IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P10

This data sheet updated: 9th August 2002.

$CH_3C(O)CH=CH_2 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)CHCH_2 + h\nu \rightarrow CH_2CHCO + CH_3$	(1)		
$\rightarrow C_3H_6 + CO$	(2)	24.7	4842
$\rightarrow C_2H_3 + CH_3CO$	(3)	405	295.3

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250-395	Gierczak *et al*., 1997[1]	(a)
235-400	Raber and Moortgat., 1996[2]	(b)

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

Measurement	Wavelength range/nm	Reference	Comments
ϕ = 0.16 (33 mbar)	308	Gierczak *et al*., 1997[1]	(c)
0.04 (33 mbar)	337		
0.01 (33 mbar)	351		
$\phi < 0.04$ (1 bar)	275 - 380	Raber and Moortgat., 1996[2]	(d)

Comments

(a) Measurements made using a diode array spectrometer with a D_2 lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 250 – 298 K. Tabulated cross sections at 1 nm intervals. $\sigma_{max} = 7.2 \times 10^{-20}$ cm^2 molecule^{-1} (±5%) at 331 nm and $\sigma = (6.6 \pm 0.35) \times 10^{-18}$ cm^{2}molecule^{-1} at 213.86 nm (Zn lamp source). Small temperature dependence at λ max (<2% increase at 250 K).

(b) Measurements made at 298 K using a diode array spectrometer with a D_2 lamp source. $\sigma_{max} = 6.5 \times 10^{-20}$ cm^{2}molecule^{-1} (±5%) at 330.7 nm.

(c) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of $CH_3C(O)CHCH_2$ (MVK) by GC. ϕ was determined at pressures of 25 and 650 Torr (33 and 850 mbar) air, and at 308, 337 and 351 nm. ϕ showed pressure quenching at 308 and 337 nm but not at 351 nm. Expression given for the variation with pressure (for air up to 1 bar)

and wavelength of ϕ: $\phi_o(\lambda,P) < \frac{\exp[-0.055(\lambda - 308)]}{(5.5 + 9.2\times10^{-19}[M])}$ where λ is in nm and M in molecule cm^{-3}.

(d) Broad band photolysis of static mixtures (bath gas is air) with measurement of the loss of $CH_3C(O)CHCH_2$ and formation of products (C_3H_6, CO, HCHO with minor amounts of CO_2, HC(O)OH, CH_3OH, $CH_3(O)OH$ and $C_2H_3C(O)OH$) by FTIR. Quantum yield from loss of $CH_2C(CH_3)CHO$ (methacrolein) and formation of CO. Indication of a weak pressure effect with ϕ(50 Torr)/ϕ(760 Torr) ~ 2. The relative importance of the photolysis channels could not be obtained accurately from the product yields.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
250	0.241	299	3.70	348	5.77
251	0.241	300	3.87	349	5.47
252	0.224	301	4.04	350	5.20
253	0.241	302	4.20	351	4.94
254	0.241	303	4.35	352	4.72
255	0.258	304	4.51	353	4.53
256	0.275	305	4.66	354	4.32
257	0.275	306	4.82	355	4.15
258	0.293	307	4.96	356	4.03
259	0.310	308	5.13	357	3.94
260	0.327	309	5.30	358	3.89
261	0.361	310	5.44	359	3.89
262	0.379	311	5.58	360	3.68
263	0.396	312	5.73	361	3.60
264	0.430	313	5.87	362	3.49
265	0.465	314	6.02	363	3.36
266	0.499	315	6.14	364	3.29
267	0.534	316	6.28	365	3.03
268	0.568	317	6.42	366	2.77
269	0.620	318	6.54	367	2.50
270	0.654	319	6.63	368	2.20
271	0.706	320	6.70	369	2.01
272	0.757	321	6.76	370	1.88
273	0.809	322	6.83	371	1.74
274	0.878	323	6.85	372	1.58
275	0.929	324	6.88	373	1.48
276	0.998	325	6.95	374	1.39
277	1.08	326	7.02	375	1.31
278	1.15	327	7.09	376	1.26
279	1.24	328	7.16	377	1.24
280	1.33	329	7.23	378	1.20
281	1.41	330	7.28	379	1.20
282	1.50	331	7.30	380	1.05
283	1.60	332	7.26	381	0.981
284	1.70	333	7.18	382	0.912
285	1.81	334	7.04	383	0.878
286	1.91	335	6.94	384	0.929
287	2.03	336	6.85	385	0.757
288	2.15	337	6.70	386	0.637
289	2.29	338	6.56	387	0.534
290	2.43	339	6.47	388	0.447

291	2.55	340	6.44	389	0.396
292	2.67	341	6.42	390	0.344
293	2.81	342	6.35	391	0.310
294	2.93	343	6.35	392	0.293
295	3.08	344	6.30	393	0.275
296	3.24	345	6.23	394	0.241
297	3.39	346	6.14	395	0.207
298	3.56	347	6.08		

Quantum Yields

$$\phi_0(\lambda,P) = \frac{\exp[-0.055(\lambda - 308)]}{(5.5 + 9.2\times10^{-19}[M])}$$

where λ is in nm and M in molecule cm^{-3}.

Comments on Preferred Values

The preferred absorption cross-sections are based on the measurements of Gierzak *et al*.[1] They agree well with the measurements of Raber and Moortgat[2] within 10% over the range 290 – 365 nm.

The two studies[1,2] of the quantum yield for photodissociation of $CH_2C(CH_3)CHO$ are essentially in agreement. Both show low efficiency for photolysis ($\phi < 0.1$) and a weak pressure dependence in ϕ (ϕ decreases with increasing pressure between 25 Torr(33 mbar) and 760 Torr (1 bar)). Gierzak *et al*.[1] also observe an increase at shorter wavelength. We recommend the empirical algorithm given by Gierzak *et al*.[1] for the overall dissociation quantum yield in air as a function of wavelength and pressure, although this should be considered an upper limit. The results of Raber and Moortgat[2] indicate that the photolysis channel leading to propene (channel 2) accounts for 60% of the $CH_2C(CH_3)CHO$ loss, with the balance occurring by the two radical channels (1) and (3) with equal probability.

References

1 T. Gierczak, J. B. Burkholder, R. K. Talukdar, A. Mellouki, S. B. Barone and A. R. Ravishankara, J. Photochem. Photobiol. A: Chem. **110** 1 (1997).

2 W.H. Raber and G.K. Moortgat, in 'Progress and Problems in Atmospheric Chemistry', edited by J. Barker, pp. 318-373, World Scientific Publ. Co., Singapore, (1996),