IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P8

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$CH_3C(O)C_2H_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)C_2H_5 + h\upsilon \rightarrow CH_3 + C_2H_5CO$	(1)	352.6	339
$\rightarrow C_2H_5 + CH_3CO$	(2)	349.4	342
$\rightarrow CH_3 + C_2H_5 + CO$	(3)	395.3	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202-355	Martinez et al., 1992	(a)
240-350	Yujing and Mellouki, 2000	(b)

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

Measurement	Wavelength range/nm	Reference	Comments
ϕ 0.34 (1000 mbar) 0.89 (68 mbar)	275 - 380	Raber and Moortgat., 1987	(c)

Comments

(a) Conventional double-beam spectrophotometric measurements on mixtures of the 2-butanone and argon at a resolution of 0.5 nm. The cross-sections are given as averages over a 1 nm ($\lambda >$ 280 nm) or 4 nm ($\lambda <$ 280 nm) region centered on the corresponding wavelength. σ_{max} = 5.77 x 10^{-20} cm^{2}molecule^{-1} at 278 nm.

(b) Diode array spectrometer measurements on pure 2-butanone at a resolution of 0.04 nm. The cross-sections are given over 1 nm intervals. Precision based on observed standard deviation was within ±5%. σ_{max} = 5.65 x 10^{-20} cm^{2}molecule^{-1} at 278 nm.

(c) 2-butanone was photolyzed in synthetic air at several pressures in the range 68 mbar to 1 bar using a broad-band radiation source (275 nm to 380 nm) and the product yields were monitored by FTIR. The quantum yield for photolysis of 2-butanone was found to be pressure dependent decreasing from 0.89 at 68 mbar to 0.34 at 1 bar. They also conclude that photolysis over the wavelength region used occurs to the extent of 80 - 90% by channel 2. These results were derived by modelling the secondary chemistry in the system.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
202	1.412	292	4.60	324	0.229
206	0.192	293	4.42	325	0.189
210	0.160	294	4.24	326	0.156
214	0.183	295	4.08	327	0.129
218	0.225	296	3.93	328	0.105
222	0.290	297	3.79	329	0.085
226	0.391	298	3.65	330	0.067
230	0.534	299	3.48	331	0.054
234	0.742	300	3.30	332	0.042
238	1.029	301	3.10	333	0.033
242	1.410	302	2.89	334	0.025
246	1.886	303	2.69	335	0.020
250	2.45	304	2.50	336	0.014
254	3.09	305	2.33	337	0.011
258	3.74	306	2.17	338	0.008
262	4.39	307	2.02	339	0.007
266	4.96	308	1.876	340	0.005
270	5.40	309	1.727	341	0.005
274	5.68	310	1.575	342	0.003
278	5.77	311	1.423	343	0.003
280	5.74	312	1.276	344	0.002
281	5.72	313	1.136	345	0.001
282	5.68	314	1.009	346	0.001
283	5.62	315	0.896	347	0.000
284	5.54	316	0.794	348	0.001
285	5.44	317	0.697	349	0.000
286	5.35	318	0.611	350	0.000
287	5.26	319	0.531	351	0.000
288	5.17	320	0.457	352	0.001
289	5.06	321	0.389	353	0.000
290	4.94	322	0.328	354	0.000
291	4.78	323	0.276	355	0.000

Quantum Yields

$\phi = 0.34$ for $\lambda = 275$ - 380 nm at 1000 mbar.

Comments on Preferred Values

The preferred absorption cross-sections are taken from the measurements of Martinez et al. (1992) over the wavelength region 220 nm to 350 nm. The values at the band maximim are 5% higher than the recent data of Yujing and Mellouki (2000), but 5% lower than those of McMillan, reported by Calvert and Pitts (1966). Raber and Moortgat (1987) have also given a spectrum which is in good agreement with these cross-sections.

The only quantum yield measurements are those of Raber and Moortgat (1987), which forms the basis for the preferred quantum yield at 1000 mbar. This data needs further experimental support.

References

Calvert, J. G. and Pitts, Jr., J. N.: Photochemistry, Wiley, New York, 1966.
Martinez, R. D., Buitrago, A.A., Howell, N. W., Hearn, C. H. and Joens, J. A.: Atmos. Environ. 26A, 785, 1992.
Raber, W. H. and Moortgat, G. K.: "Photooxidation of Selected Carbonyl Compounds in Air: Methyl Ethyl Ketone, Methyl Vinyl Ketone, Methacrolein and Methylglyoxal," Chap. 9, *In: Progress and Problems in Atmospheric Chemistry*," ed. J. Barker, World Scientific Publishing Singapore, 1987.
Yujing, M. and Mellouki, A.: J.Photochem and Photobiol.A: Chemistry, 134, 31, 2000.