

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P24

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This data sheet last evaluated: June 2010; last change in preferred values: June 2010.

i-C₃H₇CHO + hν → products

Primary photochemical transitions

Reaction		$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
<i>i</i> -C ₃ H ₇ CHO → <i>i</i> -C ₃ H ₇ + HCO	(1)		349
→ C ₃ H ₈ + CO	(2)		All
→ <i>i</i> -C ₃ H ₇ CO + H	(3)		327
→ CH ₃ + CH ₃ CHCHO	(4)		
→ C ₃ H ₆ + HCHO	(5)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
265.2-334.0	Borkowski and Ausloos, 1962	(a)
206-444	McMillan, 1966	(b)
202-365	Martinez et al., 1992	(c)
280-330	Chen et al, 2002	(d)

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

Measurement	Wavelength range/nm	Reference	Comments
$\phi(\text{HCO}) = 0.20$	253.7	Desai et al, 1986	(e)
$\phi(\text{HCO}) = 0.45$	280.3		
$\phi(\text{HCO}) = 0.55$	302.2		
$\phi(\text{HCO}) = 0.88$	312.8		
$\phi(\text{HCO}) = 0.88$	326.1		
$\phi(\text{HCO}) = 0.69$	334.1		
$\phi^0(\text{HCO}) = 0.31 \pm 0.004$	280	Chen et al, 2002	(d)
$\phi^0(\text{HCO}) = 1.10 \pm 0.10$	320		
$\phi^0(\text{HCO}) = 0.94 \pm 0.06$	330		

Comments

- (a) Conventional UV absorption measurements yielding molar extinction coefficients given in tabular form.
- (b) Conventional spectrophotometric study (Cary 17-D) using biacetyl pressures of ~4 mbar to 17 mbar. Cross-sections taken from Spectral Atlas (<http://www.atmosphere.mpg.de/enid/2295>) which gives absorption cross sections read at 1- and 2-nm intervals from figure in Calvert and Pitts, 1966.
- (c) Cross-sections determined from absorption measurements as a function of *i*-C₃H₇CHO pressure using a diode array spectrometer, with resolution of 0.25 nm.
- (d) Photolysis of *n*-butyraldehyde and *i*-butyraldehyde at 5-nm intervals in the 280-330 nm region using dye laser photolysis combined with CRDS. Absorption cross sections of *n*-butyraldehyde and *i*-butyraldehyde were obtained at each wavelength that was studied. The quantum yields of HCO and their dependences on photolysis wavelength, aldehyde pressure, and total pressure (10-525 mbar N₂) were determined, from measurement of this photoproduct by CRDS, using a probe laser at 613 - 617 nm. The time dependence of [HCO] photofragment was analysed using a model of the post flash radical chemistry and Stern-Volmer self-quenching to determine the initial, zero pressure quantum yields, ϕ^0 . Absolute absorption cross section of HCO at the probe laser wavelength was determined using HCO from the formaldehyde photolysis reaction $\text{H}_2\text{CO} + h\nu \rightarrow \text{HCO} + \text{H}$, for which the HCO quantum yield is known, or from the $\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$ reaction. Quantum yields decreased with wavelength at both the longer and shorter end of the range. ϕ^0 between 280 – 330 nm was independent of N₂ pressure. At 285 nm, ϕ^0 was independent of $p(\text{i-C}_3\text{H}_7\text{CHO})$ (1.3-13 mbar range). At 325 nm (closer to the dissociation limit), $\phi(\text{HCO})$ decreased with $p(\text{i-C}_3\text{H}_7\text{CHO})$, due to self quenching.
- (e) Steady state photolysis of *i*-C₃H₇CHO was studied in the presence of O₂ at 263 and 294 K at several incident wavelengths. The quantum yields of CO and C₃H₆ were measured using GC, and from the difference between them the primary quantum yields ϕ_1 (free radical channel) and ϕ_2 (molecular channel) were deduced. The pulsed flash photolysis of *i*-C₃H₇CHO was also studied in the presence of air at 298 K. The transient UV absorption of peroxy radicals, formed by reaction of the photo-fragments with O₂, was monitored and relative quantum yields were obtained with 284.0, 302.5, 311.7, 325.0 and 330.5 nm incident radiation. The quantum yields were not pressure quenched, except for very slightly at 330.5 nm.

