IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF9

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.

$CF_3CH_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_3CH_2CHO + h\nu \rightarrow CF_3CH_2 + HCO$	(1)		
$\rightarrow CF_3CH_2CO + H$	(2)		
$\rightarrow CF_3CH_3 + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
185-500	Sellevåg et al. (2004)	(a)
230-400	Chiappero et al. (2006)	(b)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi < 0.04$	290-400	Sellevåg et al. (2004)	(c)
$\Phi_1 = 0.38 \pm 0.09$	254	Chiappero et al. (2006)	(d)
$\Phi_3 = 0.36 \pm 0.07$	254	Chiappero et al. (2006)	(d)
$\Phi_{Total} = 0.04 \pm 0.01$	308	Chiappero et al. (2006)	(e)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of CF_3CH_2CHO shows a broad band, centered at 295 nm and extending out to approximately 350 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 CF_3CH_2CHO shows a broad band, centered at 295 nm and extending out to

approximately 350 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) Photolysis of CF_3CH_2CHO in 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 first-order loss rate of CF_3CH_2CHO during a ~3 hr period around solar noon was 7.74 x 10^{-6} s^{-1}, essentially identical to the leak rate obtained from monitoring the decay of SF_6. After correction for the leak rate and reaction with OH radicals, the observed first-order loss rate of CF_3CH_2CHO ascribed to photolysis during this ~3 hr period was J_{obs} <1.5 x 10^{-6} s^{-1}. This was compared to the maximum photolysis rate of 3.4 x 10^{-5} s^{-1} calculated using a unit quantum yield for photodissociation, the measured actinic flux within the chamber, and the measured UV absorption spectrum. Taking a ratio of J_{obs}/J_{calc} = 1.5 x 10^{-6}/3.4 x 10^{-5} gives an upper limit for the photolysis quantum yield of <0.04. Solignac et al. (2007) reported quantum yields J_{obs}/J_{calc} = (0.023 ± 0.012), (0.029 ± 0.015), and (0.046 ± 0.028) for the photodissociation of C_3F_7CHO, C_4F_9CHO and $CF_3(CF_2)_5CHO$ in the EUPHORE chamber across the atmospheric range of absorption of the aldehydes. Solignac et al. (2007) suggested that the photolytic loss of CF_3CH_2CHO may have been underestimated by Sellevåg et al. (2004).

(d) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of CF_3CH_2CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of CF_3CH_2CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of CF_3CH_2NO and CF_3CH_3 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*-CF_3CH_2CHO 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 CF_3CH_2CHO was compared to that of CH_3CHO in back-to-back experiments. There was no evidence for the formation of CF_3CH_3 (<5% yield) following the irradiation of CF_3CH_2CHO –NO–N_2 mixtures showing that process (3) is not significant.

Preferred Values

Absorption cross-sections of CF_3CH_2CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	0.64	305	1.55
205	0.48	310	1.52
210	0.36	315	1.10
215	0.27	320	0.92
220	0.21	325	0.76
225	0.16	330	0.36
230	0.13	335	0.34
235	0.14	340	0.13
240	0.17	345	0.04
245	0.24	350	0.02
250	0.34	355	0.02
255	0.48	360	0.00
260	0.67	365	0.00
265	0.88	370	0.00
270	1.07	375	0.00
275	1.38	380	0.00
280	1.51	385	0.00
285	1.73	390	0.00

290	1.81	395	0.01
295	1.80	400	0.01
300	1.82		

Quantum Yields of CF_3CH_2CHO

$\Phi_1 = 0.38$ at 254 nm
$\Phi_3 = 0.36$ at 254 nm
$\Phi_{Total} = 0.04$ at 308 nm

Reliability

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

Comments on Preferred Values

There is agreement between the absorption cross sections measured by Hashikawa et al. (2004), and Chiappero et al. (2006). Taking an average of the results from Hashikawa et al. (2004) and Chiappero et al. (2006) 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 0.04 for CF_3CH_2CHO (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 11 days at 11 km altitude and 40 days at 0 km. Photolysis is an important atmospheric fate of CF_3CH_2CHO.

