IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx6

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This data sheet updated: 16th July 2001.

$N_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$N_2O + h\nu \rightarrow N_2 + O(^3P)$	(1)	161	742
$\rightarrow N_2 + O(^1D)$	(2)	351	341
$\rightarrow N + NO$	(3)	483	248
$\rightarrow N_2 + O(^1S)$	(4)	568	211

Absorption cross-section data

Wavelength range/nm	Reference	Comments
173-240	Selwyn, Podolske, and Johnston, 1977[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(-N_2O) = 2.0$ $\phi(NO) = 1.0$ $\phi(O_2) = 0.5$	184.9	Greiner, 1967[2]	(b)
$\phi_1 \leq 0.03$	214	Paraskevopoulos and Cvetanovic, 1969[3]	(c)
$\phi_3 \leq 0.01$	185-230	Preston and Barr, 1971[4]	(d)

Comments

(a) Measured at five temperatures from 194 K to 302 K, with a resolution of 0.7 nm. Values were tabulated at 1nm intervals. A nine parameter fit expressing σ as a function of λ and T was also given.

(b) N_2O was photolyzed at 184.9 nm in a static system at temperatures in the range 299-301 K. Analysis for N_2O, NO, and O_2 was carried out by mass-spectrometry. No other products were observed but the analysis system was not sensitive to NO_2. Pressure was varied in the range 5.3-285 mbar (4-214 Torr) of N_2O. From the results obtained in this and other studies, it was concluded that $\phi(-N_2O) = 2.0$, $\phi(NO) = 1.0$, and $\phi(O_2) = 0.5$ over the range 138-210 nm.

(c) N_2O was photolyzed at 298 K in the presence of neopentane, 1-butene, and added inert gases. The yield of $O(^3P)$ atoms was determined from the yield of addition products formed with 1-butene.

(d) N_2O containing 1% ^{15}NO was photolyzed at 296 K and λ = 185 nm, 214 nm, and 229 nm. The isotopic composition of the N_2 produced was measured.

Preferred Values

Absorption cross-sections of N_2O at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

Temperature dependence of absorption cross section

$$\ln \sigma(\lambda, T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4 + (T - 300)\exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

where

$A_1 = 68.21023$ $B_1 = 123.4014$

$A_2 = -4.071805$ $B_2 = -2.116255$

$A_3 = 4.301146 \times 10^{-2}$ $B_3 = 1.111572 \times 10^{-2}$

$A_4 = -1.777846 \times 10^{-4}$ $B_4 = -1.881058 \times 10^{-5}$

$A_5 = 2.520672 \times 10^{-7}$

for λ = 173-240 nm and T = 194-302 K.

Quantum Yields

$\phi_2 = 1.0$ for λ = 185-230 nm.

Comments on Preferred Values

The preferred absorption cross-section and the expression for ln $\sigma(\lambda, T)$ are from Selwyn *et al.*[1] These cross-section values have been confirmed both at room temperature and at 208 K by the studies of Hubrich and Stuhl[5] and Mérienne *et al.*,[6] who also determined the temperature dependence.

The preferred value of the quantum yield is based on the studies of Greiner[2], Parakevopoulos and Cvetanovic[3], and Preston and Barr.[4] Greenblatt and Ravishankara[7] have also measured the quantum yield for production of NO($^2\Pi$) and N(^{4}S) atoms at 193 nm to be $< 8 \times 10^{-3}$.

Other relevant spectroscopic studies are those of Yoshino *et al.*[8] who made high-resolution room temperature cross-section measurements in the 170-222 nm range, and of Lee and Suto.[9] who measured the photoabsorption and fluorescence cross-sections in the 106-160 nm region.

The UV absorption spectrum of the heavier isotopomers of N_2O ($^{15}N^{14}NO$, $^{14}N^{15}NO$, $^{14}N^{14}N^{17}O$, $^{14}N^{14}N^{18}O$) are slightly blue shifted due to their lower zero point energies and, as a result, are expected to be photolysed more slowly in the atmosphere. This is evident in the studies of Selwyn and Johnston[10] who measured the absorption spectrum of N_2O and its ^{15}N isotopic forms over the wavelength range 172-197 nm and the temperature range 150-500 K. Isotopic fractionation is valuable as a means of investigating N_2O sources and sinks in the atmospheric cycle and, consequently, the isotope effect to be expected for the photolysis has been analysed by Yang and Miller,[11] and has been the subject a number of recent experimental studies,[12-16] which should be consulted for details.

State-resolved photofragment spectroscopy studies of N_2O photodissociation at 193 nm[17] and 205 nm[18] show that 43% of the energy deposited in the molecule appears as translational energy of the O(^{1}D) atom.

References

1. G. Selwyn, J. Podolske, and H. S. Johnston, Geophys. Res. Lett. 4, 427 (1977).
2. N. R. Greiner, J. Chem. Phys. **47**, 4373 (1967).
3. G. Paraskevopoulos, and R. J. Cvetanovic, J. Am. Chem. Soc. **91**, 7572 (1969).
4. K. F. Preston and R. F. Barr, J. Chem. Phys. **54**, 3347 (1971).
5. C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).
6. M. F. Mérienne, B. Coquart, and A. Jenouvrier, Planet. Space Sci. **38**, 617 (1990).
7. G. D. Greenblatt and A. R. Ravishankara, J. Geophys. Res. **95**, 3539 (1993).
8. K. Yoshino, D. E. Freemen, and W. H. Parkinson, Planet. Space Sci. **32**, 1219 (1984).
9. L. C. Lee and M. Suto, J. Chem. Phys. **80**, 4718 (1984).
10. G. S. Selwyn and H. S. Johnston, J. Chem. Phys. **74**, 3791 (1981).
11. Y. L. Yung and C. E. Miller, Science **278**, 1778 (1997).
12. T. Rahn, H. Zhang, M. Wahlen, and G. A. Blake, Geophys. Res. Lett. **25**, 4489 (1998).
13. H. Umemoto, Chem. Phys. Lett. **314**, 267 (1999).
14. F. Turatti, D. W. T. Griffith, S. R. Wilson, M. Besler, T. Rahn, H. Zhang, and G. A. Blake, Geophys. Res. Lett. **27**, 2489 (2000).
15. T. Roeckmann, C. A. M. Brenninkmeijer, M. Wollenhaupt, J. N. Crowley, and P. J. Crutzen, Geophys. Res. Lett. **27**, 1399 (2000).
16. H. Zhang, P. O. Wennberg, V. H. Wu, and G. A. Blake, Geophys. Res. Lett. **27**, 2481 (2000).
17. L. L. Springsteen, S. Satyapal, Y. Matsumi, L. M. Dobeck, and P. L Houston, J. Phys. Chem. **97**, 7239 (1993).
18. T. F. Hanisco and A. C. Kummel, J. Phys. Chem. **97**, 3539 (1990).