IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx7

This data sheet updated: 16th July 2001.

$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	(1)	96	1252
$\rightarrow NO_3 + NO + O$	(2)	402	298
$\rightarrow NO_3 + NO_2^* \rightarrow NO_3 + NO_2 + h\nu$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200-380	Yao, Wilson, and Johnston, 1984[1]	(a)
240-420	Harwood *et al.*, 1993[2]	(b)
208-398	Harwood, Burkholder, and Ravishankara, 1998[3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(NO_3)$	249-350	Swanson, Kan, and Johnston, 1982[4]	(d)
$\phi(NO_3)$, $\phi[O(^3P)]$	290	Barker *et al.*, 1985[5]	(e)
$\phi(NO_3)$, $\phi[O(^3P)]$	248-289	Ravishankara *et al.*, 1986[6]	(f)
$\phi(NO_3)$	248, 308, 352.5	Harwood, Burkholder, and Ravishankara, 1998[3]	(g)

Comments

(a) Measured over the temperature range 223-300 K. For the wavelength range 200-280 nm, no temperature dependence was observed and values were tabulated at 5 nm intervals. For 285-385 nm, a pronounced temperature dependence was observed and the results were presented as an equation expressing σ as a function of λ and T.

(b) Measurements were made over the temperature range 233-313 K using a dual beam diode array spectrometer. Absolute cross-sections were based on pressure measurements and determination of NO_2 and HNO_3 impurities by spectroscopic methods. For 260-380 nm, a pronounced temperature dependence was observed and the results were expressed in the form $\log_{10}(\sigma) = A + B/T$.

(c) Spectra were measured using a diode array spectrograph having a resolution of ~1 nm and were normalized to the value of σ at 280 nm reported by Harwood *et al.*[2] The N_2O_5 was analysed to check for HNO_3 impurities and found to contain <1%.

(d) Pulsed laser photolysis, mostly at 249 nm, with a few experiments at 350 nm. The NO_3 quantum yield was measured to be 0.89±0.15. At low reactant concentration, the quantum yield approached 1.0±0.1.

(e) Pulsed laser photolysis. The quantum yield for production of $O(^3P)$ atoms was determined to be < 0.1 in experiments with atomic resonance fluorescence detection of oxygen atoms. Optoacoustic techniques with added NO were used to determine $\phi(NO_3)$ to be 0.8±0.2.

(f) Pulsed laser photolysis. The quantum yield for NO_3 production at 249 nm was determined to be unity in experiments with detection of NO_3 by absorption at 662 nm. The quantum yield for $O(^3P)$ production was observed to decrease from 0.72±0.17 at 248 nm to 0.15±0.05 at 289 nm.

(g) Pulsed laser photolysis at 248 nm, 308 nm, or 352.5 nm with $[NO_3]$ monitored by absorption at 661.9 nm. At each of the three photolysis wavelengths two different actinometric methods were used to establish the laser fluence for calculating the quantum yield. Values of $\phi(NO_3)$ obtained were: at 248 nm (0.67±0.14, 0.64±0.08); at 308 nm (0.88±0.10, 1.03±0.10); at 352.5 nm (0.91±0.04, 1.21±0.04). The quantum yields were independent of pressure over the range 197-789 mbar (150-600 Torr).

Preferred Values

Absorption cross-sections of N_2O_5 at 298 K

λ/nm	$10^{20}\sigma$/cm^2	B/K	λ/nm	$10^{20}\sigma$/cm^2	B/K
210	470		315	1.62	-0.253
215	316		320	1.21	-0.294
220	193		325	0.89	-0.338
225	128		330	0.67	-0.388
230	91		335	0.50	-0.409
235	73		340	0.38	-0.492
240	60		345	0.279	-0.530
245	51		350	0.215	-0.583
250	40		355	0.164	-0.719
255	32		360	0.124	-0.770
260	25.9	-0.091	365	0.091	-0.801
265	20.4	-0.100	370	0.072	-0.885
270	16.4	-0.104	375	0.053	-0.765
275	13.2	-0.112	380	0.041	-0.992
280	11.1	-0.112	385	0.032	-0.992
285	8.59	-0.126	390	0.0228	-0.949
290	6.71	-0.135	395	0.0171	-0.845
295	5.11	-0.152	400	0.0138	-0.966
300	3.87	-0.170	405	0.0103	-1.00
305	2.91	-0.194	410	0.0080	-1.16
310	2.17	-0.226			

Temperature dependence: $\log_{10}\sigma_T$ (cm^2 molecule^{-1}) = $\log_{10}\sigma_{298} + 1000B(1/T - 1/298)$.

