IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P14

This data sheet updated: 16th May 2002.

$CH_3ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3ONO_2 + h\nu \rightarrow CH_3O + NO_2$	(1)	170.1	703
$\rightarrow HCHO + HONO$	(2)	-68.4	
$\rightarrow CH_3ONO + O(^3P)$	(3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270-315	Roberts and Fajer, 1989[1]	(a)
220-335	Rattigan *et al*., 1992[2]	(b)
236-344	Talukdar *et al*., 1997[3]	(c)

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

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 0.9 \pm 0.2$	248	Talukdar *et al*., 1997[3]	(d)
$\phi_1 = 1.3 \pm 0.3$	248		(e)
$\phi_2 < 0.05$	248		(d)
$\phi_3 < 0.1$	248		(d)

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. 4.

(b) Cross-sections were measured with a dual-beam diode array spectrometer with a spectral resolution of 0.3 nm over the temperature range 238 K to 294 K. The temperature dependence of σ was found to obey the equation, $\ln\sigma(\lambda,T) = \ln\sigma(\lambda, 298\ K) + B(\lambda)(T-298)$.

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

temperature dependence of σ was found to obey the equation ln $\sigma(\lambda,T)$ = ln $\sigma(\lambda, 298\ K)$ + $B(\lambda)$ (T-298). The absorption cross-section at 213.86 nm (Zn line) was also measured. A value of $(1.67 \pm 0.08) \times 10^{-18}$ cm^2 molecule^{-1} was obtained.

(d) Photolysis of methyl nitrate at 248 nm and 298 K in the presence of excess O_2 to scavenge radicals. Actinometry based on O_3 photolysis or N_2O photolysis in experiments carried out with 193 nm radiation. Yields of the products CH_3ONO, CH_2O, NO_2 and NO_3 were measured by UVA, NO_3 by time-resolved absorption at 662 nm, and H and O by resonance fluorescence. Channels leading to H, O, and NO_3 were found to make negligible contribution at 248 nm, but high yields of O were obtained at 193 nm. Small yields of HO observed were attributed to secondary reactions.

(e) Same technique as in (d), but NO was used to scavenge radicals instead of O_2.

Preferred Values
Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
240	5.88	295	0.568
245	4.19	300	0.360
250	3.59	305	0.214
255	3.30	310	0.134
260	3.06	315	0.0633
265	2.77	320	0.0316
270	2.39	325	0.0144
275	2.00	330	0.00661
280	1.58	335	0.00274
285	1.19	340	0.00122
290	0.85		

Temperature dependence of the absorption cross-sections over the range 240 K to 330 K

λ/nm	10^3 B/K^{-1}	λ/nm	10^3 B/K^{-1}
240	3.48	290	4.04
245	3.29	295	4.47
250	2.96	300	4.94
255	2.82	305	5.56
260	2.83	310	6.33
265	2.92	315	7.34
270	3.08	320	8.74
275	3.28	325	9.97
280	3.51	330	13.6
285	3.78		

The tabulated values of B may be used to calculate $\sigma(\lambda,T)$ using the relationship ln $\sigma(\lambda,T)$ = ln σ (λ, 298 K) + B (λ) (T-298).

Quantum Yields

$\phi_1 = 1.0$ or $\lambda \geq 248$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are average values from the data of Roberts and Fajer,[1] Rattigan *et al*.,[2] and Talukdar *et al*.,[3] which are in excellent agreement

over the whole wavelength range of the measurements. They are also in reasonable agreement with the absorption spectrum reported by Calvert and Pitts[5] and with the cross-sections reported by Maria *et al*.[6] The results of Taylor *et al*.[7] are consistently higher than the values from the other studies,[1-3,5,6] by as much as a factor of two in the region 290 nm to 330 nm.

The two studies of the effect of temperature on the cross-sections are also in very good agreement with differences only appearing at wavelengths beyond 320 nm where the absorption cross-sections become very small and the precision of the measurements falls away. The preferred values of $B(\lambda)$ are those of Talukdar *et al*.[3] averaged over 5 nm intervals around the given wavelength.

The preferred value of the quantum yield is based on the work of Talukdar *et al*.[3] who concluded that the photodissociation of methyl nitrate at 248 nm produces NO_2 and CH_3O with a quantum yield essentially of unity. This is in accord with the general assumption[4] that the lack of structure in the absorption spectrum of $RONO_2$ molecules indicates that the quantum yield for dissociation is unity, and is supported by the recently measured value for ethyl nitrate of $\phi_1 = (1.0 \pm 0.1)$ at 308 nm.[8]

References

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

2 O. Rattigan, E. Lutman, R. L. Jones, R. A. Cox, K. Clemitshaw, and J. Williams, J. Photochem. Photobiol. A: Chem. **66**, 313 (1992); *corrigendum, ibid*, **69**, 125 (1992).

3 R. K. Talukdar, J. B. Burkholder, M. Hunter, M. K. Giles, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2797 (1997).

4 J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).

5 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.

6 H. J. Maria, J. R. McDonald, and S. P. McGlynn, J. Am. Chem. Soc. **95**, 1050 (1973).

7 W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, and G. A. Takacs, Int. J. Chem. Kinet. **12**, 231 (1980).

8 L. Zhu and C.-F. Ding, Chem. Phys. Lett. **265**, 177 (1997).