IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx3

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$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$	(1)	100	1191
$\rightarrow HO + NO_3$	(2)	164	731

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190-330	Molina and Molina, 1981[1]	(a)
210-330	Singer *et al.*, 1989[2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_2	248	Mac Leod, Smith, and Golden, 1988[3]	(c)
ϕ_1	248	Roehl *et al.*, 2001[4]	(d)

Comments

(a) Measured at 298 K and 1 bar total pressure. HO_2NO_2 was prepared in a flowing N_2 stream in the presence of H_2O, H_2O_2, and HO_2. The composition of the mixture was established by FTIR spectroscopy, by the absorption spectrum in the visible, and by chemical titration after absorption in aqueous solutions. Two methods were used to prepare the HO_2NO_2. In the first, 70% nitric acid was mixed with 90% H_2O_2, while in the second method solid nitroniumtetrafluoroborate (NO_2BF_4) was added to a solution of 90% H_2O_2.

(b) Cross-sections were measured at 298 K, 273 K, and 253 K. Pernitric acid was produced *in situ* by photolysis of Cl_2-H_2-NO_2-air mixtures and averaged absorption measurements were made at small extents of reaction. The relative spectrum over the range 210-230 nm was measured at a resolution of 1 nm in flowing mixtures of pernitric acid vapour obtained from the reaction of BF_4NO_2 and H_2O_2. The spectrum was corrected for the impurities NO_2, H_2O_2, and HNO_3, which were determined by IR spectroscopy.

(c) Laser photolysis of pernitric acid at 248 nm. The HO radicals were detected by LIF and their yield determined relative to the HO yield from H_2O_2 photolysis, with the assumption that the rotational distribution of the HO from the HO_2NO_2 and the H_2O_2 was the same under the conditions of the experiment. A value of $\phi_2 = 0.34\pm0.16$ was obtained after correction for impurities in the pernitric acid sample. Fluorescence from NO_2^* was observed after photolysis and was assigned to production via channel (1). The upper limit for NO_2^* production was 30%. It was concluded that under atmospheric conditions $\phi_1 \approx 0.65$ and $\phi_2 \approx 0.35$.

(d) Laser photolysis of pernitric acid at 248 nm. The NO_2 was detected by LIF at 511 nm. The quantum yield for NO_2 production was obtained by comparison with HNO_3 photolysis under the same conditions and taking the quantum yield for NO_2 production from HNO_3 to be unity. Experiments made over a range of pressures and concentrations gave $\phi(NO_2) = 0.56 \pm 0.17$.

Preferred Values

Absorption cross-sections of HO_2NO_2 at 296 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	1010	265	22.9
195	816	270	18.0
200	563	275	13.3
205	367	280	9.3
210	239	285	6.2
215	161	290	3.9
220	118	295	2.4
225	93.2	300	1.4
230	78.8	305	0.85
235	68.0	310	0.53
240	57.9	315	0.39
245	49.7	320	0.24
250	41.1	325	0.15
255	34.9	330	0.09
260	28.4		

Quantum Yields at 298 K

$\phi_1 = 0.59$ at 248 nm.
$\phi_2 = 0.41$ at 248 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are based on the data of Molina and Molina[1] and of Singer *et al.*,[2] which are in excellent agreement at wavelengths in the range 210-300 nm. Between 300 nm and 320 nm the cross-sections of Singer *et al.*[2] are approximately a factor of 2 lower. A simple mean of the two data sets is taken over the whole wavelength range.

When the value of $\phi(HO)$ determined by Mac Leod *et al.*[3] at 248 nm is revised to take into account the present recommendation for the absorption cross-section for H_2O_2 a slightly higher value of 0.39 is obtained. This is in very good agreement with the value of 0.44 implied by the recent measurement of $\phi(NO_2)$ by Roehl *et al.*[4] at 248 nm. The preferred values of ϕ_1 and ϕ_2 are the average of the values from the studies of Roehl *et al.*[4] and MacLeod *et al.*[3] The uncertainties in the quantum yields are large and it should be noted that the recommendations are restricted to a single wavelength.

Photodissociation of HO_2NO_2 via high-lying O-H overtone absorptions in the visible region of the spectrum is energetically possible for the $3\nu_{OH}$ and higher overtones. Zhang *et al.*[5] have measured absorption cross-sections at 273 K for the $3\nu_{OH}$ and $4\nu_{OH}$ transitions using conventional long-path-length absorption spectroscopy. Assuming that such absorptions are dissociative for HO_2NO_2 the values obtained imply that these modes will play a small role in the photochemistry of the lower stratosphere,

References

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4. C. M. Roehl, T. L. Mazely, R. R. Friedl, Y. Li, J. S. Francisco, and S. P. Sander, J. Phys. Chem. A **105**, 1592 (2001).
5. H. Zhang, C. M. Roehl, S. P. Sander, and P. O. Wennberg, J. Geophys. Res. **105**, 14593 (2000).