IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P18

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$1\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$1\text{-}C_4H_9ONO_2 + h\upsilon \rightarrow 1\text{-}C_4H_9O + NO_2$ (1)		
ADVANCE \x82 $\rightarrow 1\text{-}C_3H_7CHO$ + HONO (2)		
ADVANCE \x82 $\rightarrow 1\text{-}C_4H_9ONO$ + O (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270-315	Roberts and Fajer, 1989[1]	(a)
185-320	Turberg *et al*., 1990[2]	(b)
220-340	Clemitshaw *et al*., 1997[3]	(c)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of ±0.5%. Data are presented graphically but an expression for σ as a function of λ is derived from a least squares fit to the data at λ ≥ 270 nm. Purity of the butyl nitrate was checked by FTIR.

(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells in a Varian Carey 219 spectrophotometer using a bandwidth of 1 nm.

(d) 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 ethyl 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	3.9
190	1810	270	3.4
195	1620	275	3.0

200	1300	280	2.4
205	889	285	1.9
210	518	290	1.4
215	263	295	0.89
220	111	300	0.57
225	58	305	0.34
230	30	310	0.19
235	17	315	0.10
240	9.8	320	0.051
245	6.3	325	0.031
250	5.3	330	0.021
255	4.6	335	0.016
260	4.3	340	0.013

Comments on Preferred Values

The results of Roberts and Fajer,[1] Turberg *et al*.[2] and Clemitshaw *et al*.[3] are in good agreement at wavelengths where the studies overlap (in the range 220 nm to 320 nm), except for the results of Turberg *et al*.[2] at wavelengths ≥ 300 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency to obtain higher values than others, in this wavelength region, is noticeable in the results of Turberg *et al*.[2] for all of the higher nitrates and could be due to traces of NO_2 present in their samples.

The preferred values of the absorption cross-sections are those of Turberg *et al*.[2] for the range 185 nm to 220 nm, where theirs are the only values. 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 300 nm to 400 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 the photodissociation of both ethyl and methyl nitrates 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 alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 1-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight.[4] Thus the measured rate of formation of NO_2 matched well with 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 330 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).