IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PHOx1

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$H_2O + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reactions		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$H_2O + h\upsilon \rightarrow H_2 + O(^3P)$	(1)	491.0	243
$\rightarrow H + HO$	(2)	492.8	242
$\rightarrow H_2 + O(^1D)$	(3)	680.7	176

Absorption cross-section data

Wavelength range/nm	Reference	Comments
176-185	Watanabe and Zelikoff, 1953[1]	(a)
185-198	Thompson, Harteck and Reeves, 1963[2]	(b)
175-182	Schurgers and Welge, 1968[3]	(c)
183-193	Cantrell, Zimmer and Tyndall, 1997[4]	(d)
184.9	Hofzumahaus et al, 1997[5]	(e)
184.9	Creasey, Heard and Lee, 2000[6]	(f)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 \leq 0.003$	174	Chou, Lo and Rowland, 1974[7]	(g)

Comments

(a) Static system. H_2O was determined by pressure measurement over the range 0.08-8 Torr. Resolution was approximately 0.1 nm. Only graphical presentation of data.

(b) Static system double beam spectrophotometer used with a 10 cm pathlength. H_2O pressure was 27 mbar (20 Torr). No details of pressure measurement or resolution were given. Only graphical presentation of data.

(c) Flowing system. H_2O was determined using a membrane manometer. 0.5 m grating monochromator, with 0.25 nm bandwidth. Only graphical presentation of data.

(d) Absolute cross sections measured at 184.9 nm using optically filtered Hg lamp and solar blind photomultiplier. Wide range of conditions with 4 separate methods for determination of H_2O pressure. Temperature range 273-353 K. $\sigma = (7.14 \pm 0.2) \times 10^{-20}$ $cm^2 molecule^{-1}$ at 298 K with a positive temperature dependence of 4% between 273 and 353 K. Spectrum recorded between 183-193 nm and cross sections in this range were calculated relative to σ (184.9nm).

(e) Absolute cross sections measured at 184.9 nm. $\sigma = 7.0 \times 10^{-20}$ $cm^2 molecule^{-1}$ at 298 K

(f) Absolute cross sections measured at 184.9 nm using static and H_2O/N_2 mixtures. $\sigma = (7.14 \pm 0.2) \times 10^{-20}$ $cm^2 molecule^{-1}$ at 298 K and $\sigma = 7.26 \times 10^{-20}$ $cm^2 molecule^{-1}$ at 305 K.

(g) Photolysis involved HTO. It was shown that the decomposition path is almost entirely via the reactions $HTO + h\upsilon \rightarrow H + OT$ and $HTO + h\upsilon \rightarrow T + HO$, with ≤ 0.003 of the molecules decomposing via the reaction $HTO + h\upsilon \rightarrow HT + O$.

Preferred Values

λ/nm	$10^{20}\ \sigma/cm^2$	ϕ_2
175.5	263.0	1.0
177.5	185.0	1.0
180.0	100.0	1.0
182.0	29.8	1.0
183.0	16.9	1.0
184.0	12.1	1.0
185.0	6.78	1.0
186.0	4.39	1.0
187.0	2.71	1.0
188.0	1.77	1.0
189.0	1.08	1.0
190.0	0.672	1.0
191.0	0.464	1.0
192.0	0.277	1.0
193.0	0.175	1.0

Comments on Preferred Values

Water vapour has a continuous spectrum between 175 and 190 nm, and the cross-section decreases rapidly towards longer wavelengths. The cross-section data at 184.9 nm from three recent studies[4-6] are in excellent agreement. They are all ~ 30% higher than data previously recommended by IUPAC[8], which were taken from the review of Hudson,[9] and were obtained by drawing a smooth curve through the data of Watanabe and Zelikoff,[1] Thompson *et al*.[2] and Schurgers and Welge.[3]

Recent data of Yoshino et al[10] covers wavelengths down to 120 nm but above 183 nm are scattered and give higher values of σ, but an earlier value at 184.9 from DeMore[11] is consistent with the recent data. The recommended values at 298 K in the range 180-193 nm, are those of Cantrell et al.[4] which were obtained using several independent measures of the H_2O concentration. Values at shorter wavelength based on Hudson[9]. The recommended cross section at 184.9 nm is $\sigma = 7.14 \times 10^{-20}$ $cm^2 molecule^{-1}$ at 298 K. The temperature dependence over the range 273 – 353 K is given by the expression: $\log_{10}\{\sigma(T)/\sigma(298)\} = 2.14 \times 10^{-4}\{T - 298(K)\}$, based also on the results of Cantrell et al.[4]

On the basis of the nature of the spectrum and the results of Chou *et al*.[7] on the photolysis of HTO, it is assumed that over the wavelength region 175-190 nm reaction (2) is the only primary process and that $\phi_2 = 1.0$.[7]

References

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