# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P6

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## $CH_3COCHO + h\nu \rightarrow$ products

### Primary photochemical transitions

| Reaction | | $\Delta H°_{298}$/kJ·mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|---|
| $CH_3COCHO + h\upsilon \rightarrow CH_4 + 2CO$ | (1) | -24.7 | |
| $\rightarrow CH_3CO + HCO$ | (2) | 304.2 | 393 |
| $\rightarrow CH_3CHO + CO$ | (3) | -5.2 | |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 220-480 | Meller *et al*., 1991[1] | (a) |
| 205-480 | Staffelbach *et al*., 1995[2] | (b) |
| 290-440 | Chen, Wang and Zhu, 2000[3] | (c) |

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

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi(2)$ | | | |
| 0.14 | 240 – 420 | Staffelbach *et al*., 1995[2] | (d) |
| 1.0 | 260 – 320 | Koch and Moortgat, 1998[4] | (e) |
| 1.10±0.14 | 380 | | |
| 0.47±0.09 | 400 | | |
| 0.21±0.06 | 420 | | |
| 0.08±0.02 | 440 | | |
| 0.82±0.06 | 290 | Chen, Wang and Zhu, 2000[3] | (f) |
| 0.89±0.10 | 300 | | |
| 0.97±0.08 | 320 | | |
| 0.92±0.10 | 380 | | |
| 0.56±0.09 | 400 | | |
| 0.27±0.04 | 420 | | |
| 0.17±0.02 | 440 | | |

### Comments

(a) Measured over the range 220 nm to 480 nm by conventional UV spectroscopy in a cell of path length 63 cm. Light was detected by a diode array camera and the spectral resolution was 0.07 nm. As well as using methylglyoxal prepared external to the cell, methylglyoxal was generated *in situ* by the Cl atom-initiated modulated photo-oxidation of hydroxyacetone and the cross-sections were measured over the range 390 nm to 460 nm in these *in situ* studies.

(b) Cross-sections measured in a 90 cm cell using a diode array spectrometer. The spectral resolution was estimated to be 0.6 nm. Pressures in the range 0.13 mbar to 8.0 mbar were used and measurements were made at 248 K, 273 K and 298 K.

(c) Cross-sections determined from transmission of UV light at 5 nm intervals from tunable dye laser, as a function of $CH_3COCHO$ pressure. Overall uncertainty estimated to be ~10% at all wavelengths, except at 280 and 330 nm, where uncertainties are 20-30% higher.

(d) Low concentrations of methyl glyoxal in an $O_2$ (20%)/$N_2$ (80%) mixture at 1 bar were photolysed with an Xe arc equipped with filters to isolate specific wavelength regions. Products (HCHO, $CH_3COOH$, $CH_3COO_2H$, $CH_3OH$, HCOOH, CO, $CO_2$) were monitored by FTIR. Light intensity calibrated by photolysis of $Cl_2/CH_3OH/O_2/N_2$ mixture. Quantum yields were derived by modeling product yields taking into account a number of important secondary reactions. Average $\phi$ value quoted.

(e) Static photolysis of $CH_3COCHO$ in synthetic air. Quantum yields of molecular products CO and HCHO determined by GC. Pressure range 30-900 Torr (0.039-1.2 bar). For the short wavelength band $\phi$ was independent of pressure and wavelength; in the long wavelength band $\phi$(CO) showed Stern-Volmer pressure quenching and $\phi$ (HCHO) *increased* with methyl glyoxal pressure; zero pressure values of $CH_3COCHO$ are quoted here. The primary process was attributed to reaction (2) at all wavelengths

