IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P3

This data sheet updated: 16th May 2002.

$C_2H_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_2H_5CHO \rightarrow C_2H_5 + HCO$	(1)	351.4	340
$\rightarrow C_2H_6 + CO$	(2)	-7.1	
$\rightarrow C_2H_4 + HCHO$	(3)	131.0	913
$\rightarrow CH_3 + CH_2CHO$	(4)	344.3	347

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202-365	Martinez *et al*., 1992[1]	(a)
280-330	Chen and Zhu, 2001[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1		Heicklen *et al*., 1986[3]	(c)
0.89	294		
0.50	302		
0.26	325		
0.15	334		
ϕ_1		Chen and Zhu, 2001[2]	(d)
0.85±0.06	280		
1.01±0.07	285		
0.95±0.06	290		
0.98±0.06	295		
0.92±0.06	300		
0.95±0.08	305		
0.98±0.11	310		
0.91±0.05	315		
1.08±0.07	320		
1.07±0.14	325		
0.84±0.08	330		

Comments

(a) Absorption measurements as a function of C_2H_5CHO pressure using a diode array spectrometer. Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

(b) Cross-sections determined from transmission of UV light at 5 nm intervals from tunable dye laser, as a function of C_2H_5CHO pressure. Overall uncertainty estimated to be 5-10% at all wavelengths. Results agree with those from ref 1 except at 280 and 330 nm, where values are 20-30% higher.

(c) Laser flash photolysis of C_2H_5CHO in the presence of air and steady-state photolysis of C_2H_5CHO in the presence of O_2 at 263 K or 298 K, as a function of wavelength and of O_2 pressure. Quantum yields for radical channel from measurement of $C_2H_5O_2$ and HO_2 by UV absorption following LP. Quantum yields for CO and C_2H_6 were measured by GC. From the proposed mechanism it was deduced that $\phi_1 = (\phi_\infty - \phi[C_2H_6])$. The values of ϕ quoted are for 1 bar air.

(d) Tunable dye laser photolysis of C_2H_5CHO with time resolved measurement of HCO concentration by cavity ring down spectroscopy at 613.8 nm. Absorbed flux was determined from photon fluence measurements using a calibrated Joulemeter. Absolute yields of HCO calculated from absorption cross sections, σ(HCO) determined *in situ* from either photo-dissociation of HCHO or Cl_2+HCHO mixtures (at 310-330 nm). A weak dependence of ϕ on $P_{C2H5CHO}$was observed but no dependence of ϕ on N_2 up to 1 bar. The values of ϕ quoted are for zero pressure, but the same values apply at 1 bar N_2.

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	0.049	295	5.57	330	0.575
206	0.049	296	5.37	331	0.494
210	0.057	297	5.16	332	0.466
214	0.069	298	5.02	333	0.430
218	0.080	299	5.02	334	0.373
222	0.091	300	5.04	335	0.325
226	0.115	301	5.09	336	0.280
230	0.163	302	5.07	337	0.230
234	0.257	303	4.94	338	0.185
238	0.407	304	4.69	339	0.166
242	0.622	305	4.32	340	0.155
246	0.909	306	4.04	341	0.119
250	1.287	307	3.81	342	0.076
254	1.745	308	3.65	343	0.045
258	2.25	309	3.62	344	0.031
262	2.88	310	3.60	345	0.025
266	3.43	311	3.53	346	0.019
270	4.12	312	3.50	347	0.016
274	4.59	313	3.32	348	0.014
278	5.17	314	3.06	349	0.013
280	5.16	315	2.77	350	0.010
281	5.21	316	2.43	351	0.008
282	5.35	317	2.18	352	0.007
283	5.57	318	2.00	353	0.005

284	5.78	319	1.864	354	0.004
285	5.86	320	1.831	355	0.002
286	5.82	321	1.777	356	0.001
287	5.72	322	1.662	357	0.001
288	5.59	323	1.577	358	0.000
289	5.52	324	1.488	359	0.000
290	5.56	325	1.300	360	0.000
291	5.68	326	1.129	361	0.000
292	5.81	327	0.996	362	0.000
293	5.88	328	0.828	363	0.000
294	5.80	329	0.685	364	0.000

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1
280	0.85
285	0.90
290	0.95
295	1.00
300	1.00
305	1.00
310	1.00

Preferred Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez *et al*.[1] Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of the earlier data of Calvert and Pitts[4], and the less precise measurements of Chen and Zhu.[2]

The quantum yields, ϕ_1, reported by Chen and Zhu[2] at wavelengths less than 310 nm and at 1 bar N_2, agree well with those obtained for 1 bar air in the less direct study of Heicklen *et al*.[3] However at wavelengths >310 nm the results of Chen and Zhu[2] do not show the fall off observed by Heicklen *et al*.[3] in air. This could be due to quenching by O_2 of the excited triplet state, which is believed to dissociate to give radical products (channel 1), or to errors in the interpretation of the more complex chemistry in the presence of O_2. There are significant experimental uncertainties at the longer wavelengths associated with the weak absorption by propionaldehyde. Further work is needed to resolve this issue and we are unable to recommend values for ϕ_1 in this region.

References

1 R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

2 Y. Chen and L. Zhu, J.Phys.Chem.A 105, 9689, (2001).

3 J. Heicklen, J. Desai, A. Bahta, C. Harper, and R. Simonaitis, J. Photochem. **34**, 117 (1986).

4 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.