

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P11

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$n\text{-C}_3\text{H}_7\text{CHO} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction		$\Delta H^\circ_{298}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$n\text{-C}_3\text{H}_7\text{CHO} \rightarrow n\text{-C}_3\text{H}_7 + \text{HCO}$	(1)	355.7	336
$\rightarrow \text{C}_3\text{H}_8 + \text{CO}$	(2)	-3.2	
$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{CHOH}$	(3)	~136	880
$\rightarrow \text{CH}_3 + \text{CH}_2\text{CH}_2\text{CHO}$	(4)		
$\rightarrow \text{C}_3\text{H}_6 + \text{HCHO}$	(5)	123.4	969

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202-365	Martinez <i>et al.</i> , 1992 ¹	(a)
240-350	Tadic <i>et al.</i> , 2001 ²	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.48 \pm 0.02$ (100 Torr air)	275-380	Tadic <i>et al.</i> , 2001 ²	(c)
$\phi = 0.38 \pm 0.02$ (700 Torr air)	275-380		
$\phi_1 = 0.21$ (1 bar, air)	275-380		
$\phi_3 = 0.10$ (1 bar, air)	275-380		

Comments

- Absorption measurements as a function of $\text{C}_3\text{H}_7\text{CHO}$ 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.
- Cross-sections determined from absorption measurements as a function of $\text{C}_3\text{H}_7\text{CHO}$ pressure using a diode array spectrometer, with resolution of 0.25 nm.
- Broad band (275 – 280 nm) steady-state photolysis of $\text{C}_3\text{H}_7\text{CHO}$ in the presence of air at 298 K. Products measured by FTIR were CO, C_2H_4 , CH_3CHO , CH_2CHOH and CO_2 . Quantum

yields of CO and C₂H₆ were measured as a function of wavelength and pressure, to provide values of ϕ_1 and ϕ_3 . Over all quantum yields were pressure dependent over range 100 – 700 torr, with the following Stern-Volmer expression: $1/\phi = 1.81 + (1.931 \times 10^{-3}) P[\text{Torr}]$.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
202	0.0178	295	6.03	330	0.868
206	0.0316	296	5.87	331	0.734
210	0.0475	297	5.69	332	0.647
214	0.0623	298	5.56	333	0.602
218	0.0771	299	5.46	334	0.554
222	0.0850	300	5.42	335	0.485
226	0.102	301	5.43	336	0.417
230	0.133	302	5.44	337	0.346
234	0.202	303	5.43	338	0.285
238	0.316	304	5.32	339	0.242
242	0.488	305	5.08	340	0.215
246	0.724	306	4.79	341	0.191
250	1.05	307	4.50	342	0.144
254	1.45	308	4.29	343	0.093
258	1.93	309	4.15	344	0.059
262	2.52	310	4.07	345	0.041
266	3.09	311	4.00	346	0.031
270	3.81	312	3.92	347	0.026
274	4.34	313	3.82	348	0.023
278	5.02	314	3.69	349	0.018
280	5.18	315	3.46	350	0.015
281	5.22	316	3.17	351	0.014
282	5.30	317	2.85	352	0.012
283	5.45	318	2.57	353	0.010
284	5.65	319	2.37	354	0.008
285	5.81	320	2.25	355	0.006
286	5.90	321	2.18	356	0.005
287	5.89	322	2.07	357	0.004
288	5.85	323	1.96	358	0.003
289	5.80	324	1.82	359	0.002
290	5.78	325	1.69	360	0.002
291	5.83	326	1.55	361	0.002
292	5.93	327	1.39	362	0.001
293	6.05	328	1.22	363	0.001
294	6.10	329	1.04	364	0.001

Quantum Yields

$\phi_3 = 0.10$; $\phi_1 = 0.21$ for 1 bar air, over the wavelength range 290 – 380 nm.

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez *et al.*¹ The cross-section data of Tadic *et al.*² are within 5% of the Martinez data over the wavelength region 260 nm to 350 nm.

The photolysis of long chain (>C₄) aldehydes undergo Norrish type I (ϕ_1) and Norrish type II (ϕ_3) dissociation in the first absorption band (260–340 nm). Channels 2, 4 and 5 are unimportant at wavelengths > 280 nm. The indirect quantum yield measurements for the two channels, ϕ_1 and ϕ_3 , reported by Tadic *et al.*² for photolysis of *n*-C₃H₇CHO appear reliable and are recommended here. Quantum yield measurements for the channel producing HCO (ϕ_1) from *n*-pentanal, obtained in the same study, agree with direct measurements for *n*-pentanal obtained by Cronin and Zhu³ using cavity ring-down detection of HCO. Weak pressure quenching of ϕ reported by Tadic *et al.*² for photolysis of *n*-C₃H₇CHO can be used to obtain quantum yields at lower atmospheric pressures, assuming constant branching ratio for channels 1 and 3.

References

- ¹ R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, *Atmos. Environ.* **26A**, 785 (1992).
- ² J. Tadic, I. Juranic and G. K. Moortgat, *J. Photchem. Photobiol. A: Chemistry*, **143** 169, (2001).
- ³ T. J. Cronin and L. Zhu, *J. Phys. Chem. A* **102**, 10274, (1998).