Quantum Yields at 298 K

λ/nm	ϕ (NO_3)	ϕ (O)
248	0.8	0.72
266		0.38
287		0.21
289		0.15
300	1.0	
350	1.0	

Comments on Preferred Values

The absorption cross sections reported by Harwood *et al.*[2] are in excellent agreement with the earlier data of Yao *et al.*[1] and the more recent values obtained by Harwood *et al.*[3] at wavelengths > 240 nm. At wavelengths shorter than 240 nm the values obtained by Harwood *et al.*[3] are lower than those of Yao *et al.*,[1] the divergence between the two studies increasing with decreasing wavelength, so that at 210 nm the absorption cross-section obtained by Yao *et al.*[1] is ~ 50% greater than that of Harwood *et al.*[3] The preferred values for the cross-sections at

298 K were obtained by averaging the values obtained by Yao *et al.*,[1] Harwood *et al.*,[2] and Harwood *et al.*[3] for $\lambda \geq 240$ nm and averaging those of Yao *et al.*[1] and Harwood *et al.*[3] in the range 210-240 nm.

The temperature dependences of the cross-sections measured by Harwood *et al.*[2] agree well with the values obtained by Yao *et al.*[1] except at the longer wavelengths where the results in the former study show a slightly larger dependence. Thus, using the expressions for the temperature dependence and the A values given in the two studies, the σ values calculated at 380 nm differ by about 30%. The preferred values of the temperature coefficients are taken from Harwood *et al.*[2]

The quantum yields for NO_3 and O atom formation have been measured at a number of wavelengths in the range 248-352.5 nm. The preferred value of $\phi(NO_3)$ =1.0 at 300 nm and 350 nm are based on the results of Swanson *et al.*[4] at 350 nm, Barker *et al.*[5] at 290 nm, and Harwood *et al.*[3] at 308 nm and 352.5 nm, which agree within the fairly substantial error limits. The value of $\phi(NO_3)$ at wavelengths below 300 nm is less certain. A quantum yield close to unity has been reported by Swanson *et al.*[4] at 249 nm and by Ravishankara *et al.*[6] over the range 248-289 nm, but the recent study of Harwood *et al.*[3] suggests a substantially lower value at 248 nm. Our preferred value of 0.8, with suggested error limits of at least 10%, reflects the findings of all of these studies.[3,4,6]

The preferred quantum yields for O atom production are those reported by Ravishankara *et al.*[6] Barker *et al.*[5] also report a quantum yield for O atom production of < 0.1 at 290 nm in agreement with the findings of Ravishankara *et al.*[6] that $\phi(O)$ is substantial at 248 nm but decreases with increasing wavelength, approaching zero in the neighbourhood of the thermodynamic threshold for O atom production at 298 nm.

The study of Oh *et al.*[7] indicates that electronically excited NO_2 in the $^2B_1$ state is produced, and photolysis induced fluorescence (PIF) quantum yield values are reported.

References

1 F. Yao, I. Wilson, and H. S. Johnston, J. Phys. Chem. **86**, 3611 (1982).

2 M. H. Harwood, R. L. Jones, R. A. Cox, E. Lutman, and O. V. Rattigan, J. Photochem. Photobiol. A **73**, 167 (1993).

3 M. H. Harwood, J. B. Burkholder, and A. R. Ravishankara, J. Phys. Chem. A **102**, 1309 (1998).

4 D. Swanson, B. Kan, and H. S. Johnston, J. Phys. Chem. **88**, 3115 (1984).

5 J. R. Barker, J. Brouwer, R. Patrick, M. J. Rossi, P. L. Trevor, and D. M. Golden, Int. J. Chem. Kinet. **17**, 991 (1985).

6 A. R. Ravishankara, P. H. Wine, C. A. Smith, P. E. Barbone, and A. Torabi, J. Geophys. Res. **91**, 5355 (1986).

7 D. Oh, W. Sisk, A. Young, and H. S. Johnston, J. Chem. Phys. **85**, 7146 (1986).