

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P25

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### $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH} + h\nu \rightarrow \text{products}$

#### Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O}) + \text{CH}_2\text{OH}$ (1)		
$\rightarrow \text{CH}_3 + \text{HOCH}_2\text{CO}$ (2)		
$\rightarrow \text{C}_3\text{H}_8\text{OH} + \text{CO}$ (3)		

#### Absorption cross-section data

Wavelength range/nm	Reference	Comments
207 - 333	Mellor and Crowley, 1990	(a)
235 - 340	Orlando et al. 1999	(b)
240 - 350	Butovskaya et al., 2006	(c)
184.9	Dillon et al., 2006	(d)

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

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.65 \pm 0.25$ (750 Torr air)	240-420	Orlando et al., 2006	(e)

#### Comments

- (a) Cross-sections determined from absorption measurements as a function of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$  pressure using a diode array spectrometer, with resolution of 0.25 nm. These results are reported in the on-line Mainz Spectral Atlas (see [http://www.atmosphere.mpg.de/enid/201aae7d473a97fc66e7686c134902ed,0/Spectra/Introduction\\_1rr.html](http://www.atmosphere.mpg.de/enid/201aae7d473a97fc66e7686c134902ed,0/Spectra/Introduction_1rr.html))

- (b) Diode array spectrometer, with spectral resolution of the instrument about 0.6 nm. UV absorption cross sections for hydroxyacetone measured over the wavelength range 235 to 340 nm; the spectrum is blue-shifted by about 15 nm relative to that of acetone and peaks at 266 nm, with a maximum absorption cross section of  $(6.7 \pm 0.1) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ . Measurable absorption extends out to about 330 nm
- (c) Both absolute and relative measurements of the cross section at 184.9 nm. In the absolute determination, i.e., measurement of the attenuation of 184.9 nm light by undiluted, static samples of hydroxyacetone at pressures of 0.28-0.501 Torr, a mean value of  $\sigma = (5.43 \pm 0.08) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  was obtained. In the second experiment, measurement in a flowing system with the hydroxyacetone diluted in nitrogen relative to the spectrum of Orlando et al., (2006) gave  $\sigma = (5.44 \pm 0.02) \text{ cm}^2 \text{ molecule}^{-1}$
- (d) The spectrum was measured by conventional diode array spectrometry in both static and flowing mixtures containing known concentrations of HAC. Measurements were performed at two temperatures: 294 and 328 K. The standard deviation was less than 5% over the wavelengths between 250 nm and 300 nm, and larger than 10% at wavelength greater than 300 nm.
- (e) Broad band steady-state photolysis of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$  in the presence of air at 298 K. Products measured by FTIR were CO,  $\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}_2\text{H}$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{OH}$ . Average quantum yields of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$  decay were measured for wavelength range 240 – 420 nm.

### Preferred Values

#### Absorption cross-sections at 298 K

$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$10^{20}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	
236	2.13	270	6.61	304	0.652
237	2.29	271	6.53	305	0.569
238	2.43	272	6.42	306	0.493
239	2.59	273	6.30	307	0.431
240	2.78	274	6.18	308	0.379
241	2.94	275	6.05	309	0.331
242	3.14	276	5.90	310	0.287
243	3.34	277	5.73	311	0.249
244	3.55	278	5.54	312	0.219
245	3.74	279	5.33	313	0.192
246	3.95	280	5.12	314	0.177
247	4.14	281	4.91	315	0.157
248	4.34	282	4.69	316	0.142
249	4.56	283	4.48	317	0.133
250	4.76	284	4.27	318	0.117
251	4.98	285	4.05	319	0.104
252	5.18	286	3.82	320	0.095
253	5.36	287	3.58	321	0.087
254	5.54	288	3.34	322	0.078
255	5.72	289	3.11	323	0.072
256	5.89	290	2.87	324	0.067
257	6.06	291	2.66	325	0.063
258	6.19	292	2.45	326	0.065
259	6.30	293	2.26	327	0.057
260	6.41	294	2.06	328	0.051

261	6.50	295	1.87	329	0.051
262	6.61	296	1.69	330	0.046
263	6.68	297	1.52	331	0.041
264	6.72	298	1.36	332	0.037
265	6.74	299	1.22	333	0.036
266	6.74	300	1.08	334	0.037
267	6.74	301	0.961	335	0.035
268	6.71	302	0.843	336	0.031
269	6.67	303	0.743		

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### Quantum Yields

$\phi = 0.60$  over the wavelength range 240 – 380 nm.

$\phi_1 = 0.31$  for 1 bar air,

#### *Comments on Preferred Values*

UV absorption spectrum of hydroxyacetone consists of a broad structureless band over the wavelength range 230 to 340 nm; the spectrum is blue-shifted by about 15 nm relative to that of acetone and peaks at 266 nm. The three reported spectra show similar shape but the cross-sections at the maximum of absorption near 266 nm differ, covering the range  $5.43 \times 10^{-20}$  (Butkovskaya et al. 2006) to  $6.74 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  (Orlando et al, 1999). . Uncertainties ( $2\sigma$ ) in the cross sections reported by Orlando et al. are  $\sim \pm 10\%$  near the peak of the spectrum and increase to about  $\pm 35\%$  at the longest wavelengths measured. The errors are dominated by possible systematic errors associated with sample purity. Only experimental statistical errors were reported by Butkovskaya et al. and the results from the two methods did not agree very well. The JPL evaluation recommended a mean of the 3 cited studies, in the overlapping range. However the excellent agreement between the absolute and relative determinations of  $\sigma$  at 184.9nm of Dillon et al. (2006) provides an indirect confirmation of the UV spectrum reported by Orlando et al. (1999), and we recommend these cross sections.

The quantum yields from the same study of Orlando et al.(1999) are the only reported data, and form the basis of our recommendation for calculation of atmospheric photolysis rates. The product analysis in that work suggest that <50% photodissociation proceeds via channel (1), and significant formation of HOCH<sub>2</sub>CO radicals.

### References

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