

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PHOx2

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This data sheet updated: 2nd October 2001.

H₂O₂ + hν → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
H ₂ O ₂ + hν → HO + HO	(1)	215	557
→ H ₂ O + O(¹ D)	(2)	333	359
→ H + HO ₂	(3)	369	324
→ HO + HO(² Σ)	(4)	606	197

Quantum Yield Data

$$(\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4)$$

Measurement	Wavelength Range/nm	Reference	Comments
$\phi_3 = 0.12$	193	Gerlach-Meyer <i>et al.</i> , 1987 ¹	(a)
$\phi_1 = 1.04 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990 ²	(b)
$\phi_2 < 0.002$	248		
$\phi_3 < 0.0002$	248		
$\phi_1 = 1.01 \pm 0.17$	222	Vaghjiani <i>et al.</i> , 1992 ³	(c)
$\phi_2 < 0.002$	222		
$\phi_3 = 0.024 \pm 0.012$	222		
$\phi_3 = 0.16 \pm 0.04$	193		
$\phi_1 = 0.79 \pm 0.12$	248	Schiffman, Nelson and Nesbitt, 1993 ⁴	(d)

Comments

- (a) Pulsed laser photolysis of H₂O₂ with H-atom detection by laser-induced fluorescence.
- (b) Pulsed photolysis of flowing mixtures of H₂O₂-H₂O-N₂ (or He) and of O₃-H₂O-N₂ (or He) at 298 K. H₂O₂ and O₃ were determined by UV absorption at 213.9 nm or 228.8 nm. Quantum yield of HO radical formation from H₂O₂-H₂O mixture was measured relative to that from O₃-H₂O mixture. These relative yields were placed on an absolute basis using the known quantum yield of HO radical production from the photolysis of O₃-H₂O mixtures at 248 nm, taken as $\phi(\text{HO}) = 1.73 \pm 0.09$.^{2,5} O and H atom yields were determined by resonance fluorescence.
- (c) Pulsed laser photolysis of H₂O₂-N₂ or SF₆ mixtures at 222 nm and 248 nm. [HO] monitored by LIF. The quantum yield of HO radical production at 248 nm was assumed to be 2.0 and the value

at 222 nm was determined from this and the relative HO yields at the two wavelengths. H atom concentrations were monitored by resonance fluorescence. The quantum yield was determined by reference to CH₃SH photolysis at 193 nm. O(³P) atom formation was investigated using resonance fluorescence but only a very small signal was detected, possibly due to secondary chemistry.

- (d) Pulsed laser photolysis of H₂O₂ mixtures. Energy, and hence number of photons, of laser pulse absorbed determined by calorimetry. HO radical concentrations were monitored by infrared absorption using a color center dye-laser (2.35-3.40 μm) and interferometer for wavelength measurement. Absolute HO radical concentrations were obtained using integrated absorption cross-sections measured in the same laboratory.

Preferred Values

Absorption Cross-sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	ϕ_1	$10^{20} \lambda/\text{nm}$	σ/cm^2	ϕ_1
190	67.2		275	2.6	1.0
195	56.3		280	2.0	1.0
200	47.5		285	1.5	1.0
205	40.8		290	1.2	1.0
210	35.7		295	0.90	1.0
215	30.7		300	0.68	1.0
220	25.8	1.0	305	0.51	1.0
225	21.7	1.0	310	0.39	1.0
230	18.2	1.0	315	0.29	1.0
235	15.0	1.0	320	0.22	1.0
240	12.4	1.0	325	0.16	1.0
245	10.2	1.0	330	0.13	1.0
250	8.3	1.0	335	0.10	1.0
255	6.7	1.0	340	0.07	1.0
260	5.3	1.0	345	0.05	1.0
265	4.2	1.0	350	0.04	1.0
270	3.3	1.0			

Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 230$ nm; $\phi_1 = 0.85$, $\phi_3 = 0.15$ at 193 nm.

Comments on Preferred Values

There have been no new measurements of the absorption cross-sections and our recommendations are unchanged from those in our previous evaluation, IUPAC, 1997.⁷ The preferred values are the mean of those determined by Lin *et al.*,⁸ Molina and Molina,⁹ Nicovich and Wine¹⁰ and Vaghjiani and Ravishankara.¹¹ These agree with the earlier values of Holt *et al.*¹² The absorption cross-sections have also been measured at other temperatures by Troe¹³ (220—290 nm at 600 K and 1100 K) and by Nicovich and Wine¹⁰ (260-250 nm, 200-400 K). Both Nicovich and Wine¹⁰ and Troe¹³ have expressed their results in an analytical form. It has long been assumed that channel (1) is the only significant primary photochemical channel at $\lambda > 200$ nm. There are measurements by Vaghjiani and Ravishankara² and Vaghjiani *et al.*³ at

248 nm and 222 nm which support this. However, measurements at 193 nm by Vaghjiani *et al.*³ show a decline in the HO radical quantum yield (1.51 relative to an assumed value of 2 at 248 nm) with a growth in the H atom quantum yield, a feature previously observed by Gerlach-Meyer *et al.*¹ The results of Schiffman *et al.*⁴ also agree well with this relative change in HO radical production in going from 248 nm to 193 nm. However, Schiffman *et al.*⁴ obtain much lower absolute values for the quantum yield of HO radical production than obtained by Vaghjiani and Ravishankara.²

The evidence therefore indicates that there is a decline in the relative importance of channel (1) in going from 248 nm to 193 nm but the point of onset of this decline and its form are uncertain. Furthermore, the reason for the difference in the absolute values of the quantum yield between the studies of Schiffman *et al.*⁴ and Vaghjiani and Ravishankara² is unclear; further work is urgently required to clarify this. Recent measurements¹⁴ of the translational energy of the H-atom photofragments from 193 nm photolysis of H₂O₂ originate from the same upper state (\tilde{A}^1A) which is responsible for OH production at longer wavelengths.

We recommend the use of a quantum yield of 2 for HO radical production ($\phi_1 = 1.0$) at $\lambda > 230$ nm.

References

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