IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P15

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$C_2H_5ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_2H_5ONO_2 + h\upsilon$	$\rightarrow C_2H_5O + NO_2$	(1)	171.7	697
	$\rightarrow CH_3CHO + HONO$	(2)	-91.3	
	$\rightarrow C_2H_5ONO + O(^3P)$	(3)	299.4	400

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270-315	Roberts and Fajer, 1989[1]	(a)
185-330	Turberg *et al*., 1990[2]	(b)
265-340	Zhu and Ding, 1997[3]	(c)
265-340	Clemitshaw *et al*., 1997[4]	(d)
265-340	Talukdar *et al*., 1997[5]	(e)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.0 \pm 0.1$	308	Zhu and Ding, 1997[3]	(f)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from ref. 6.

(b) Absorption cross-sections were measured in cells of 2 cm and 10 cm pathlengths with a range of pressures of $C_2H_5ONO_2$. The spectral resolution was not specified.

(c) Cross-sections measured at 10 nm intervals, between 238 K and 298 K, using cavity ring- down spectroscopy. Absorption cross-sections were obtained by measuring optical loss as a function of sample gas pressure (0.013 mbar to 18 mbar). The purity of ethyl nitrate was checked by FTIR and cavity ring-down spectroscopy.

(d) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm, over the temperature range 233 K to 298 K. The purity of the ethyl nitrate was checked by NMR and FTIR.

(e) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and six other temperatures in the range 240 K to 360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum. Corrections were made for contributions to the spectrum from NO_2 present in the ethyl nitrate.

(f) Excimer laser used to photodissociate ethyl nitrate in a cavity ring-down spectrometer. Time-resolved spectra of products observed. Only NO_2 found as product, with undetectable yields of HONO and C_2H_5ONO. Quantum yield measurements were made at 278 K, 283 K, 288 K, 293 K and 298 K with ethyl nitrate pressures of 1.3 mbar to 13 mbar in a buffer gas of N_2 at total pressures of 16 mbar to 1 bar. ϕ_1 was found to be pressure and temperature independent.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233 K to 360 K and 235 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	1710		265	3.6	2.9
190	1710		270	3.1	3.1
195	1490		275	2.7	3.3
200	1140		280	2.2	3.6
205	738		285	1.7	3.8
210	400		290	1.2	4.2
215	195		295	0.85	4.7
220	91		300	0.55	5.1
225	45		305	0.33	5.8
230	24		310	0.19	6.7
235	11.9	1.4	315	0.10	7.9
240	7.7	2.8	320	0.051	8.6
245	5.4	2.9	325	0.026	10.4
250	4.5	2.8	330	0.012	12.9
255	4.1	2.6	335	0.0049	14.1
260	3.9	2.6	340	0.0025	15.6

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

Quantum Yields

$\phi_1 = 1.0 \pm 0.1$ at 308 nm, independent of pressure over the temperature range 278 K to 298 K.

Comments on Preferred Values

The preferred values of the cross-sections at 298 K are those obtained by Turberg *et al*.[2] over the range 185 nm to 230 nm, where this is the only study, and for the range 235 nm to 340 nm averages are taken of the values from all of the five studies[1-5] at the wavelengths where they overlap.

The temperature variation of the cross-sections has been studied by Zhu and Ding,[3] Clemitshaw *et al*.[4] and Talukdar *et al*.[5] These studies together cover the temperature range 233 K to 360 K and the wavelength range 235 nm to 340 nm. It is found in all of the studies that the

temperature variation of σ can be expressed as ln σ(λ,*T*) - ln σ(λ, 298 K) = *B*(λ)(*T*-298). The results from the three studies[3-5] are in good agreement and the preferred values of *B* have been obtained by averaging values from the three studies.[3-5]

The only direct measurement of the quantum yield is that of Zhu and Ding.[3] Their finding that at 308 nm the sole photodissociation channel was that leading to NO_2 production with a quantum yield of unity is accepted for our preferred value of the quantum yield. It is in accord with the studies of Luke *et al*.[7,8] who concluded that the measured rates of NO_2 production from ethyl nitrate photolysis in sunlight could be accounted for by assuming that $\phi_1 = 1$ throughout the region 290 nm to 340 nm. This is also supported by the measured value of unity for the same channel in the 248 nm photolysis of methyl nitrate.[5]

References

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