IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P12

This data sheet updated: 16th May 2002.

$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3OOH + h\upsilon \rightarrow CH_3O + HO$	(1)	185	645
$\rightarrow CH_3 + HO_2$	(2)	292	410
$\rightarrow CH_3O_2 + H$	(3)	358	334

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210-365	Vaghjiani and Ravishankara, 1989[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.00 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990[2]	(b)

Comments

(a) CH_3OOH prepared by methylation of H_2O_2 and shown by ^1H NMR to be > 97% pure [major impurity $C_2H_5OC_2H_5$]. A diode-array spectrometer was used to make relative absorption measurements over the whole wavelength range and the results were put on an absolute basis by measurement of the cross-sections at 213.9 nm (Zn line), and at 298.1 nm, 326.1 nm, 340.4 nm and 361.1 nm using Cd lines. The CH_3OOH concentration was determined by trapping the vapor at 77 K and titrating with Fe^{2+} or I^-.

(b) Direct measurement of products, OH by LIF, and $O(^3P)$ and H atoms by resonance fluorescence. Quantum yields for the formation of $O(^3P)$ and H atoms of < 0.007 and 0.038 ± 0.007, respectively, were obtained.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 290$ nm.

Comments on Preferred Values

The preferred absorption cross-section data are those of Vaghjiani and Ravishankara,[1] which are approximately 25% lower than the previously recommended data of Molina and Arguello.[3] The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello[3] used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara[1] showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara,[2] who showed that $\phi_{OH} \sim 1.0$ at $\lambda = 248$ nm, we recommend that the atmospheric photolysis of CH_3OOH ϕ_1 be taken to be unity for wavelengths > 290 nm.

References

1 G. L. Vaghjiani and A. R. Ravishankara, J. Geophys. Res. **94**, 3487 (1989).

2 G. L. Vaghjiani and A. R. Ravishankara, J. Chem. Phys. **92**, 996 (1990).

3 M. J. Molina and G. Arguello, Geophys. Res. Lett. **6**, 953 (1979).