IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx1

This data sheet updated: 16th July 2001.

HONO + hν → products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
HONO + hν → HO + NO	(1)	207	578
→ H + NO_2	(2)	331	361
→ HNO + O(^{3}P)	(3)	442	271

Absorption cross-section data

Wavelength range/nm	Reference	Comments
185-270	Kenner, Rohrer, and Stuhl, 1986[1]	(a)
300-400	Bongartz *et al.*, 1991;[2] 1994[3]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 0.92 \pm 0.16$	365±5	Cox and Derwent, 1976[4]	(c)
ϕ(HO*)	193	Kenner, Rohrer, and Stuhl, 1986[1]	(d)
ϕ(H)	351	Wollenhaupt *et al.*, 2000[5]	(e)

Comments

(a) A relative absorption spectrum was measured in the range 185-270 nm with absolute determinations at 193 nm and 215 nm. A value of $\sigma = 1.6 \times 10^{-18}$ cm^2 molecule^{-1} was obtained at 193 nm. Two different methods used to prepare HONO gave similar results. The σ values agree with those of Cox and Derwent[4] in the wavelength region 220-270 nm, but the peak at

215 nm, seen in the Cox and Derwent[4] study, which could have been due to NO absorption, was not observed.

(b) Absolute absorption cross-sections were determined using conventional absorption spectroscopy, and with low, non-equilibrium concentrations of HONO determined by a combination of gas-phase and wet chemical analysis. Spectral resolution was 0.1 nm; cross sections averaged over 0.5 nm are given in a table. In their later work, improved conditions were used, specifically, higher HONO mole fractions, greater stability of HONO in the absorption chamber, and determination of the NO_2 present by interference free optical absorption at 440 nm.

(c) Rates of photon absorption and decomposition of NO_2 and HONO were measured in the same photolysis cell. The value of ϕ obtained supersedes an earlier estimate[6] using the same technique but based on less reliable absorption cross-section data.

(d) Laser photolysis of HONO at 193 nm. HO* was measured by emission spectroscopy. A small quantum yield of ~ 10^{-5} was determined.

(e) Pulsed laser photolysis at 351 nm of flowing HONO - N_2 (or Ar) mixtures was used to generate HO and the system was investigated using resonance absorption at 121.6 nm to discover the extent of any concommittent production of H. The system was calibrated for [H] by 248 nm photolysis of CH_3SH. An upper limit of 1% was obtained for ϕ(H).

Preferred Values

Absorption cross-sections of HONO at 298 K

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{-20}\sigma/cm^2$
190	127	260	8.0	330	9.3
195	172	265	5.2	335	6.5
200	197	270	3.4	340	16.8
205	220	275	2.5	345	9.6
210	214	280	-	350	11.5
215	179	285	-	355	23.6
220	146	290	-	360	8.0
225	120	295	-	365	16.1
230	86	300	0.0	370	20.5
235	60	305	0.7	375	4.9
240	42	310	1.6	380	9.2
245	30	315	2.5	385	14.5
250	18.5	320	4.4	390	2.4
255	12.4	325	5.0	395	0.6

Quantum Yields at 298 K

ϕ_1 = 1.0 throughout the wavelength range 190-400 nm.

Comments on Preferred Values

Since our previous evaluation, IUPAC 1997,[7] Wang and Zhang[8] have measured the absorption cross-sections at 352.2 nm, 354.2 nm and 357.0 nm and there have been three other new

determinations by Stutz *et al.*,[9] Pagsberg *et al.*,[10] and Brust *et al.*,[11] of the absorption cross-sections over a range of wavelengths in the 300-400 nm range. The results of Wang and Zhang,[8] Stutz *et al.*[9] and Pagsberg *et al.*[10] are in good agreement but the values obtained by Brust *et al.*[11] are much lower. The reason for this discrepancy is not clear.

The studies of Wang and Zhang,[8] Stutz *et al.*,[9] and Pagsberg *et al.*[10] are also in agreement with the earlier studies of Stockwell and Calvert,[12] Vasudev,[13] and Bongartz *et al.*[2,3] which were the basis of the preferred values for the absorption cross-section given in our previous evaluation, IUPAC, 1997,[7] which are therefore unchanged. The preferred values of the cross-sections tabulated for the 300-395 nm range are obtained from the data of Bongartz *et al.*[2,3] In their later work,[3] cross-sections were measured under better controlled conditions than in their earlier study[2] and it was shown that their earlier data were consistently too high by, on average, 14.5%. The preferred values have been obtained, therefore, by averaging the data from Ref. 2 over 5 nm intervals centred on the wavelength specified in the Table and reducing these values by 14.5% as directed in Ref. 3.

The HONO spectrum consists of a diffuse structured band between 300 and 390 nm and a broad structureless band from 270 nm to below 180 nm, peaking at ~210 nm. The only direct determination of the ϕ(HO) in this region is that of Cox and Derwent[4] who showed that channel (1) is the dominant process between 330 nm and 380 nm and obtained a quantum yield for HO production of 0.92 ± 0.16 at 365 nm. There is some indirect evidence for H atom production at ~ 350 nm[14] but Wollenhaupt *et al.*[5] have shown ϕ(H) to be less than 0.01. We therefore take ϕ(HO) to be unity throughout this band.

In the second absorption band, cross-sections over the range 185-275 nm are based on the data of Kenner *et al.*,[1] which show that channel (1) is the main photodissociation channel in this region also, but minor H atom producing channels in the 193.3 nm photodissociation of a beam of jet-cooled HONO[15] have also been observed.

References

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