IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet PF6

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$C_2F_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			$\Delta H°/kJ\cdot mol^{-1}$	$\lambda_{threshold}/nm$
$C_2F_5CHO + h\nu$	$\rightarrow C_2F_5 + HCO$	(1)		
	$\rightarrow C_2F_5CO + H$	(2)		
	$\rightarrow C_2F_5H + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
265-334	Borkowski and Ausloss, (1962)	(a)
319	Pritchard et al. (1962)	(b)
185-500	Hashikawa et al. (2004)	(c)
230-400	Chiappero et al. (2006)	(d)
230-376	Antinolo et al. (2014)	(e)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi_1 = 0.38\pm0.08$	254	Chiappero et al. (2006)	(f)
$\Phi_3 = 0.43\pm0.08$	254	Chiappero et al. (2006)	(f)
$\Phi_1 = 0.30\pm0.02$	308	Antinolo et al. (2014)	(g)

Comments

(a) Absolute absorption cross-sections at 334, 313, 280.4, and 265.2 nm were measured using a UV spectrometer with the sample at 305 K.

(b) An absolute absorption cross-section at 319 nm was measured using a UV spectrometer

(c) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of C_2F_5CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(d) Absolute absorption cross-sections were measured using a diode array spectrometer at 269-297 K. The UV spectrum of C_2F_5CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals. There was no discernable effect of temperature over the range 248-297 K on the UV spectrum, however for reasons which are unclear the UV spectra at 308 K and 323 K reported in the supporting information are approximately 10% more intense than that at 298 K.

(e) Absolute absorption cross-sections were measured using a 0.5-m spectrograph with a coupled-charge device (CCD) detector with 0.5−9.8 Torr of C_2F_5CHO. The temperature range specified in the text of the paper is 269 – 298 K, but data in the supporting information cover the range 269 – 323 K. The spectrum had a peak at 308.13 ± 0.76 nm. Values of σ were given at 1 nm intervals.

(f) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of C_2F_5CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of C_2F_5CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of C_2F_5NO and C_2F_5H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(g) Photolysis quantum yield measured using acetaldehyde as a chemical actinometer with pulsed laser photolysis of C_2F_5CHO at 308 nm in 75 – 760 Torr (100 – 1013 mbar) of air at 298 K. The quantum yield at λ=308 nm was pressure dependent, ranging from (0.94 ± 0.28) at 75 Torr to (0.30 ± 0.02) at 760 Torr. The pressure dependence is characterized by the Stern−Volmer expression with a Stern-Volmer constant of (1.22 ± 0.52) × 10^{-19} cm^3 $molecule^{-1}$. FTIR spectroscopy was used to identify the products following photolysis of C_2F_5CHO in air. From the observed product distribution it was concluded that photolysis at 308 nm occurs predominantly, if not exclusively, via channel (1) to give C_2F_5 + HCO radicals.

Preferred Values

Absorption cross-sections of C_2F_5CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
230	0.15	305	5.64
235	0.15	310	5.78
240	0.21	315	5.38
245	0.29	320	5.36
250	0.40	325	4.47
255	0.60	330	3.64
260	0.89	335	3.16
265	1.26	340	2.01
270	1.75	345	1.37
275	2.34	350	1.05
280	2.99	355	0.44
285	3.68	360	0.14
290	4.36	365	0.08
295	4.97	370	0.07
300	5.41	375	0.05

Quantum Yields of C_2F_5CHO

$\Phi_1 = 0.38$ at 254 nm
$\Phi_3 = 0.43$ at 254 nm
$\Phi_1 = 0.30$ at 308 nm

Reliability

$\Delta\Phi_1 = \pm 0.10$
$\Delta\Phi_3 = \pm 0.10$

Comments on Preferred Values

There is good agreement in the absorption cross sections measured at 298 K by Borkowski and Ausloss, (1962), Pritchard et al. (1962), Hashikawa et al. (2004), Chiappero et al. (2006), and Antinolo et al. (2014). Taking an average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Antinolo et al. (2014) gives the recommended values. The quantum yield measurements at 254 nm reported by Chiappero et al. (2006) and at 308 nm by Antinolo et al. (2014) are recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.14 for C_2F_5CHO (based upon a linear interpolation of the measured quantum yields for CF_3CHO and C_4F_9CHO) at 308 nm and estimated the photolysis lifetimes in the summer and winter solstices and the fall and spring equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages of approximately 0.9 days at 11 km altitude and 2.5 days at 0 km. Antinolo et al. (2014) assumed an exponential decrease of photolysis quantum yield with increasing wavelength from 0.81 at 254 nm (Chiappero et al., 2006) to 0.30 at 308 nm (Antinolo et al., 2014) and lower for wavelengths longer than 308 nm. Antinolo et al. (2014) estimated a photolysis lifetime of 3.5 hours at a altitude of 3.5 km and solar zenith angle of 16° (local noon in Ciudad Real, Spain, in summer). Photolysis is the dominant atmospheric fate of C_2F_5CHO.

