IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx2

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$$HONO_2 + h\nu \rightarrow products$$

Primary photochemical transitions

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HONO_2 + h\nu \rightarrow HO + NO_2(X\ ^2A_1)$	(1)	198	604
$\rightarrow HONO + O(^3P)$	(2)	305	393
$\rightarrow HO + NO_2(1\ ^2B_2)$	(3)	314	381
$\rightarrow H + NO_3$	(4)	427	278
$\rightarrow HONO + O(^1D)$	(5)	495	242
$\rightarrow HONO(a^3A'') + O(^3P)$	(6)	554	216

Absorption cross-section data

Wavelength range/nm	Reference	Comments
195-350	Burkholder et al., 1993[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(OH) = 1.0$	200-315	Johnston, Chang, and Whitten, 1974[2]	(b)
$\phi(OH) = 0.89\pm0.08$	222	Jolly et al., 1986[3]	(c)
$\phi[HO], \phi[O(^3P)]$	248, 222, 193	Turnipseed et al., 1992[4]	(d)
$\phi[O(^1D)], \phi[H(^2S)]$			
$\phi(1), \phi(2), \phi(3), \phi(5), \phi(6)$	193	Myers et al., 1997[5]	(e)
$\phi(4)$	193	Li, Carter, and Huber, 2001[6]	(f)

Comments

(a) The temperature dependences of HNO_3 absorption cross-sections were measured between 240 K and 360 K using a diode array spectrometer with a resolution of < 0.4 nm. Absorption cross-sections were determined using both absolute pressure measurements at 298 K and a

dual cell arrangement to measure absorptions at various temperatures relative to 298 K. A review of all previous experimental values was given together with an assessment of temperature-dependence effects on the stratospheric photolysis rate of HNO_3.

(b) Photolysis of HNO_3 in the presence of excess CO and excess O_2 to prevent complications due to secondary reactions. Results were interpreted by a complex reaction scheme.

(c) Pulsed laser photolysis with a KrCl excimer laser. HO radicals were detected by time-resolved resonance absorption at 308.3 nm. The error estimate quoted does not include the uncertainty of + 17%, - 8% resulting from an analysis of potential systematic errors.

(d) Quantum yields for HO radicals, $[O(^3P)+O(^1D)]$ atoms, $O(^1D)$ atoms, and H atoms were measured in pulsed laser photolysis systems at 248 nm, 222 nm, and 193 nm, using LIF detection for $HO(X^2\Pi)$ radicals and atomic resonance fluorescence for $O(^3P)$ and $H(^2S)$ atoms. $\phi(HO)$ was measured relative to the yield of HO radicals from H_2O_2 photolysis at 248 nm $[\phi(HO) = 2.00 \pm 0.05]$[7] and at 193 nm $[\phi(HO) = 1.51 \pm 0.18]$.[8] $\phi [O(^3P) + O(^1D)]$ was measured relative to the O atom yield from O_3 photolysis at 248 nm ($\phi = 1$) and 193 nm ($\phi = 1.20 \pm 0.15$).[9] $\phi[H(^2S)]$ was measured relative to the H atom yield from the photolysis of O_3-H_2 mixtures where the H atoms are produced in the $O(^1D) + H_2$ reaction. Measurements gave: $\phi(HO) = 0.95 \pm 0.09$ at 248 nm, 0.90 ± 0.11 at 222 nm, and 0.33 ± 0.06 at 193 nm. $\phi[O(^3P) + O(^1D)]$ was observed to be 0.031 ± 0.010, 0.20 ± 0.03, and 0.81 ± 0.13, at 248nm, 222nm, and 193 nm respectively, with exclusively $O(^3P)$ production at 248 nm. $\phi[O(^1D)]$ was 0.074 ± 0.03 at 222 nm and 0.28 ± 0.13 at 193 nm. H atom yields were low; only at 193 nm were any H atoms detected, with $\phi[H(^2S)] \leq 0.012$.

(e) Photofragment translational spectroscopy investigation of $HONO_2$ photolysis at 193 nm. The primary processes and their relative yields were deduced from photofragment time-of-flight signals at masses 16 (O^+), 17 (HO^+), 30 (NO^+), and 46 (NO_2^+). Two HO distributions arising from channels (1) and (3) were resolved and gave $\phi_1+\phi_3 = 0.33 \pm 0.04$, $\phi_3/\phi_1 = 0.45$. Two main O–atom producing channels were identified and attributed to channels (5) and (6), with quantum yields $\phi_5+\phi_6 = 0.67 \pm 0.04$, $\phi_5/\phi_6 = 4.0$.

(f) Photodissociation at 193 nm in a supersonic jet was studied using LIF and REMPI-TOF techniques. A bimodal rotational state distribution was observed for HO, consistent with the bimodal translational distribution found for HO by Myers et al.[5] An additional decay channel yielding $O(^3P)$ was observed and attributed to channel (2), with a quantum yield of ~ 0.06.

Preferred Values

Absorption cross-sections at 298 K [a]

λ/nm	$10^{20}\,\sigma/cm^2$	$10^3\,B/K^{-1}$	λ/nm	$10^{20}\,\sigma/cm^2$	$10^3\,B/K^{-1}$
190	1360	0	270	1.62	1.45
195	1016	0	275	1.38	1.60
200	588	1.66	280	1.12	1.78
205	280	1.75	285	0.858	1.99
210	104	1.97	290	0.615	2.27
215	36.5	2.17	295	0.412	2.61
220	14.9	2.15	300	0.263	3.10
225	8.81	1.90	305	0.150	3.64
230	5.78	1.80	310	0.081	4.23
235	3.75	1.93	315	0.041	5.20
240	2.58	1.97	320	0.020	6.45
245	2.11	1.68	325	0.0095	7.35
250	1.97	1.34	330	0.0043	9.75
255	1.95	1.16	335	0.0022	10.1
260	1.91	1.14	340	0.0010	11.8
265	1.80	1.20	345	0.0006	11.2
			350	0.0004	9.30

[a] Temperature dependence given by the expression: $\log_e\sigma = \log_e\sigma(298) + B(T - 298)$ with T in K.

