

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P27

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4-oxo-pent-2-enal (CH₃C(O)CH=CHC(O)H) + hν → products

Primary photochemical transitions

Reaction	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
<i>trans</i> -/ <i>cis</i> - CH ₃ COCH=CHCHO	<i>cis</i> -/ <i>trans</i> - CH ₃ COCH=CHCHO (1)	
→	→ 5-methyl-3 <i>H</i> -furan-2-one (2)	
	→ CH ₃ + COCH=CHCHO (3)	~351
	→ CH ₃ CO + CH=CHCHO (4)	<346
	→ CH ₃ COCH=CH + HCO (5)	<346
	→ CH ₃ COCH=CH ₂ + CO (6)	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190-460	Xiang, Zhu, and Tang, 2007	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$)

Measurement	Wavelength range/nm	Reference	Comments
<i>absolute quantum yields</i>			
$\phi(\text{HCO}) = 0.13 \pm 0.02$ (<i>trans</i> -)	193	Xiang, Zhu, and Tang, 2007	(b)
$\phi(\text{HCO}) = 0.078 \pm 0.012$ (<i>cis</i> -)			
$\phi(\text{HCO}) = 0.014 \pm 0.003$ (<i>trans</i> -)	248		(b)
$\phi(\text{HCO}) = 0.018 \pm 0.007$ (<i>cis</i> -)			
<i>relative quantum yields</i> (ϕ %)			
$\phi(1) = \sim 20 - 30$ (<i>cis</i> - <i>trans</i> & <i>trans</i> - <i>cis</i>)	320 - 480	Bierbach et al., 1994	(c)
$\phi(1) = \leq 20$ (<i>cis</i> - <i>trans</i> & <i>trans</i> - <i>cis</i>)	254		

$\phi(\text{CH}_3\text{CO})= 11\pm 3$	193	Xiang, Zhu, and Tang, 2007	(d)
$\phi(\text{CH}_3\text{CO})= 17\pm 9$	248		
$\phi(2)= 1.2\pm 0.1$	193		
$\phi(2)= 2.1\pm 1.5$	248		
$\phi(2)= 5.3\pm 1.3$	308		
$\phi(2)= 5.5\pm 1.7$	351		
$\phi(3)= 25\pm 8$	193		
$\phi(3)= 33\pm 10$	248		
$\phi(3)= 31\pm 12$	308		
$\phi(3)= 23\pm 9$	351		
$\phi(6)= 25\pm 10$	193		
$\phi(6)= 23\pm 8$	248		
$\phi(6)= 40\pm 10$	308		
$\phi(6)= 33\pm 9$	351		

Comments

- (a) Three techniques - conventional UV-Vis absorption spectrometry, laser fluence attenuation, and cavity ringdown spectroscopy- were used to determine absorption cross sections of purified samples of 4-oxo-pent-2-enal containing known amounts of *cis*- and *trans*- isomers defined by NMR. Cross section data at 1 nm intervals in the 190-250 nm region were determined by absorption in a 10 cm cell placed in a UV/visible spectrometer, with variation of the 4-oxo-2-pentenal pressure (mainly the *trans*- isomer) in the cell. The absolute uncertainty in these cross section data is about 40-70%. Cross section data at 193 and 248 nm were determined by monitoring transmitted laser photolysis fluence as a function of 4-oxo-2-pentenal pressure in the cell. The absolute cross section for 4-oxo-2-pentenal with a *trans/cis* ratio of 0.082:1 was: $4.79 \times 10^{-19} \text{ cm}^2/\text{molecule}$ at 248 nm. The overall uncertainties in the determination of *cis*-4-oxo-2-pentenal cross sections were $\pm 10\%$ at 193 and 248 nm, and for *trans*-4-oxo-2-pentenal were $\pm 15\%$ at 193 nm and $\pm 25\%$ at 248 nm. Cross section data at 10 nm intervals in the 280-460 nm region were determined by cavity ring-down spectroscopy (CRDS). The method was calibrated using measurements of the cross section for acetone at 298 K and 300 nm which was within 14% of the preferred value. Some differences were obtained in the CRDS absorbances of samples containing either mainly *cis*-isomer and containing mainly *trans*-isomer, especially at $\lambda > 400 \text{ nm}$. The relative amounts of *cis*- and *trans*-isomer in the mixtures was determined, which allowed the isomer-specific cross sections for 4-oxo-2-pentenal to be extracted.
- (b) Quantum yield of HCO production determined from CRDS measurement of HCO concentration at 613.80 nm., using an absorption cross section of $\sim 2.0 \times 10^{-18} \text{ cm}^2/\text{molecule}$ at this wavelength, calibrated relative to formaldehyde photolysis at 248 nm, for which the recommended $\phi(\text{HCO})= 0.29$.
- (c) Photo-oxidation studies in 1080 L quartz glass chamber surrounded by actinic fluorescent or low pressure mercury lamps. Total pressure 1000 mbar synthetic air and $296 \pm 2 \text{ K}$. Loss of 4-oxo-pent-2-enal (*cis*- & *trans*- isomers) and formation of products, from time-dependence of

FTIR absorption. The main products formed included maleic anhydride, HCHO, CH₃OH and CH₃OOH, with minor amounts of 5-Methyl-3H-furan-2-one.