(f) Tunable dye laser photolysis of $CH_3COCHO$ with time resolved measurement of HCO concentration by cavity ring down spectroscopy at 613.8 nm. Absorbed flux was determined from photon fluence measurements using a calibrated Joulemeter. Absolute yields of HCO calculated from absorption cross sections, $\sigma$(HCO), determined by *in situ* calibration using either photo-dissociation of HCHO (at 290–310 nm) or $Cl_2$+HCHO mixtures (at 310-440 nm) to produce known amounts of HCO. A weak dependence of $\phi$(HCO) on $P_{CH3COCHO}$ was observed and the values of $\phi$ quoted at selected wavelengths are for zero pressure, derived from Stern-Volmer plots. No dependence of $\phi$(HCO) on $N_2$ pressure up to 520 mbar was observed in the 270-390 nm region. Pressure quenching by $N_2$ was observed in the long wavelength band (380-440 nm) and expressions were reported for the wavelength-dependent zero pressure quantum yield ($\phi(HCO)_0 = (3.63 \pm 0.32) \times 10^{-7}$ [exp(5693 ± 533)/$\lambda$(nm)] and Stern-Volmer quenching constant by $N_2$ ($k_Q$ (Torr$^{-1}$)= (1.93 ± 0.24) x $10^4$ [exp(-(5639 ± 497)/$\lambda$(nm)]). Values of $\phi$(2) for 1 bar air were obtained by extrapolation, and atmospheric photolysis rates were calculated.

## Preferred Values

### Absorption cross-sections at 298 K at 5 nm intervals between 225 nm and 410 nm

| $\lambda$/nm | $10^{20}$ $\sigma$/cm$^2$ | $\lambda$/nm | $10^{20}$ $\sigma$/cm$^2$ |
|---|---|---|---|
| 225 | 1.268 | 320 | 1.511 |
| 230 | 1.477 | 325 | 0.938 |
| 235 | 1.803 | 330 | 0.652 |
| 240 | 2.071 | 335 | 0.482 |
| 245 | 2.304 | 340 | 0.323 |
| 250 | 2.612 | 345 | 0.300 |
| 255 | 2.859 | 350 | 0.394 |
| 260 | 3.280 | 355 | 0.560 |
| 265 | 3.618 | 360 | 0.695 |
| 270 | 4.159 | 365 | 1.077 |
| 275 | 4.413 | 370 | 1.475 |
| 280 | 4.877 | 375 | 1.911 |
| 285 | 4.719 | 380 | 2.429 |
| 290 | 4.838 | 385 | 3.221 |
| 295 | 4.362 | 390 | 4.029 |

| | | | |
|---|---|---|---|
| 300 | 3.754 | 395 | 4.732 |
| 305 | 3.361 | 400 | 5.664 |
| 310 | 2.365 | 405 | 6.923 |
| 315 | 1.891 | 410 | 8.459 |

## Preferred Values

### Absorption cross-sections at 298 K at 1 nm intervals between 401 nm and 475 nm

| λ/nm | $10^{20}$ σ/cm$^2$ | λ/nm | $10^{20}$ σ/cm$^2$ |
|---|---|---|---|
| 401 | 5.90 | 439 | 11.01 |
| 402 | 6.07 | 440 | 9.94 |
| 403 | 6.35 | 441 | 10.39 |
| 404 | 6.54 | 442 | 10.20 |
| 405 | 6.91 | 443 | 10.17 |
| 406 | 7.20 | 444 | 11.17 |
| 407 | 7.58 | 445 | 9.61 |
| 408 | 7.94 | 446 | 8.90 |
| 409 | 8.12 | 447 | 9.84 |
| 410 | 8.52 | 448 | 9.18 |
| 411 | 8.63 | 449 | 10.13 |
| 412 | 9.07 | 450 | 8.67 |
| 413 | 9.37 | 451 | 6.34 |
| 414 | 9.62 | 452 | 6.33 |
| 415 | 9.68 | 453 | 6.08 |
| 416 | 9.71 | 454 | 4.46 |
| 417 | 10.04 | 455 | 3.69 |
| 418 | 10.07 | 456 | 3.08 |
| 419 | 10.12 | 457 | 2.46 |
| 420 | 10.21 | 458 | 1.81 |
| 421 | 10.34 | 459 | 1.28 |
| 422 | 10.51 | 460 | 0.914 |
| 423 | 10.45 | 461 | 0.795 |
| 424 | 10.15 | 462 | 0.642 |
| 425 | 10.34 | 463 | 0.479 |
| 426 | 10.24 | 464 | 0.332 |
| 427 | 9.84 | 465 | 0.268 |
| 428 | 10.01 | 466 | 0.227 |
| 429 | 9.94 | 467 | 0.187 |
| 430 | 10.41 | 468 | 0.160 |
| 431 | 10.53 | 469 | 0.133 |
| 432 | 9.79 | 470 | 0.108 |
| 433 | 10.64 | 471 | 0.099 |
| 434 | 10.54 | 472 | 0.089 |
| 435 | 10.81 | 473 | 0.077 |
| 436 | 11.13 | 474 | 0.067 |
| 437 | 9.99 | 475 | 0.062 |
| 438 | 10.59 | | |