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	0.93	273	4.05	321	2.280
206	0.40	274	4.14	322	2.175
208	0.28	275	4.35	323	2.076
210	0.23	276	4.69	324	1.951
212	0.20	277	4.91	325	1.842
214	0.17	278	4.81	326	1.710
216	0.15	279	5.03	327	1.584
218	0.12	287	5.73	328	1.397
220	0.12	288	5.79	329	1.195

222	0.09	289	5.85	330	0.950
224	0.11	290	5.87	331	0.785
226	0.09	291	5.84	332	0.672
228	0.12	292	5.84	333	0.567
230	0.12	293	5.88	334	0.490
232	0.16	294	5.92	335	0.425
234	0.18	295	5.94	336	0.357
236	0.24	296	5.86	337	0.297
238	0.27	297	5.78	338	0.257
240	0.34	298	5.73	339	0.215
242	0.41	299	5.69	340	0.173
244	0.51	300	5.59	341	0.147
246	0.61	301	5.48	342	0.123
248	0.77	302	5.43	343	0.081
250	0.91	303	5.36	344	0.059
252	1.11	304	5.29	345	0.034
254	1.27	305	5.15	346	0.025
256	1.51	306	4.98	347	0.019
258	1.71	307	4.73	348	0.015
260	1.96	308	4.57	349	0.013
261	2.11	309	4.41	350	0.011
262	2.13	310	4.27	351	0.010
263	2.43	311	4.13	352	0.009
264	2.60	312	3.99	353	0.008
265	2.79	313	3.86	354	0.005
266	2.88	314	3.73	355	0.004
267	3.16	315	3.61	356	0.003
268	3.33	316	3.48	357	0.001
269	3.45	317	3.26	358	0.001
270	3.49	318	2.82	359	0.001
271	3.75	319	2.60		
272	3.84	320	2.41		

Quantum Yields

λ/nm	ϕ_1
280	0.31 ± 0.04
285	0.50 ± 0.07
290	0.71 ± 0.04
295	0.91 ± 0.04
300	1.00 ± 0.14
305	0.92 ± 0.08
310	1.06 ± 0.07
315	1.06 ± 0.13
320	1.10 ± 0.10
325	1.10 ± 0.10
330	0.94 ± 0.06

Comments on Preferred Values

The absorption spectrum of i-butyraldehyde shows a single broad band between 230 and 350 nm, with a maximum at 294 nm. The cross-sections from earlier scanning UV spectrometer measurements of McMillan (1966) agree well with the diode array measurements of Martinez et al. (1992), although there are small differences in the details of the weak structure near the maximum and on the long wavelength side of the band. The less well λ -resolved measurements of Chen et al. (2002) suggest a systematic red-shift of the band compared to these data. The preferred absorption cross-sections are a simple average of the measurements of Martinez *et al.* (1992) and McMillan (1966) at each corresponding wavelength. The uncertainty on the cross-sections near the band centre are better than 4%.

The two studies cited reporting quantum yields both show wavelength dependence of the HCO radical channel, with $\phi(\text{HCO})$ near unity around 310 nm, declining at both ends of the range 280 – 330 nm. The absolute values of the quantum yield of HCO at zero pressure measured directly by Chen et al. (2002) was generally slightly higher than the indirect determinations reported by Desai et al. (1986), but overall the agreement is good. Chen et al estimate and overall uncertainty of ~50%, comprising $\pm 10\%$ experimental error and 38% systematic error arising mostly from the cross sections for HCO ($\pm 20\%$) and i-C₃H₇CHO (10%; note that the σ values of Chen differ from the above IUPAC preferred values near the maximum). Both studies concluded that pressure quenching by N₂ or O₂ was negligible except near the photodissociation threshold, but efficient quenching of excited i-butyraldehyde by ground state i-butyraldehyde occurs at $\lambda < 310$ nm. The reduced $\phi(\text{HCO})$ at $\lambda < 295$ nm is accounted for by the opening up of an additional photodissociation pathway (2) forming C₃H₈ + CO at higher photon energy. The Norrish Type II dissociation channel involving α -H transfer to give C₂H₄ + CH₂CHOH products is not available for i-butyraldehyde and it can be concluded that the overall quantum yield $\phi (= \phi_1 + \phi_2) = 1.0$. The slight fall off in ϕ at the longest wavelengths near the photodissociation threshold could result from quenching by N₂

The preferred values of ϕ_1 are the direct measurements of Chen et al. for $\phi(\text{HCO})$. For atmospheric photolysis of i-butyraldehyde the overall photolysis can be calculated with $\phi = 1.0$, with the second contributing channel $\phi_2 = (1 - \phi_1)$.

References

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