References

Antinolo, M., Jiménez, E., Gonzalez, S., and Albaladejo, J.: J. Phys. Chem. A, 118, 178, 2014.

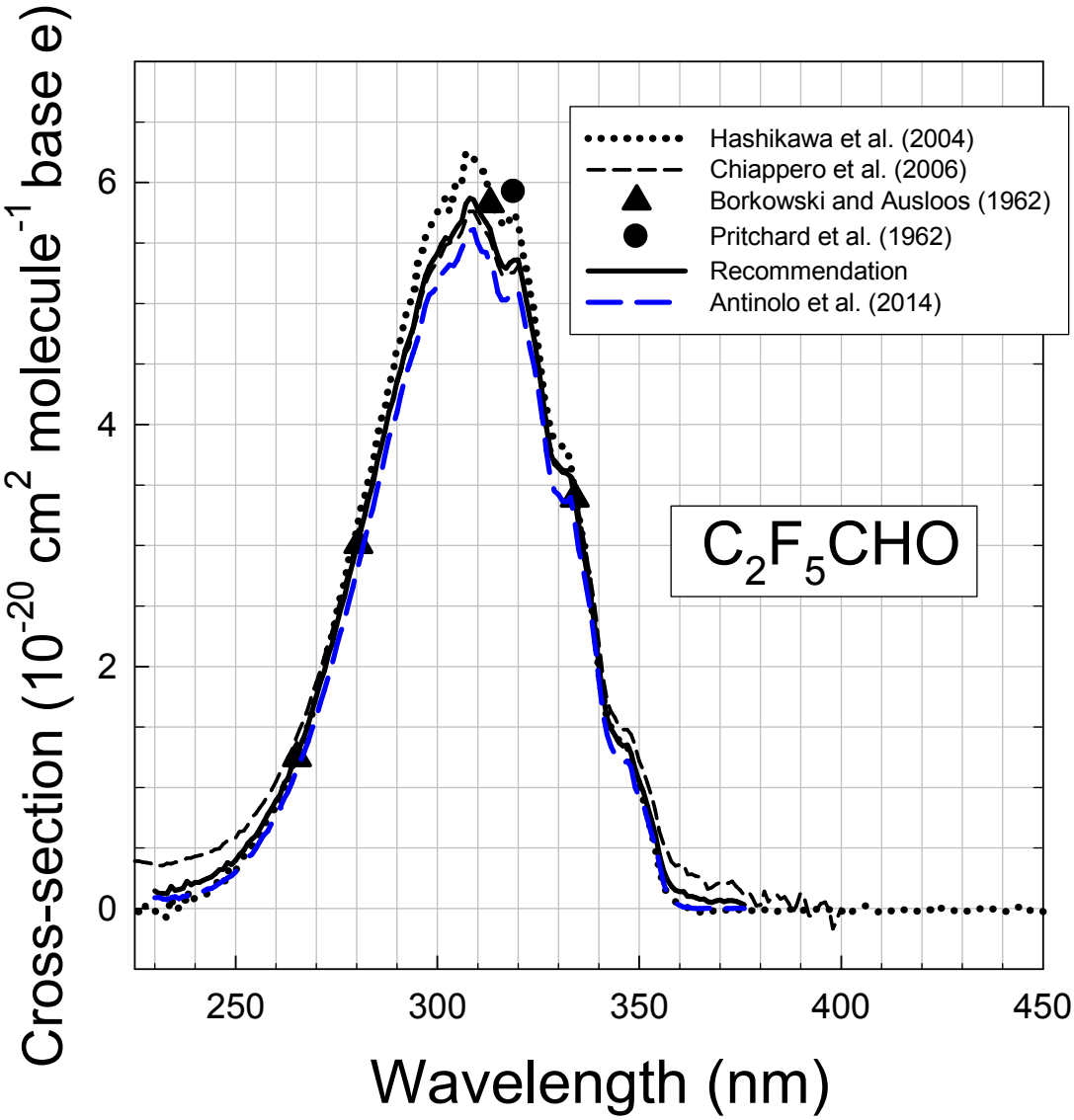
Borkowski, R. P., Ausloss, P.: J. Am. Chem. Soc., 1962, 84, 4044.

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2010.

Chiappero M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., Buck, R. C.: J. Phys. Chem. A, 110, 11944, 2006.

Hashikawa, Y., Kawasaki, M., Waterland, R. L., Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M. D.; Ball, J. C.; Wallington, T. J.: J. Fluorine Chem., 2004, 125, 1925.

Pritchard, G. O., Miller, G. H., Foote, J. K.: Can. J. Chem., 1962, 40, 1830.


Hashikawa et al. (2004)
Chiappero et al. (2006)
Borkowski and Ausloos (1962)
Pritchard et al. (1962)
Recommendation
Antinolo et al. (2014)
C2F5CHO
Cross-section (10-20 cm2 molecule-1 base e)
Wavelength (nm)
0
2
4
6
250
300
350
400
450