IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF8

The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.

This datasheet last evaluated: June 2015; last change in preferred values: June 2010.

n-C_4F_9CHO + hν → products

Primary photochemical transitions

Reaction		ΔH°/kJ·mol^{-1}	$\lambda_{threshold}$/nm
n-C_4F_9CHO + hν → *n*-C_4F_9 + HCO	(1)		
→ *n*-C_4F_9CO + H	(2)		
→ *n*-C_4F_9H + CO	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
185-500	Hashikawa et al. (2004)	(a)
230-400	Chiappero et al. (2006)	(b)
230-390	Solignac et al. (2007)	(c)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
Φ_1 = 0.31±0.08	254	Chiappero et al. (2006)	(d)
Φ_3 = 0.29±0.07	254	Chiappero et al. (2006)	(d)
Φ_{Total} = 0.08±0.02	308	Chiappero et al. (2006)	(e)
Φ_{Total} = 0.029±0.015	290-390	Solignac et al. (2007)	(f)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of *n*-C_4F_9CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum of *n*-C_4F_9CHO 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 studied on the UV spectrum.

(c) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for 1.5–11.0 Torr (2.0-14.7 mbar) samples of *n*-C_4F_9CHO at 298 K. The UV spectrum of *n*-C_4F_9CHO 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) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of *n*-C_4F_9CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of *n*-C_4F_9CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of *n*-C_4F_9NO and *n*-C_4F_9H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(e) Photolysis quantum yield measured using CH_3CHO as a chemical actinometer. Mixtures of *n*-C_4F_9CHO and NO (added as radical scavenger) in 700 Torr of N_2 diluent were irradiated using the 308 nm output of an eximer laser. The rate of loss of *n*-C_4F_9CHO was compared to that of CH_3CHO in back-to-back experiments. There was no evidence for the formation of *n*-C_4F_9H (<5% yield) following the irradiation of *n*-C_4F_9CHO–NO–N_2 mixtures showing that process (3) is not significant.

(f) Photolysis of *n*-C_4F_9CHO in one atmosphere of pure dry air in the presence of an OH radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured rate of photolysis of *n*-C_4F_9CHO was $(1.9 \pm 0.8) \times 10^{-5}$ s^{-1}. When compared to the maximum photolysis rate calculated using unit quantum yield for photodissociation across the atmospheric range of absorption of *n*-C_4F_9CHO a quantum yield of 0.029 ± 0.015 was derived.

Preferred Values

Absorption cross-sections of *n*-C_4F_9CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	0.41	305	9.44
205	0.30	310	9.87
210	-0.03	315	9.22
215	0.11	320	9.32
220	-0.02	325	7.59
225	-0.03	330	6.31
230	-0.02	335	5.61
235	-0.02	340	3.46
240	0.05	345	2.33
245	0.19	350	1.80
250	0.40	355	0.69
255	0.73	360	0.08
260	1.19	365	0.00
265	1.79	370	-0.08
270	2.53	375	-0.05
275	3.47	380	-0.04
280	4.52	385	-0.05
285	5.69	390	-0.05
290	6.84	395	-0.03

295	8.01	400	-0.04
300	8.82		

Quantum Yields of n-C_4F_9CHO

$\Phi_1 = 0.31$ at 254 nm
$\Phi_3 = 0.29$ at 254 nm
$\Phi_{Total} = 0.08$ at 308 nm
$\Phi_{Total} = 0.03$ at 290-390 nm

Reliability

$\Delta\Phi_1 = \pm\ 0.10$ at 254 nm
$\Delta\Phi_3 = \pm\ 0.10$ at 254 nm
$\Delta\Phi_{Total} = \pm\ 0.04$ at 308 nm
$\Delta\Phi_{Total} = 0.02$ at 290-390 nm

Comments on Preferred Values

There is agreement between the absorption cross sections measured by Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007). Taking an average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007) gives the recommended values. The quantum yield measurements at 254 and 308 nm reported by Chiappero et al. (2006) are recommended.

