

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P2

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CH₃CHO + hv → products

Primary photochemical transitions

Reaction	$\Delta H^\circ_{298}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ CHO + hv → CH ₄ + CO (1)	-19.5	
→ CH ₃ + HCO (2)	355.3	337
→ CH ₃ CO + H (3)	373.8	320

Absorption cross-sections

Wavelength range/nm	Reference	Comments
202-365	Martinez <i>et al.</i> , 1992 ¹	(a)
308 nm	Yang <i>et al.</i> , 2006	(b)

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

Measurement	Wavelength range/nm	Reference	Comments
$\phi(\text{CH}_4)$ 0.46-0.005 0.0	260 – 295 300 - 330	Meyrahn, Moortgat and Warneck, 1982	(c)
$\phi(\text{CO})$ 0.31-0.48 0.48-0			
$\phi^\circ(\text{HCO})$ 0.91±0.10	308	Yang <i>et al.</i> , 2006	(d)
$\phi(\text{CH}_4)^*$ 0.475-0.027 0.027-0.003 0.003-<0.001	257 – 287 287 – 313 313 - 330	Moortgat, Meyrahn, and Warneck, 2010	(e)
$\phi(\text{CO})^*$ 0.726-0.681 0.681-0.219 0.219-0.014			
$\phi(\text{CO}_2)^*$ 0.085-0.055 0.055–0.027 -			

* in air at 1 bar

Comments

- (a) Double beam spectrophotometric measurements with 10 cm pathlength. Data obtained at 0.1 nm intervals with 0.5 nm resolution. Argon-acetaldehyde mixtures used at a total pressure of 133 mbar and several acetaldehyde pressures in the range 1.3 mbar to 2.6 mbar. Cross-sections tabulated are averages over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered on the corresponding wavelength (see Preferred Values).
- (b) Laser absorption measurements at 308 nm and 243 K and 293 K. cross sections are $(3.00 \pm 0.09) \times 10^{-20}$ and $(3.24 \pm 0.14) \times 10^{-20}$ cm²/molecule, at 243 and at 293 K, respectively, where the error represents 1 σ standard deviation of 12 repeated measurements. Our acetaldehyde absorption cross section at 308 nm and 293 K agrees well with the value of 3.33×10^{-20} cm²/molecule reported by Martinez et al. (1992).
- (c) Quantum yields of CH₄ and CO determined from the photolysis of 100 ppm of CH₃CHO in air or N₂ at a total pressure of 1 bar. H₂ was found only in trace quantities and hence it was concluded that the photolytic channel giving CH₃CO + H ($\lambda_{\text{threshold}} = 320$ nm) is negligible. Quantum yield data based on the assumption that $\phi_1 + \phi_2 + \phi_a = 1$, where ϕ_a refers to the quenching process CH₃CHO* + M → CH₃ + CHO + M. Quantum yield data at 1 bar pressure were found to be independent of the diluent, N₂, or air. ϕ_{CO} both in N₂ and in air increased as the total pressure was lowered.
- (d) PLP-CRDS; HCO product detected by CRDS at 613.8 nm; yield determined by modelling post-photolysis chemistry showed Stern-Volmer quenching by the process CH₃CHO* + M → CH₃ + CHO + M; $\phi^{\text{O}}(\text{HCO}) = 0.87 \pm 0.11$ and 0.91 ± 0.10 at 243 and at 293 K respectively.
- (e) The quantum yields for CO and CH₄, formed in the steady state photolysis of about 200 ppm of acetaldehyde in air at 1 bar pressure, were determined by GC analysis at 15 wavelengths in the range: 250–330 nm. The quantum yields for CO₂ were determined at nine wavelengths in the range: 250–315 nm. The products CH₄, CO, and CO₂ were assigned to the three primary processes: $\phi_1 + \phi_2 + \phi_3$ respectively, with dissociation occurring from the initially populated S¹ singlet state of acetaldehyde. The wavelength dependence of individual primary quantum yields was derived. The pressure dependence of the quantum yields at wavelengths of 270, 304.4, and 313 nm exhibited Stern–Volmer behavior in all cases. Quenching coefficients as a function of excitation energy were obtained by comparison with literature data.

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	0.056	297	4.38	334	0.363
206	0.053	298	4.41	335	0.350
210	0.049	299	4.26	336	0.238
214	0.048	300	4.16	337	0.222
218	0.052	301	3.99	338	0.205
222	0.065	302	3.86	339	0.219
226	0.096	303	3.72	340	0.150
230	0.151	304	3.48	341	0.074
234	0.241	305	3.42	342	0.042
238	0.375	306	3.42	343	0.031
242	0.564	307	3.36	344	0.026
246	0.818	308	3.33	345	0.021
250	1.128	309	3.14	346	0.019
254	1.524	310	2.93	347	0.015

