IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet P9

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This datasheet updated: 16th May 2002.

$CH_2=C(CH_3)CHO + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH^o_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_2C(CH_3)CHO + h\nu \rightarrow CH_2CCH_3 + HCO$ (1)	320.5	373.1
$\rightarrow C_3H_6 + CO$ (2)	16.1	7428
$\rightarrow H + CH_2CCH_3CO$ (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250-395	Gierczak *et al.*, 1997[3]	(a)
235-400	Raber and Moortgat., 1996[2]	(b)

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

Measurement	Wavelength range/nm	Reference	Comments
ϕ = 0.008 (865 mbar)	308	Gierczak *et al.*, 1997[3]	(c)
= 0.005 (33 mbar)	308		
= 0.005 (865 mbar)	351		
= 0.003 (33 mbar)	351		
$\phi < 0.05$ at 1 bar	275-370	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. σ_{max} = 7.2 x 10^{-20} cm^2 $molecule^{-1}$ (±5%) at 331 nm and σ = (2.21±0.03) x 10^{-17} cm^2 $molecule^{-1}$ at 213.86 nm (Zn lamp source). Small increase with decreasing temperature at λ max.

(b) Measurements made at 298 K using a diode array spectrometer with a D_2 lamp source. σ_{max} = 7.64 x 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 $CH_2C(CH_3)CHO$ (methacrolein) by GC. ϕ was determined at pressures of 25 and 650 Torr (33 and 865 mbar) air, and at 308 and 351 nm. ϕ increased with pressure by a factor of ~2 over the range. Propene not observed as a product, in contrast to other studies.

(d) Broad band photolysis of static mixtures (bath gas is air) with measurement of the loss of $CH_2C(CH_3)CHO$ and formation of products (C_2H_4, C_3H_6, C_2H_2, CO, CO_2, HCHO) by FTIR. Quantum yield from loss of $CH_2=C(CH_3)CHO$ and formation of CO. Indication of a weak pressure effect with ϕ(50 Torr)/ϕ(760 Torr) ~ 2. No firm information on the relative importance of the photolysis channels could be obtained 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	0.207	300	3.44	350	4.16
251	0.194	301	3.61	351	3.85
252	0.187	302	3.76	352	3.89
253	0.180	303	3.91	353	4.35
254	0.178	304	4.04	354	4.31
255	0.177	305	4.19	355	4.14
256	0.180	306	4.40	356	3.62
257	0.180	307	4.58	357	3.53
258	0.186	308	4.71	358	3.46
259	0.193	309	4.81	359	3.81
260	0.201	310	4.92	360	5.05
261	0.211	311	5.13	361	4.28
262	0.224	312	5.35	362	3.61
263	0.241	313	5.50	363	2.86
264	0.263	314	5.61	364	2.68
265	0.283	315	5.70	365	2.33
266	0.305	316	5.87	366	1.92
267	0.333	317	6.04	367	1.62
268	0.363	318	6.19	368	1.40
269	0.398	319	6.28	369	1.31
270	0.436	320	6.27	370	1.42
271	0.479	321	6.18	371	1.67
272	0.520	322	6.21	372	1.53
273	0.567	323	6.34	373	1.43
274	0.616	324	6.58	374	1.08
275	0.673	325	6.74	375	0.977
276	0.732	326	6.73	376	1.000
277	0.793	327	6.68	377	1.07
278	0.863	328	6.83	378	1.35
279	0.936	329	7.07	379	2.18
280	1.01	330	7.15	380	1.30
281	1.09	331	7.16	381	0.984
282	1.18	332	7.03	382	0.555
283	1.26	333	6.69	383	0.456
284	1.35	334	6.41	384	0.364
285	1.45	335	6.08	385	0.331
286	1.56	336	5.97	386	0.246
287	1.67	337	6.25	387	0.205
288	1.79	338	6.38	388	0.181
289	1.90	339	6.37	389	0.161
290	2.03	340	6.24	390	0.147
291	2.16	341	6.02	391	0.156
292	2.28	342	5.98	392	0.159
293	2.40	343	6.58	393	0.153
294	2.52	344	6.79	394	0.149
295	2.68	345	6.53	395	0.123
296	2.85	346	6.11		
297	2.99	347	5.63		
298	3.13	348	5.22		
299	3.26	349	4.55		

Quantum Yields

No recommendation

Comments on Preferred Values

The preferred absorption cross-sections are based on the measurements of Gierzak *et al*.[1] The peak cross section agrees within 10% with the measurements of Raber and Moortgat.[2]

The two studies[1,2] of the quantum yield for photodissociation of $CH_2C(CH_3)CHO$ are not in good agreement, although both indicate very low quantum efficiencies with $\phi < 0.05$. No firm recommendation can be given.

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).