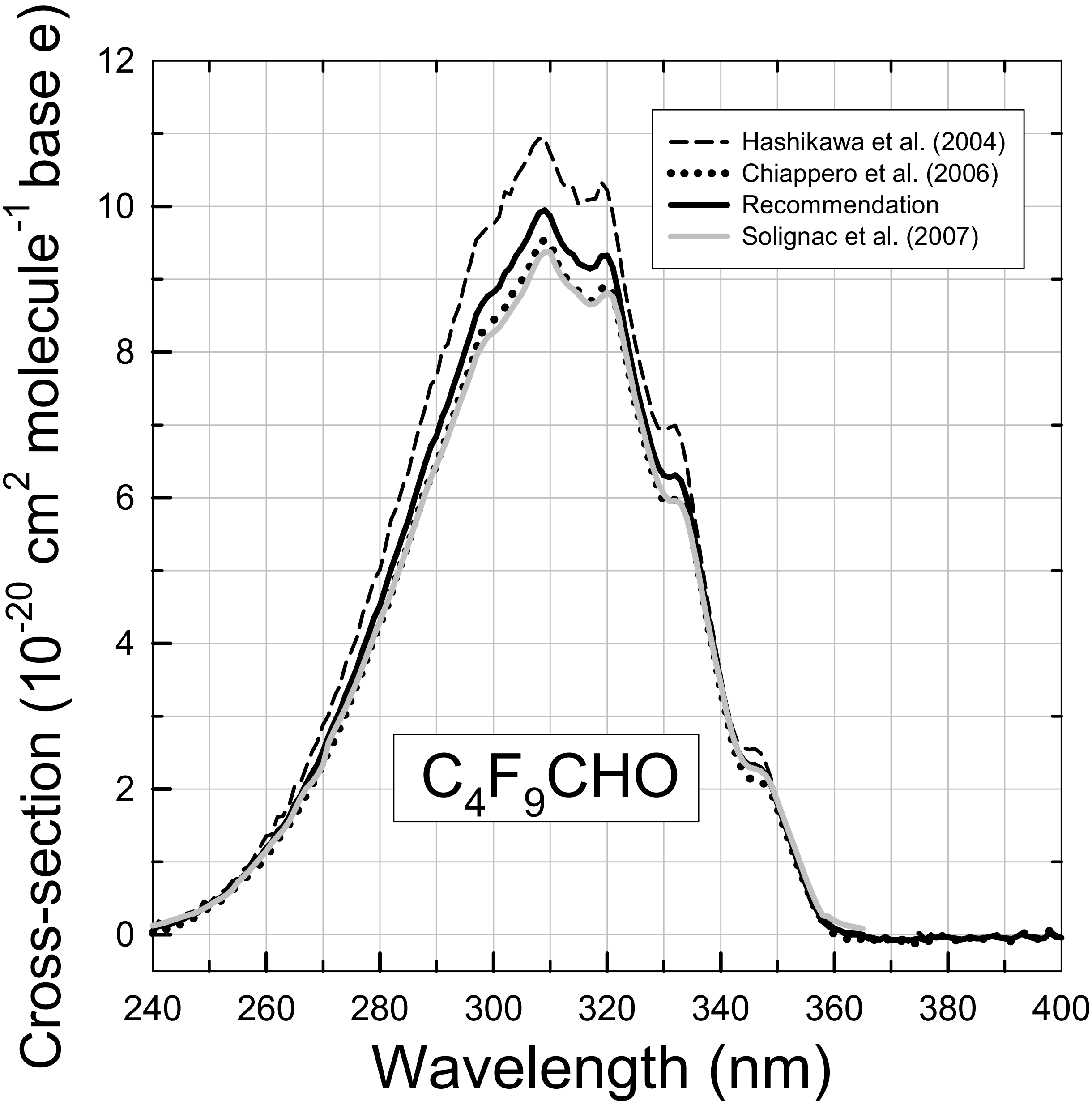
Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.08 for n-C_4F_9CHO (based on their data measured at 308 nm) and estimated the photolysis lifetimes in the summer and winter solstices and the fall and spring equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages of approximately 0.75 days at 11 km altitude and 2 days at 0 km. Use of the recommended quantum yield of 0.03 in place of the value of 0.11 used by Chiappero et al. (2006) will increase the photolytic lifetimes by approximately a factor of 4. In either case, photolysis is the dominant atmospheric fate of n-C_4F_9CHO.

References

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.

Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., and Sidebottom, H.: Phys. Chem. Chem. Phys., 9, 4200, 2007.



Hashikawa et al. (2004)
Chiappero et al. (2006)
Recommendation
Solignac et al. (2007)
C_4F_9CHO
Cross-section (10^{-20} cm^2 molecule^{-1} base e)
Wavelength (nm)
0
2
4
6
8
10
12
240
260
280
300
320
340
360
380
400