258	1.994	311	2.76	348	0.016
262	2.44	312	2.53	349	0.010
266	3.05	313	2.47	350	0.008
270	3.42	314	2.44	351	0.007
274	4.03	315	2.20	352	0.006
278	4.19	316	2.04	353	0.005
280	4.50	317	2.07	354	0.005
281	4.69	318	1.979	355	0.004
282	4.72	319	1.874	356	0.005
283	4.75	320	1.723	357	0.003
284	4.61	321	1.484	358	0.004
285	4.49	322	1.402	359	0.002
286	4.44	323	1.244	360	0.003
287	4.59	324	1.091	361	0.002
288	4.72	325	1.136	362	0.001
289	4.77	326	1.074	363	-
290	4.89	327	0.858	364	-
291	4.78	328	0.747	365	-
292	4.68	329	0.707		
293	4.53	330	0.688		
294	4.33	331	0.588		
295	4.27	332	0.530		
296	4.24	333	0.398		

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1	ϕ_2	ϕ_3	ϕ_{total}
255	0.46	0.30	0.12	0.88
260	0.44	0.31	0.11	0.86
265	0.39	0.35	0.10	0.84
270	0.30	0.41	0.10	0.81
275	0.17	0.51	0.09	0.77
280	0.05	0.59	0.09	0.73
285	0.02	0.58	0.08	0.68
290	0.01	0.55	0.07	0.63
295	-	0.50	0.07	0.57
300	-	0.44	0.06	0.50
305	-	0.36	0.06	0.42
310	-	0.28	0.04	0.32
315	-	0.18	0.02	0.20
320	-	0.09	0.01	0.10
325	-	0.04	-	0.04
330	-	0.01	-	0.10
335	-	-	-	-

Pressure dependence of quantum yields in air at 298 K

λ /nm	ϕ^0	$10^{21}k_M/k_D/$ $\text{cm}^3\text{molecule}^{-1}$
255	1.000	5
260	1.000	6
265	1.000	8
270	1.000	10
275	1.000	13
280	1.000	16
285	1.000	19
290	1.000	25
295	0.999	32
300	0.995	45
305	0.983	71
310	0.941	129
315	0.811	260
320	0.537	562
325	0.238	1253
330	0.078	2802
335	0.022	6204
340	0.006	13519

Total dissociation quantum yield, ϕ_{diss} , is given by the expression:

$$\frac{1}{\phi_{\text{diss}}} = \frac{1}{\phi_0} + \left(\frac{k_M}{k_D} \right) [M]$$

where ϕ_0 is the the total dissociation quantum yield at zero bath gas concentration, and $[M]$ the concentration of air molecules in molecule cm^{-3} .

Comments on Preferred Values

The preferred absorption cross-sections are from the extensive measurements of Martinez *et al.* (1992). Resolution is 0.5 nm. Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of the data of Calvert and Pitts (1966) and Weaver *et al.* (1976). The absorption cross section at 308 nm and 293 K measured by LAS (Tang *et al.*, 2006), agrees well with the value of $3.33 \times 10^{-20} \text{ cm}^2/\text{molecule}$ reported by Martinez *et al.* (1992).

Studies of the photodecomposition of acetaldehyde following absorption in the 255 – 350 nm regions shows the existence of all three energetically feasible dissociation pathways defined above (Calvert *et al.*, 2008). The first reaction is negligible for $\lambda > 300$ nm and only becomes prominent at $\lambda < 285$ nm. This channel can therefore be ignored for tropospheric photolysis. In the region $\lambda > 290$ nm reaction (2) dominates and reaction (3) contributes ~10% overall; the total photodissociation quantum yield in this region, ϕ_{diss} is given by $(\phi_2 + \phi_3)$. Many studies have shown that the quantum yields, either the total quantum yield or that of the dominant products CO or HCO, are pressure dependent exhibiting Stern-Volmer behaviour at all wavelengths in the spectral region 270–331 nm. Thus the data can be used to determine the quenching parameters k_M/k_D (i.e. the ratio of the rate constants for collisional quenching and for dissociation of excited CH_3CHO molecules) and ϕ^0 (the zero pressure quantum yield for dissociation), from the slope and intercept of plots of $1/\phi_{\text{diss}}$ versus pressure of quenching gas, p . The quenching parameters depend on the excitation wavelength.

The preferred values for the quantum yields at 1 bar air for each channel ϕ_1 , ϕ_2 and ϕ_3 are those reported by Moortgat *et al.* (2010) based on their measurements of the quantum yields for CH_4 , CO and CO_2 , from low $[\text{CH}_3\text{CHO}]$ in the presence of air and N_2 as bath gas. Their results are in close agreement with the earlier data of Meyrahn *et al.* (1982) and of Horowitz and Calvert (1982), which were evaluated together with early data by Atkinson and Lloyd (1984). The zero pressure HCO

yields and their pressure dependence, measured by Tang et al.(2006), provide support for the recommended value of ϕ_2 at 1 bar.