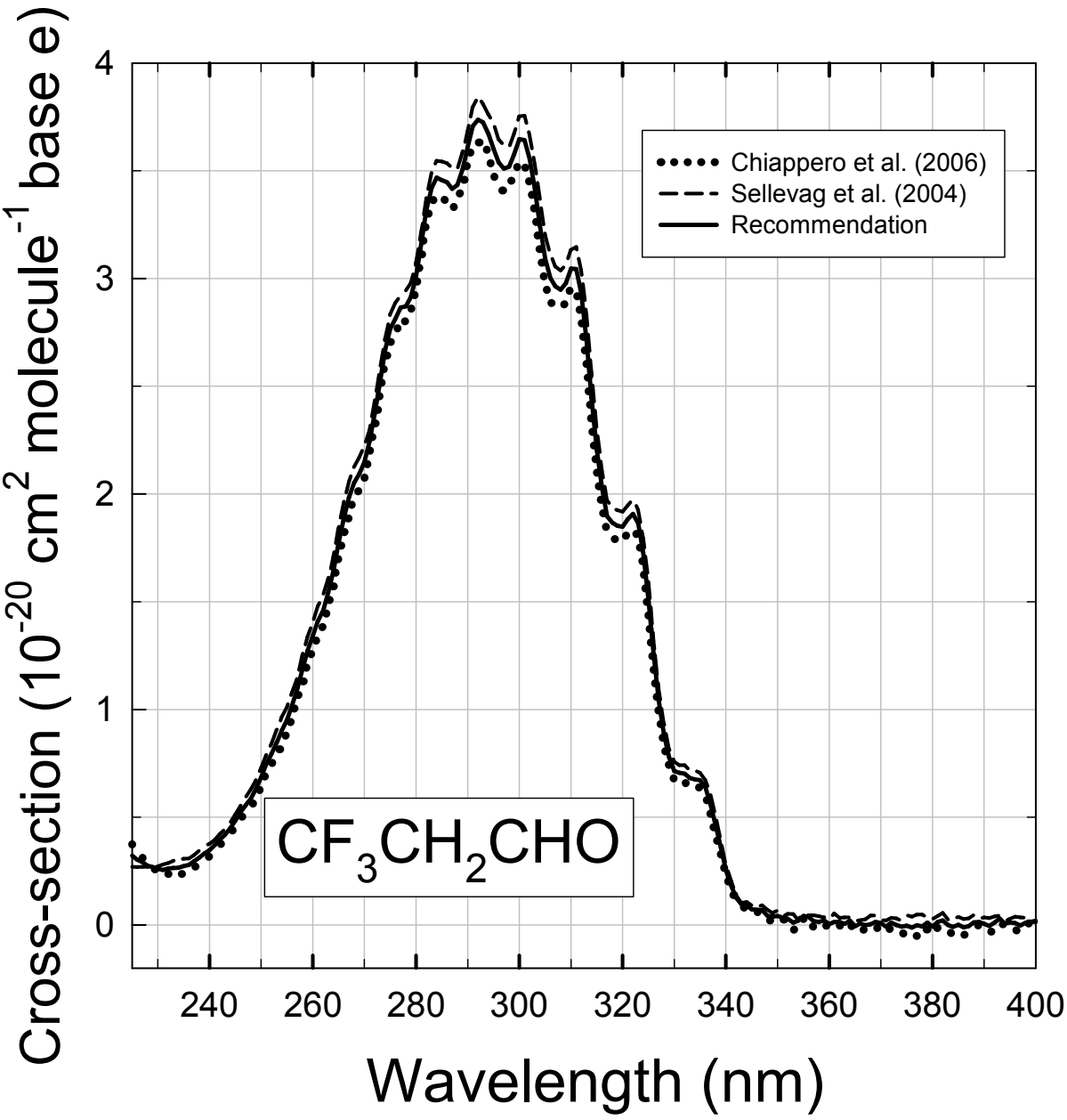
References

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.

Sellevåg, S. R., Kelly, T., Sidebottom, H., and Nielsen, C. J.: Phys. Chem. Chem. Phys., 6, 1243, 2004.

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


Cross-section (10^{-20} cm^2 $molecule^{-1}$ base e)
Wavelength (nm)
CF_3CH_2CHO
Chiappero et al. (2006)
Sellevag et al. (2004)
Recommendation
0
1
2
3
4
240
260
280
300
320
340
360
380
400