IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P21

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$CH_3C(O)OONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CO_3NO_2 + h\upsilon \rightarrow CH_3CO_3 + NO_2$	(1)	119	1004
$\rightarrow CH_3CO_2 + NO_3$	(2)	124	963

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220-325	Libuda and Zabel, 1995	(a)
196-350	Talukdar et al., 1995	(b)

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

Measurement	Wavelength range/nm	Reference	Comments
$\phi(NO_2)$	248	Mazely, Friedl and Sander, 1995	(c)
$\phi(NO_3)$	248	Mazely, Friedl and Sander, 1997	(d)
$\phi(NO_3)$	248, 308	Harwood et al., 2003	(e)

Comments

(a) Longpath (39.1 m) UV absorption cell with diode array detector used. The concentration of the $CH_3C(O)OONO_2$ was determined by FTIR (pathlength = 51.6 m) in the same cell. The UV spectral resolution was 0.6 nm.

(b) Diode array spectrometer with a resolution of 0.2 nm used with temperature controlled (±1 K) absorption cells of pathlengths 100 cm and 25 cm. $CH_3C(O)OONO_2$ concentrations were determined by pressure measurements. Cross-sections were measured at 250 K, 273 K and 298 K.

(c) Pulsed laser photolysis of PAN with LIF detection of NO_2. The quantum yield for NO_2 formation was measured relative to the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see HNO3 photolysis data sheet http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/photol/PNOx2_HONO2.pdf). A value of $\phi(NO_2) = 0.83 \pm 0.09$ for the photolysis of PAN at 248 nm was obtained.

(d) Pulsed laser photolysis of PAN at 248 nm with LIF detection of NO_3. The quantum yield for NO_3 formation was determined by comparison to the photodissociation of N_2O_5, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see HNO3 photolysis data sheet

http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/photol/PNOx2_HONO2.pdf). A value of $\phi(NO_3) = 0.3 \pm 0.1$ was obtained for PAN.

(e) Pulsed laser photolysis of PAN with LIF detection of NO_3. The quantum yield for NO_2 formation was measured relative to the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see HNO3 photolysis data sheet http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/photol/PNOx2_HONO2.pdf). Values of $\phi(NO_3) = 0.19 \pm 0.04$ and $\phi(NO_3) = 0.41 \pm 0.10$ were obtained for the photolysis of PAN at 248 nm and 308 nm respectively.

Preferred Values

Absorption cross-sections at 298 K and the temperature coefficient B[a]

λ/nm	10^{20} σ/cm^2	$10^3 B/K^{-1}$	λ/nm	10^{20} σ/cm^2	10^3 B/K^{-1}
196	429	2.02	274	2.45	5.55
198	398	1.73	276	2.07	5.76
200	361	1.36	278	1.74	5.98
202	325	1.07	280	1.46	6.20
204	292	0.86	282	1.21	6.43
206	261	0.75	284	1.01	6.67
208	226	0.71	286	0.81	6.90
210	196	0.75	288	0.648	7.15
212	168	0.84	290	0.537	7.39
214	143	0.97	292	0.447	7.63
216	122	1.12	294	0.369	7.86
218	104	1.29	296	0.297	8.08
220	89.7	1.47	298	0.245	8.27
222	77.7	1.64	300	0.189	8.44
224	67.6	1.81	302	0.152	8.61
226	59.3	1.98	304	0.125	8.76
228	52.0	2.14	306	0.0998	8.87
230	45.8	2.30	308	0.0816	9.01
232	40.4	2.46	310	0.0666	9.13
234	35.5	2.63	312	0.0538	9.30
236	31.4	2.80	314	0.0462	9.46
238	27.9	2.96	316	0.0363	9.57
240	24.4	3.11	318	0.0300	9.75
242	21.5	3.25	320	0.0252	10.0
244	18.8	3.39	322	0.0199	10.2
246	16.6	3.52	324	0.0166	10.4
248	14.6	3.64	326	0.0140	10.6
250	12.9	3.76	328	0.0117	10.7
252	11.4	3.87	330	0.0106	10.9
254	10.0	3.98	332	0.00857	11.2
256	8.86	4.10	334	0.00676	11.5
258	7.8	4.23	336	0.00615	11.7
260	6.85	4.38	338	0.00526	11.9
262	6.01	4.53	340	0.00502	12.2
264	5.23	4.68	342	0.00360	12.4
266	4.54	4.82	344	0.00241	12.5
268	3.94	4.97	346	0.00231	-
270	3.37	5.14	348	0.00247	-
272	2.87	5.34	350	0.00165	-

[a]Absorption cross-sections at temperatures in the range 250 K to 298 K are calculated using the equation

$\ln[\sigma(T)/\sigma(298\ K)] = B(T - 298)$.

Quantum Yields

$\phi_1 = 0.76$; $\phi_2 = 0.24$ at 248 nm
$\phi_1 = 0.61$; $\phi_2 = 0.41$ at 308 nm

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are based on the work of Libuda and Zabel (1995) and Talukdar et al. (1995), which agree to within a few percent at wavelengths below 290 nm and only slightly less well at longer wavelengths where the error limits on the measurements increase because of the difficulty of measuring the small cross-sections in that region of the spectrum.

Talukdar et al. (1995) have also measured the cross-sections at three temperatures and expressed their results in the form $\ln[\sigma(T)/\sigma(298\ K)] = B(T-298)$ where B is a constant at a particular wavelength. The values of B and $\sigma(298\ K)$ obtained by Talukdar et al. (1995) are listed as our preferred values.

Combination of the NO_2 and NO_3 formation quantum yields measured by Mazely et al. in their 1995 and 1997 studies suggests NO_2 and NO_3 are the sole N-containing photoproducts. at 248 nm. It is therefore suggested that $(\phi_1 + \phi_2) = 1$ following absorption in the UV region. The values of ϕ_2 from Harwood et al. (2003) and Mazely et al. (1997) are averaged for the recommended value at 248 nm, and ϕ_1 obtained by difference. The Harwood value for ϕ_2 at 308 nm is accepted and ϕ_1 obtained by difference.

References

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