### Quantum yields for zero pressure at 298 K

$\phi(2)_0 = (3.63 \pm 0.32) \times 10^{-7} [\exp(5693 \pm 533)/\lambda(\text{nm})]$ for $380 < \lambda < 440$ nm

$\phi(2)_0 = 1.0$ for $280 < \lambda < 380$ nm

*Comments on Preferred Values*

The preferred values of the absorption cross-sections are taken from the work of Meller *et al*.[1] The cross-sections of Staffelbach *et al*.[2] and Chen *et al*.[3] agree to within <10% of those of Meller *et al*.[1] across the whole range of the three studies. Staffelbach *et al*.[2] also studied the cross-sections at three different temperatures: 248 K, 273 K, and 298 K. They found little variation in the cross-sections (≤10%) over this temperature range.

The recent studies of Koch and Moortgat[4] and Chen *et al*.[3] provide for the first time information on the wavelength-resolved quantum yields for methyl glyoxal photolysis, and the latter study gives direct measurements of the initial product of photodissociation by reaction (2), HCO. This demonstrates conclusively that reaction (2) is the predominant dissociation channel over the wavelength range 280 - 440 nm. These results supercede the earlier work of Staffelbach *et al*.,[2] Raber and Moortgat[5] and Plum *et al*.,[6] which used broad-band excitation.

The results of Koch and Moortgat[4] and Chen *et al*.[3] are in good agreement regarding both the zero pressure quantum yields, and the absence of a dependence on pressure of $\phi(2)$ at $\lambda < 380$ nm. At the longer wavelengths ($380 < \lambda < 440$ nm) both studies observed a fall off in $\phi(2)$ with wavelength, and a complex pressure dependence. Koch and Moortgat[4] interpret their HCHO yields using a mechanism with a reaction of excited methyl glyoxal with the ground state. The quenching by $N_2$ observed by Chen *et al*.[5] in the long wavelength band (380-440 nm) did not exhibit Stern-Volmer behaviour, indicating the involvement of more than one excited precursor for HCO. There is a difference of up to a factor of 4 in the extrapolated values for the quantum yields in the range $\lambda$ = 380-400 nm at atmospheric pressure, reported from the two studies.

The preferred values are taken from Chen *et al*.[3], since they were determined directly. The expression for the wavelength dependence of $\phi(2)_0$ (zero pressure) at $\lambda > 380$ nm is taken from their work. Values at higher pressures (of air) can be calculated using the expression for the wavelength dependence of the quenching constant obtained by approximating to the Stern Volmer relationship:

$$1/\phi(2) = 1/\phi(2)_0 + k_Q \; P[N_2(\text{Torr})]$$

$k_Q$ (Torr$^{-1}$) = $(1.93 \pm 0.24) \times 10^4 [\exp(-(5639 \pm 497)/\lambda(\text{nm})]$. In view of the departure from linearity this leads to an estimated uncertainty up to ±50% in the overall quantum yield at 1 bar.

## References


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