th November 2001.

CH₃SSCH₃ + hν → products

Primary photochemical processes

Reaction			ΔH°/kJ·mol ⁻¹	λ _{threshold} /nm
CH ₃ SSCH ₃	→ CH ₃ SS + CH ₃	(1)	238	502
	→ 2CH ₃ S	(2)	274	437

Absorption cross-section data

Wavelength/nm	Reference	Comments
201-360	Hearn, Turcu and Joens, 1990 ¹	(a)

Quantum yield data

Wavelength/nm	Reference	Comments
193-248	Barone <i>et al.</i> , 1994 ²	(b)

Comments

- (a) Cary 2300 double beam UV spectrophotometer used with a resolution of 0.10 nm. Photolysis of (CH₃)₂S₂-N₂ mixtures at a constant pressure of 133 mbar (100 Torr). Temperature = 300 ± 2 K.
- (b) Primary quantum yields for formation of H(²S) and CH₃S(²E) from photodissociation at excimer wavelengths 193, 222, and 248 nm were measured, with H atom detection by RF and CH₃S detection by pulsed LIF.

Preferred Values

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
201	1053.0	280	49.8
205	850.0	285	36.0
210	630.0	290	25.15
215	312.0	295	17.06
220	138.7	300	11.27
225	85.6	305	7.24
228 (min)	82.3	310	4.57
230	84.2	315	2.85
235	96.0	320	1.79
240	110.0	325	1.09
245	120.7	330	0.67
250	125.4	335	0.38
251 (max)	125.6	340	0.22
255	123.3	345	0.14
260	113.9	350	0.07
265	99.3	355	0.04
270	82.7	360	<0.01
275	65.4		

Comments on Preferred Values

The preferred values for σ are those of Hearn *et al.*¹ which agree well with the earlier values cited in Calvert and Pitts.³ Sheraton and Murray's spectrum⁴ agrees qualitatively with the other studies, but the reported absorption coefficients are significantly lower.

Barone *et al.*² report the primary quantum yield for CH_3S production to be 1.65 ± 0.38 at 248 nm and 1.20 ± 0.14 at 193 nm. These authors report that no H atoms were observed at 248 nm, and that at 193 and 222 nm H atom production was only a minor process and could be due to sample impurities. These results and those of Balla and Heicklen⁵ indicate that at wavelengths of importance to atmospheric photochemistry dissociation occurs primarily by S-S bond scission to give 2 CH_3S . The significantly lower value of $\phi(\text{CH}_3\text{S})$ at 193 nm implies the existence of an additional channel at these short wavelengths.

References

- ¹ C. H. Hearn, E. Turcu, and J. A. Joens, *Atmos. Environ.* **24A**, 1939 (1990).
- ² S. B. Barone, A. A. Turnipseed, T. Gierczak, and A. R. Ravishankara, *J. Phys. Chem.* **98**, 11969 (1994).
- ³ J. G. Calvert and J. N. Pitts, Jr., *"Photochemistry,"* (Wiley), 1966, p. 490.
- ⁴ D. F. Sheraton and F. E. Murray, *Can J. Chem.* **59**, 2750 (1981).
- ⁵ R. J. Balla and J. Heicklen, *Can. J. Chem.* **62**, 162 (1984).