IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P17

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i-$C_3H_7ONO_2$ + hν → products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
i-$C_3H_7ONO_2$ + hυ → 2-C_3H_7O + NO_2	(1)	171.7	697
→ CH_3COCH_3 + HONO	(2)	-105.9	
→ *i*-C_3H_7ONO + O	(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)
240-360	Talukdar *et al*., 1997[4]	(d)

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%. Numerical data for cross-sections are available from ref. 5. Samples were checked by FTIR for the presence of NO_2, which was not found.

(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells, with a range of pressures of *i*-$C_3H_7ONO_2$, at a bandwidth of 1 nm.

(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 *i*-propyl nitrate was checked by NMR and FTIR.

(d) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and 6 other temperatures in the range 240 K to 360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233 K to 360 K and 240 nm to 340 nm

λ/nm	10^{20} σ/cm^2	$10^3 B/K^{-1}$	λ/nm	10^{20} σ/cm^2	10^3 B/K^{-1}
185	1790		275	3.4	3.3
188	1810		280	2.8	3.6
190	1790		285	2.2	4.0
195	1610		290	1.6	4.4
200	1260		295	1.2	4.8
205	867		300	0.78	5.4
210	498		305	0.50	6.1
215	247		310	0.29	6.9
220	125		315	0.17	8.1
225	62		320	0.085	9.4
230	34		325	0.044	11.1
235	18		330	0.022	11.9
240	11	2.8	335	0.011	14.0
245	7.0	2.7	340	0.0053	13.9
250	5.4	2.5	345	0.0018	
255	4.9	2.5	350	0.00080	
260	4.6	2.6	355	0.00029	
265	4.3	2.8	360	0.00018	
270	3.9	3.1			

The temperature variation of the absorption cross-section at a particular wavelength in the range 240 nm to 340 nm is expressed as $\ln \sigma(T) - \ln \sigma(298\ \mathrm{K}) = B(T\text{-}298)$.

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 and Talukdar *et al*.[4] have measured both the cross-sections at 298 K over the range 240 nm to 360 nm and their temperature dependence at temperatures in the range 240 K to 360 K. The results of Clemitshaw *et al*.[3] and of Talukdar *et al*.[4] are in excellent agreement with the earlier results of Roberts and Fajer[1] and Turberg *et al*.[2] at wavelengths where they overlap (in the range 220 nm to 330 nm), except for the results of Turberg *et al*.[2] at wavelengths ≥ 310 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 at 298 K 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 305 nm averages are taken of the results of Roberts and Fajer,[1] Turberg *et al*.,[2] Clemitshaw *et al*.,[3] and Talukdar *et al*.,[4] where their studies overlap, and over the range 310 nm to 360 nm the preferred values are based on the results of Roberts and Fajer,[1] Clemitshaw *et al*.[3] and Talukdar *et al*.[4]

The preferred values of the constant B, which characterize the temperature dependence of the absorption cross-sections are those of Talukdar *et al*.[4]

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 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 structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for isopropyl 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.[6] Thus the measured rate of formation of NO_2 matched well with calculated rates of photolyses based on measurements of the absorption cross-section, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290 nm to 330 nm.[6]

References

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