IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P16

This data sheet updated: 16th May 2002.

n-$C_3H_7ONO_2$ + hν → products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
n-$C_3H_7ONO_2$ + hυ → *n*-C_3H_7O + NO_2	(1)	165.9	721
→ C_2H_5CHO + HONO	(2)	-92.8	
→ C_3H_7ONO + $O(^3P)$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270-330	Roberts and Fajer, 1989[1]	(a)
185-330	Turberg *et al*., 1990[2]	(b)
220-340	Clemitshaw *et al*., 1997[3]	(c)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single-beam spectrometer with a photometric accuracy of ±0.5%. No NO_2 could be detected by FTIR in the *n*-propyl nitrate.

(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells with a range of pressures of *n*-$C_3H_7ONO_2$ at an unspecified spectral resolution.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the *n*-propyl nitrate was checked by NMR and FTIR.

Preferred Values
Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
185	1810	265	3.6
190	1800	270	3.2
195	1600	275	2.8
200	1260	280	2.3
205	855	285	1.8
210	489	290	1.3
215	244	295	0.95
220	105	300	0.57
225	50	305	0.34
230	27	310	0.19
235	15	315	0.10

240	8.9	320	0.053
245	6.0	325	0.031
250	4.8	330	0.022
255	4.4	335	0.018
260	4.0	340	0.016

Comments on Preferred Values

Clemitshaw *et al*.[3] have measured the absorption cross-sections at 298 K over the range 220 nm to 340 nm. In the wavelength region where their measurements overlap with those of Roberts and Fajer[1] (270 nm to 320 nm), the two studies are in excellent agreement. Agreement with the results of Turberg *et al*.[2] is also very good in the range 220 nm to 295 nm, but the results of Turberg *et al*.[2] deviate significantly from those of both Clemitshaw *et al*.[3] and Roberts and Fajer[1] at $\lambda > 295$ nm. This tendency to obtain higher values than others of the absorption cross-section at longer wavelengths is noticeable in the results of Turberg *et al*.[2] in all of their studies of the higher nitrates and could be due to traces of NO_2 in their samples.

The preferred values of the absorption cross-section are those of Turberg *et al*.[2] for the range 185 nm to 220 nm where theirs are the only measurements. Over the range 220 nm to 295 nm averages are taken of the results of Roberts and Fajer,[1] Turberg *et al*.[2] and Clemitshaw *et al*.[3] where their studies overlap, and over the range 295 nm to 340 nm the preferred values are based on the results of Roberts and Fajer[1] and Clemitshaw *et al*.[3]

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for photodissociation of both ethyl and methyl nitrate to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar, with structureless continua occurring in the same region of the spectrum, it seems likely that the photodissociation quantum yield for *n*-propyl nitrate will also be unity. Further support for this conclusion comes from direct measurements[4] of the rate of formation of NO_2 from the photolyses of n-$C_3H_7ONO_2$ in sunlight. These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290 nm to 340 nm.[4]

References

1 J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

2 M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

3 K. C. Clemitshaw, J. Williams, O. V. Rattigan, D. E. Shallcross, K. S. Law, and R. A. Cox, J. Photochem. Photobiol. A: Chemistry **102**, 117 (1997).

4 W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).