- (d) Relative yields based on measurements, using FTIR, of photolysis of 4-oxo-2-pentenal and amounts of its end products: 5-Methyl-3H-furan-2-one, methyl vinyl ketone and ethane. The former two products are assumed to result directly from channels (2) and (6); ethane indicates CH₃ production in channel (3) or by dissociation of 'hot' CH₃CO in channel (4). Significantly increased CO yields were observed at 193 and 248 nm. If the *trans/cis* isomerisation yields of Bierbach et al. are included, the total photolysis yield of 4-oxo-2-pentenal is close to unity, based on these results.

Preferred Values

Absorption cross-sections at 294 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		$10^{20} \sigma/\text{cm}^2$
	<i>cis</i> - isomer	<i>trans</i> - isomer	50/50 <i>cis/trans</i>
193	849	444	644
248	66.2	37.8	52
280	3.72	1.39	2.56
290	1.33	2.09	1.71
300	1.18	2.74	1.96
310	1.51	4.76	3.14
320	2.37	2.42	2.40
330	3.99	4.37	4.18
340	4.36	4.63	4.50
350	5.08	3.69	4.39
360	4.47	3.69	4.08
370	4.07	2.67	3.37
380	2.47	3.26	2.87
390	2.53	2.54	2.54
400	2.22	1.94	2.08
410	1.82	0.75	1.29
420	1.22	0.59	0.91
430	1.14	0.29	0.72
440	0.73	0.29	0.51
450	0.6	0.13	0.36
460	0.38	0.11	0.24

Quantum Yields

λ/nm	350-460	193	248	308	351
ϕ_1	0.3	-	<0.2	-	-
ϕ_2	0.05	0.01	0.02	0.05	0.05
ϕ_3	-	0.25	0.33	0.30	0.23
ϕ_4	0	0.11	0.17	-	-
ϕ_5	-	0.13	0.02	0	0
ϕ_6	0.33	0.25	0.25	0.40	0.33

Comments on Preferred Values

The cited data is the only reported quantitative study of gas-phase UV/visible absorption spectrum of 4-oxo-2-pentenal. It is composed of an absorption band in the shorter wavelength region ($\lambda_{\text{max}} = 215 \text{ nm}$; $\pi \rightarrow \pi^*$ transition) and broad absorption bands in the longer wavelength region ($\lambda_{\text{max}} = \sim 350 \text{ nm}$; most likely composed of two partially overlapping $n \rightarrow \pi^*$ transitions).

The absolute cross-sections for the wavelengths: 193nm, 248 nm and 280 – 460 nm (10 nm intervals) are listed in the paper of Xiang et al. (2007), together with the cross sections determined at 1 nm intervals by UV absorption on the 190 – 250 nm region for the mainly *trans*- isomer of 4-oxo-2-pentenal. Results using the different methods in the different spectral regimes were in reasonable agreement. A detailed account of the uncertainties in the experimental data was also given.

The preferred cross-sections are the isomer specific values reported by Xiang et al (2007), based on their measurements using CRDS and LAS. A simple average of these recommended values applies to a 50:50 mixture of *cis/trans* isomers, which corresponds approximately to an equilibrium mixture for ambient conditions.

The only direct determination of primary quantum yields are those for HCO production reported by Xiang et al. (2007), and these results show that this channel only occurs at $\lambda < 308 \text{ nm}$ and remains a minor channel even at 193 nm. However the analysis of the relative yields of the photolysis products by Xiang et al. (2007), together with the *cis/trans* isomerisation yields reported by Bierbach et al (1994), give a consistent picture of the photolysis channels in the absence of O_2 ; the preferred quantum yields are based on the assumption that the overall photolysis quantum yield of *cis* and *trans* 4-oxo-2-pentenal is unity. The major products observed from the photo-oxidation in synthetic air, reported by Bierbach et al., can be rationalised from secondary reactions of the primary photofragments.

References

Bierbach, A., Barnes, Ian, Becker, K.H., and Wiesen, Evelyn, *Environ.Sci.Technol.*, 1994, 28, 715 - 729.

Xiang, B., Zhu, L., and Tang, Y., *J Phys. Chem. A*, 2007, 111, 9025 - 9033.

Figure 1: Absorption Spectrum of 4-oxo-penten-2-dial