Quantum Yields at 298 K

	λ/nm		
	≥ 248	222	193
$\phi(OH)$	> 0.97	0.90±0.10	0.33±0.06
$\phi[O(^1D) + O(^3P)]$	0.03±0.03	0.20±0.03	0.81±0.13
$\phi(O^1D)$	< 0.003	0.08±0.01	0.28±0.11
$\phi(H)$	< 0.01	< 0.01	< 0.01

Comments on Preferred Values

The results of Burkholder et al.[1] for the cross-sections provide a high quality and comprehensive data set over the range of temperatures and wavelengths of significance for atmospheric photolysis of HNO_3. Over the wavelength range 205-310 nm there is good agreement with the earlier studies of Rattigan et al.,[10] Biaume,[11] Molina and Molina,[12] and Johnston and Graham.[13] At λ < 205 nm, the data from different studies show small and unexplained discrepancies. At λ > 310 nm the room temperature results of Burkholder et al.[1] are increasingly higher than all previously reported data except those of Rattigan et al.,[10] which are in good agreement. The preferred values are those given by Burkholder et al.[1]

The temperature dependences reported by Burkholder *et al.*[1] are weaker than those reported by Rattigan *et al.*[10] However, if the data at the lowest temperature (239 K) in the study of Rattigan *et al.*[10] are omitted, the agreement is good. Burkholder *et al.*[1] give values for the temperature coefficient, B, based on the two data sets[1,10] (excluding the 239 K data of Rattigan *et al.*[10]), and these are adopted here.

The quantum yield measurements confirm that, although channels (1) and (3) are the dominant channels at $\lambda > \sim 260$ nm with $\phi(OH)$ close to unity, other channels become important at shorter wavelengths as suggested by the earlier work of Kenner *et al.*[14] The quantum yield measurements of Turnipseed *et al.*[4] and Schiffman *et al.*[15] are in excellent agreement at 248 nm when the two sets of measurements are normalized to the same value of the quantum yield for HO radical production from H_2O_2. The agreement is less good at 193 nm, where the direct measurements of Schiffman *et al.*[15] give an HO radical yield higher by about 50%. The value of $\phi(H_2O_2)$ obtained by Schiffman *et al.*[15] is about 25% lower at both 248 nm and 193 nm than the values obtained by Vaghjiani *et al.*[8,9] (2.0 at 248 nm and 1.5 at 193 nm). The preferred values for the quantum yields at $\lambda \geq 248$ nm are based on the indirect studies of Johnston *et al.*[2] and the direct observation of Turnipseed *et al.*[4] The small yield of O atoms observed by Turnipseed *et al.*[4] is in agreement with the value of $\phi(O) = 0.03$ at 266 nm obtained by Margitan and Watson.[16] At 222 nm the preferred values are based on the data of Turnipseed *et al.*[4] and Jolley *et al.*[3]

The photolysis of $HONO_2$ at 193 nm has been clarified by recent the recent molecular beam studies of Myers *et al.*[5] and Li *et al.*[6] which employed LIF and TOF techniques to detect the photolysis products and to measure their energy distributions. They obtained evidence for the occurrence of channels (1), (2), (3), (5), and (6), with O atom production becoming a major process at this wavelength, directly through channels (2), (5), and (6), and indirectly through dissociation of the internally excited NO_2 produced via channel (1). The minor pathway ($\phi_2 = \sim 0.06$), detected by Li *et al.*,[6] also produces internally excited HONO capable of subsequent dissociation. There are also pulsed laser photolysis studies at 193 nm on bulk gas samples from Turnipseed *et al.*[4] and Schiffman *et al.*[16] As previously mentioned, in the study of Schiffman *et al.*[16] there are inconsistencies in the measurements of HO yields from H_2O_2 dissociation at $\lambda \geq 260$ nm. The results of Turnipseed *et al.*[4] are therefore preferred and are the basis of our preferred values for the quantum yields at 193 nm. The value $\phi(OH)$ obtained by Turnipseed *et al.*[4] is the same as that from the molecular beam study of Myers *et al.*[5] and the value of $\phi[O(^3P)+O(^1D)]$ of Turnipseed *et al.*[4] can also be reconciled with the molecular beam results when production of O atoms from dissociation of internally excited NO_2 from channel (1) is allowed for. However the value of $\phi(O^1D) = 0.28$ obtained by Turnipseed *et al.*[4] is much smaller than the value of $\phi_5 = 0.52$ found by Myers *et al.*[5] and this discrepancy remains to be resolved. The upper limits to the H-atom yield obtained by Turnipseed *et al.*[4] suggest that channel (4) is unimportant at $\lambda \geq 193$ nm.

Photodissociation of $HONO_2$ via high-lying O-H overtone absorptions in the visible region of the spectrum is energetically possible for the $5\nu_{OH}$ and higher overtones. Brown *et al.*[17] have used cavity ring down spectroscopy to measure absorption cross-sections at 296 K and 251 K for the $4\nu_{OH}$ and $5\nu_{OH}$ transitions. The values obtained agree well with those from other studies[18,19] and imply that the contribution of these absorptions to HO production in the atmosphere is small, but larger than previous calculations[18,20] suggest.

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