Warneck and Moortgat (2013) have evaluated the available laboratory data and have developed functional relationships for the wavelength dependence of the quenching parameters, ϕ^o and k_M/k_D in units of $\text{cm}^3/\text{molecule}$, which can be used to calculate the overall dissociation quantum yield, using the Stern-Volmer model. In their analysis it is assumed that only the S_1 state is involved in the quenching, which along with intersystem crossing, competes with internal conversion followed by rapid dissociation. Their analysis provides the following expressions:

$$\phi^o = [1 + \exp((\lambda - \lambda_0)/c)]^{-1}$$

where $\lambda_0 = 320.55 \pm 0.59$ nm, $c = 3.82 \pm 0.52$; and:

$$10^{21} k_M/k_D = A \exp(-\alpha/\lambda) + B \exp(-\beta/\lambda)$$

where $A = (1.04 \pm 0.26) \times 10^{27}$, $\alpha = 17918 \pm 1179$, $B = (1.48 \pm 0.15) \times 10^6$, $\beta = 3210.8 \pm 322.1$.

These expressions give the values of ϕ^o and k_M/k_D tabulated in the table of preferred values, which can be used to evaluate the pressure dependence of the overall photo-dissociation quantum yields. The expression for the wavelength dependence of ϕ^o was obtained from a least squares fit to the zero pressure values derived from Stern-Volmer plots from the following studies: Weaver et al. (1976/77), Horowitz et al. (1982), Horowitz and Calvert (1982), Simonaitis and Heicklen (1983), Moortgat et al, (2010), and the sensitised emission data of Gandini and Hackett. The expression for the wavelength dependence of k_M/k_D was obtained from a least squares fit to a bi-exponential expression, which best describes the semi-logarithmic plot of the k_M/k_D values obtained from the Stern-Volmer plots, vs $1/\lambda$, which exhibits two regions of approximate linearity in the ranges 312–333 nm and 270–295 nm. Figure 2 shows pressure dependence of ϕ^o calculated for selected wavelengths in the atmospheric photolysis region.

References

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Figure 1: Absorption cross sections; resolution : 0.5 nm

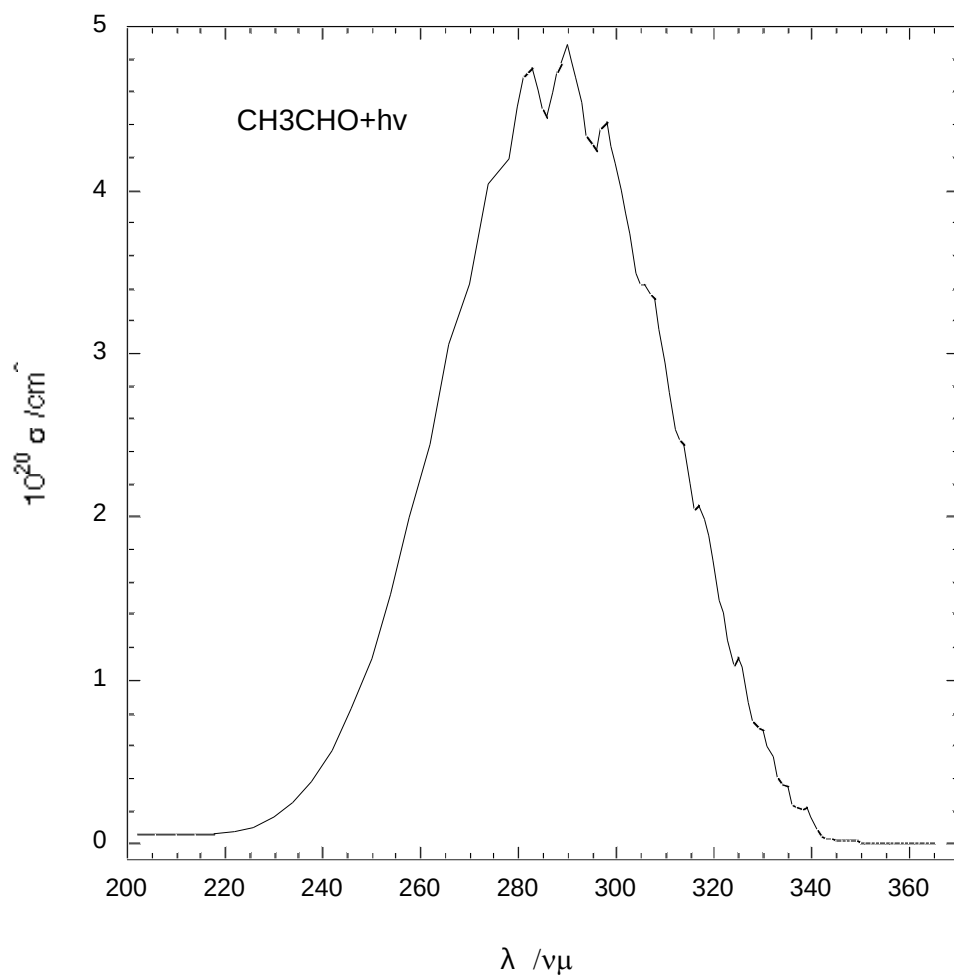


Figure 2 shows pressure dependence of ϕ^0 calculated for selected wavelengths in the atmospheric photolysis region, calculated using the parameterisation of Warneck and Moortgat (2012).

