IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet PSOx2

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.

$CS_2 + h\upsilon \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CS_2 + h\nu \rightarrow CS$	(1)		>277
$\rightarrow CS + S(^3P)$	(2)	432	281
$\rightarrow CS + S(^1D)$	(3)	543	223

Absorption cross-section data

Wavelength/nm	Reference	Comments
180-230	Chen and Wu, 1995[1]	(a)
187-230	Xu and Joens, 1993[2]	(b)
185-220	Molina, Lamb and Molina, 1981[3]	(c)
188-213, 287.5-339.5	Ahmed and Kumar, 1992[4]	(d)
271-374	Hearn and Joens, 1991[5]	(e)
318-350	Wu and Judge, 1981[6]	(f)
280-360	Wine, Chameides and Ravishankara, 1981[7]	(g)
315-330	Leroy *et al.*, 1983[8]	(h)

Comments

(a) Spectral resolution 0.08 nm. Synchroton radiation was used as a continuum light source. Measurements were made at 203, 295, and 385 K. Significant temperature effects and hot bands were observed. Results were presented in graphical form in paper but authors provide data points at 0.005 nm intervals on request.

(b) Spectral resolution of 0.2 nm. Deuterium lamp as continuum light source.

(c) As part of their study of the OCS spectrum. Spectral resolution of 0.2 nm. Results in graphical form.

(d) Spectral resolution of 0.2 nm. Ar-arc lamp as continuum light source.

(e) Spectral resolution 0.06 nm. Deuterium lamp as continuum light source. Results presented in graphical form in paper but authors provide data points at 0.02 nm intervals on request.

(f) Spectral resolution 0.06 nm. Synchroton radiation was used as a continuum light source.

(g) Spectral resolution 0.4 nm.

(h) Spectral resolution 0.2 nm.

Preferred Values

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
275	0.017	299	2.017	323	5.180	347	0.328
276	0.020	300	1.879	324	3.517	348	0.109
277	0.027	301	3.269	325	8.628	349	0.368
278	0.043	302	3.166	326	5.023	350	0.239
279	0.050	303	3.131	327	3.481	351	0.127
280	0.053	304	4.438	328	2.849	352	0.255
281	0.062	305	4.461	329	2.848	353	0.066
282	0.080	306	3.658	330	3.802	354	0.172
283	0.103	307	5.122	331	1.301	355	0.247
284	0.122	308	7.101	332	3.057	356	0.052
285	0.158	309	4.930	333	1.552	357	0.133
286	0.209	310	8.838	334	1.506	358	0.055
287	0.254	311	5.611	335	1.375	359	0.059
288	0.309	312	6.692	336	0.861	360	0.119
289	0.445	313	8.148	337	1.377	361	0.042
290	0.438	314	7.842	338	0.591	362	0.048
291	0.635	315	9.440	339	1.121	363	0.021
292	0.640	316	7.039	340	0.489	364	0.037
293	0.878	317	9.462	341	0.386	365	0.012
294	0.801	318	7.159	342	0.573	366	0.036
295	1.137	319	9.803	343	0.387	367	0.023
296	1.134	320	4.518	344	0.556	368	0.020
297	1.861	321	6.122	345	0.353	369	0.011
298	2.287	322	4.221	346	0.350	370	0.018

Quantum Yields

$\phi_{OCS} < 1.2 \times 10^{-2}$ for 290-360 nm region in 1 bar air.

Comments on Preferred Values

The UV absorption spectrum of CS_2 shows two absorption bands at ≈ 180-210 nm and ≈ 290-340 nm, both have fine structure superimposed on a continuum. The cross-sections in both bands display some temperature dependence[1,7] and dependence on instrumental resolution. The measurements of Hearn and Joens[5] on the absorption spectrum were carried out using similar conditions of temperature, resolution, pathlength, and gas pressure to those used by Wu and Judge.[6] In both cases the resolution used (0.06 nm) is higher than in the other studies. The values of the cross-section obtained by Hearn and Joens[5] are some 10-15% higher than those obtained by Wu and Judge[6] and there are minor differences in the band structures observed. The preferred values in the long-wavelength band are those of Hearn and Joens[5] whose data set covers the largest spectral region. The data listed are averaged over 1 nm intervals.

The recommended quantum yield for OCS production from the photoinitiated oxidation of CS_2 in air is that reported by Jones *et al*.,[9] which is in good agreement with the value estimated by Wine *et al*.[7] from the earlier data of Wood and Heicklen[10] (i.e., ϕ_{OCS} = 0.01 - 0.015). The recommended value might best be considered an upper limit since the observed slow oxidation of the CS_2 could have been due, at least in part, to other mechanisms, possibly involving excited CS_2.[11]

References

[1] F. Z. Chen and C. Y. R. Wu, Geophys. Res. Lett. **22**, 2131 (1995).
[2] H. Xu and J.A. Joens, Geophys. Res. Lett. **20**, 1035 (1993).
[3] L.T. Molina, J.J. Lamb and M.J. Molina, Geophys. Res. Lett. **8**, 1008 (1981).
[4] S.M. Ahmed and V. Kumar, Pramana-J. Phys., **39**, 367 (1992).
[5] C. H. Hearn and J. A. Joens, J. Quant. Spectrosc. Radiat. Trans. **45**, 69 (1991).
[6] C. Y. R. Wu and D. L. Judge, Geophys. Res. Lett. **8**, 769 (1981).
[7] P. H. Wine, W. L. Chameides, and A. R. Ravishankara, Geophys. Res. Lett. **8**, 543 (1981).
[8] B. Leroy, P. Rigaud, J.L. Jourdain and G. Le Bras, Moon Planet, **29**, 177, (1983).
[9] B. M. R. Jones, R. A. Cox, and S. A. Penkett, J. Atmos. Chem. **1**, 65 (1983).
[10] W. P. Wood and J. Heicklen, J. Phys. Chem. **75**, 854 (1971).
[11] L. M. Goss, G. J. Frost, D. J. Donaldson, and V. Vaida, Geophys. Res. Lett. **22**, 2609 (1995).