IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P30

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$C_6H_5C(O)H + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_6H_5C(O)H \rightarrow C_6H_5 + HC(O)$	(1)	408.6	292
$\rightarrow C_6H_5CO + H$	(2)	363.9	328
$\rightarrow C_6H_6 + CO$	(3)	9.1	13.1 (μm)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220 - 300	Nozière et al.,1994	(a)
245 - 300	Caralp et al.,1999	(b)
255 - 296	Etzkorn et al.,1999	(c)
280 - 308	Zhu and Cronin, 2000	(d)
252 - 368	Thiault et al.,2004	(e)
220 - 280	El Dib et al.,2006	(f)
280 - 400	Xiang et al., 2009	(g)
320 - 450	Chen et al., 2011	(h)

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

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1(HCO) = 0.32±0.05	280	Zhu and Cronin, 2000	(d)
ϕ_1 (HCO) = 0.45±0.05	285		
ϕ_1 (HCO) = 0.29±0.05	308		

Comments

(a) The absorption cross sections were determined by flowing nitrogen containing a calibrated concentration of benzaldehyde through a 70 cm reaction cell. UV light from a D_2 lamp passed twice through the cell into a monochromator/photomultiplier unit for conventional absorption measurements. Resolution not given.

(b) Same set up as (a); no experimental details given.

(c) UV absorption cross sections were determined using a 1080 l quartz cell with a 0.5 m Czerny-Turner spectrometer coupled with a photodiode array detector (spectral resolution 0.15 nm). The maximum absolute absorption cross section for benzaldehyde at the 284.1 nm peak was $\sigma = (4.40 \pm 1.82) \times 10^{-18}$)cm^{2}molecule^{-1}.

(d) The UV photodissociation of benzaldehyde was investigated wavelengths of 280, 285 and 308 nm by employing excimer or dye laser photolysis in combination with CRDS. Absorption cross-sections of benzaldehyde were obtained from attenuation of the photolysis light. The HCO radical photofragmentation product was detected by CRDS at 614 nm and amounts formed after 10 μs were determined using the absorption cross-section of HCO at the probe laser wavelength, determined relative to the photolysis reaction: $H_2CO + h\nu \rightarrow HCO + H$, for which the HCO quantum yield is known. The uncertainty on the quantum yields reflects experimental scatter.

(e) Absorption cross-sections for benzaldehyde were measured in the wavelength region 252–368 nm using two different systems (D_2 lamp-diode array and D_2 lamp-monochromator). In addition, cross sections at 253.7 ($(8.5 \pm 1.3) \times 10^{-19}$), 312.2 ($(6.6 \pm 0.1) \times 10^{-20}$) and 365 nm ($(2.2 \pm 0.4) \times 10^{20}$) were measured using a Hg pen ray lamp and were found in good agreement with those obtained using the D_2 lamp-diode array system. The absorption spectra of aromatic aldehydes have been found to exhibit fine structures similarly to aromatic hydrocarbons.

(f) Photolysis of a slow flowing mixture of Cl_2, N_2, O_2, and $C_6H_5CH_3$. Absorption cross sections were determined by the "factor analysis method". Using factor analysis, the spectrum obtained is refined and the concentrations of the main absorbing species in a omplex mixture are extracted.

(g) Absorption measurements by CRDS. Cross sections and error limits (standard deviations in the precision of the measurements) given at 5 nm intervals in the range.

(h) Absorption cross sections of benzaldehyde were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 m^3 FEP chamber which contained the benzaldehyde (>99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1σ).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
220	21.000	310	0.0480
225	32.000	315	0.0658
230	39.000	320	0.0576
235	32.000	325	0.0649
240	24.000	330	0.0667
245	2.080	335	0.0677
250	1.300	340	0.0627
255	0.920	345	0.0471
260	1.300	350	0.0508
265	1.640	355	0.0385
270	1.990	360	0.0468
275	2.270	365	0.0418
280	1.720	370	0.0130

285	1.830	375	0.0043
290	0.120	380	0.0007
295	0.053	385	0.0002
300	0.043	390	0.0001
305	0.056	395	0.0002

Quantum Yields

Wavelength /nm	ϕ_1(HCO)
308	0.29±0.05

Comments on Preferred Values

The absorption spectrum of benzaldehyde consists of three distinct regions; an intense band between 200 - 250 nm (σ_{max} = 3.9 x 10^{-17} cm^2 at 230 nm); a second band between approx. 250 - 290 nm (σ_{max} = 3.9 x 10^{-17} cm^2 at 230 nm); and a weaker absorbing plateau region with superimposed structure between 300 - 370 nm. The cross-section data of most of the studies are in reasonable agreement except for those of Noziere et al. (1999) which are systematically higher over the range studied by them, and those of Zhu and Cronin which were significantly lower, except ar 318 nm where they were slightly higher than other measurements. Part of the differences arise from different resolution of the measurements using narrow band (laser) and broad-band techniques, especially in regions with discrete absorption features. The most recent CEAS measurements of Chen at al.(2011) confirm the detailed structure in the near UV observed by Thiault *et al*.(2004), but the authors note a blue-shift in the wavelength calibration in the Thiault *et al*. results at λ >335 nm, and an offset in their absorption at λ >380 nm resulting from a baseline shift.

The preferred absorption cross-sections at λ > 295 nm are averaged values from the measurements of Thiault *et al*.(2004) (blue shifted by 4nm between 335 – 375 nm), Xiang et al (2009) and Chen at al.(2011) in the regions of data overlap. Between 255 nm < λ < 295 nm the preferred values are average values of the data from Etzkorn *et al* (1999), Thiault *et al* (2004) , and El Dib *et al*. (2006). The data of El Dib *et al*. (2006) are recommended for λ < 255 nm.

The recommended quantum yield ϕ(HCO) at 308 nm is the wavelength resolved value reported by Zhu and Cronin (2000). This gives a lower limit to the overall ϕ. The values at at shorter wavelength may be in unrepresentative due to fine structure effects in this structured part of the spectrum. Nevertheless these results indicate that photolysis is a potentially important removal process for aromatic aldehydes in the troposphere.

References

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Figure 1: Absorption Spectrum of Benzaldehyde