IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PSOx1

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OCS + hυ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
OCS + hν → CO + S(^{3}P)	(1)	308	388
→ CO + S(^{1}D)	(2)	419	286

Absorption cross-section data

Wavelength/nm	Reference	Comments
185-300	Molina, Lamb and Molina, 1981[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength region	Reference	Comments
$\phi_1/\phi_2 = 0.055$	222	Nan, Burak and Houston, 1993[2]	(b)
$\phi = 1.04 \pm 0.09$	248	Zhao, Stickel and Wine, 1995[3]	(c)

Comments

(a) At a spectral resolution of 0.2 nm, at temperatures of 295 and 225 K. Data were given in figures and tables showing values averaged over 1 nm and averaged over wavelength intervals generally used in stratospheric photodissociation calculations. A value of $\sigma_{max} = 3.27 \times 10^{-19}$ cm^2 molecule^{-1} was determined at 223 nm.

(b) Pulsed laser photolysis of OCS at 222 nm. Doppler profile of S($^3P_2$) was monitored by LIF at 147 nm. CO used to quench S(^{1}D). S($^3P_2$) yield of 0.050 relative to S(^{1}D) obtained. S($^3P_1$) and S($^3P_0$) were not monitored but if they were present in statistical amounts then total triplet yield = 0.055.

(c) Excimer laser flash photolysis of flowing OCS-N_2-N_2O and $C(O)Cl_2$-N_2-N_2O gas mixtures at 248 nm. Concentration of CO was monitored by TDLS. ϕ was measured relative to the quantum yield

for production of CO from photolysis of $C(O)Cl_2$, which is known to be unity. Measurements were carried out at 297 K and pressures of 5-133 mbar (4 to 100 Torr) $N_2 + N_2O$.

Preferred Values

λ/nm	10^{21} σ/cm^2 (295 K)	10^{-3} B / K^{-1}	ϕ
300	0.0009		
295	0.0023	8.15	
290	0.0077	11.3	
285	0.0218	13.6	
280	0.0543	13.85	
275	0.1504	12.96	
270	0.376	12.57	
265	0.960	1.17	
260	2.52	1.11	1.0
255	6.64	9.31	1.0
250	16.5	7.46	1.0
245	38.2	6.00	1.0
240	81.3	4.51	1.0
235	153.6	3.09	1.0
230	243.8	2.01	1.0
225	310.4	1.32	1.0
220	304.8	0.835	1.0
215	241.6	0.323	1.0
210	150.8	-0.0756	
205	82.0	-0.0868	
200	39.3	0	
195	20.2	0.950	
190	39.7	5.61	
185	190.3	4.83	

Comments on Preferred Values

There is good agreement among all cross-section measurements for $\lambda < 280$ nm obtained since 1970.[1,4-9] The data of Molina *et al*. is the only data set that extends beyond 280 nm, and provides the basis of the recommendation. The temperature dependence of the cross-sections of Molina *et al*.[1] are described by $\sigma(\lambda,T) = \sigma(\lambda,295)\exp[B(\lambda)(T-295)]$ where T is in K and wavelength dependent values of B are taken from the Table above. This simple parameterisation perfectly reproduces the data of Molina at 225 K and accurately reproduces the temperature dependence of the Wu *et al*. data at 170 to 370 K at $\lambda > 230$ nm.

The preferred overall quantum yield of 1.0 is based on results reported recently by Zhao *et al*.[3] Results of all studies indicate that S atoms are produced predominately in the S(^{1}D) electronically excited state. Sidhu *et al*.[10] reported $\phi_2/\phi \geq 0.74$ and Breckenridge and Taube[4] reported $\phi_2/\phi = 0.74 \pm 0.04$. Nan *et al*.[2] reported $\phi_1/\phi_2 = 0.055$, which when combined with the preferred value of $\phi = \phi_1 + \phi_2 = 1.0$ yields $\phi_2/\phi = 0.95$.

References

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