IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF5

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

$CHF_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CHF_2CHO + h\nu$	$\rightarrow CHF_2 + HCO$	(1)	305.6	392
	$\rightarrow CHF_2CO + H$	(2)	373.5	320
	$\rightarrow CH_2F_2 + CO$	(3)	-17.3	----

Absorption cross-section data

Wavelength range/nm	References	Comments
190-400	Sellevåg et al. (2005)	(a)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi = 0.30 \pm 0.05$	295-400	Sellevåg et al., 2005	(b)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of difluoroacetaldehyde shows a broad band, centered at 310 nm and extending out to approximately 355 nm. Values of σ were given at 1 nm intervals.

(b) Photolysis of CHF_2CHO in pure dry air in the presence of an inert tracer (SF_6) added to monitor leakage from the chamber and an OH radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured loss rate of CHF_2CHO during a ~5 hr period around solar noon was corrected for loss via leakage from the chamber and reaction with OH radicals to yield $J_{obs} = (2.91 \pm 0.09) \times 10^{-5}$ s^{-1}. This was compared to the maximum photolysis rate of 9.8×10^{-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 $J_{obs}/J_{calc} = 2.9 \times 10^{-5}/9.8 \times 10^{-5}$ gives the effective photolysis quantum yield from wavelengths relevant to the troposphere of 0.30 ± 0.05.

Preferred Values

Absorption cross-sections of CHF_2CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	0.27	300	4.34
195	0.20	305	4.49
200	0.12	310	4.53
205	0.08	315	4.07
210	0.06	320	4.22
215	0.05	325	3.37
220	0.05	330	2.92
225	0.06	335	2.07
230	0.06	340	1.11
235	0.07	345	0.97
240	0.11	350	0.55
245	0.17	355	0.09
250	0.28	360	0.04
255	0.44	365	0.01
260	0.68	370	0.01
265	1.01	375	0.02
270	1.40	380	0.01
275	1.87	385	0.01
280	2.43	390	0.01
285	2.95	395	0.01
290	3.54	400	0.00
295	3.97		

Quantum Yields of CHF_2CHO

$\Phi_1 = 0.30$ at 295- 360 nm

Reliability

$\Delta\Phi_1 = \pm 0.10$

Comments on Preferred Values

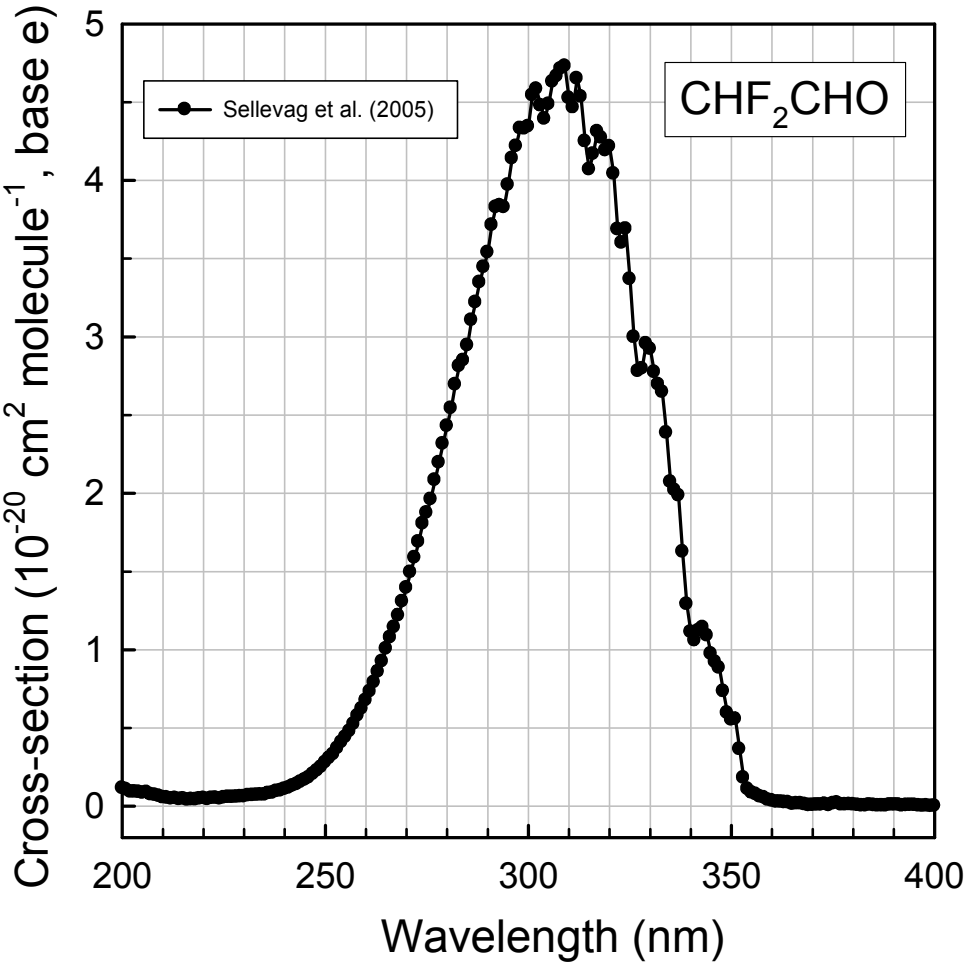
The preferred values for the cross-sections and quantum yield are taken from the study by Sellevåg et al. (2005). The photolysis of CHF_2CHO, presumable in air diluent (although this was not specified), at 310 nm was investigated by Sellevåg et al. (2005) and the formation of COF_2 and CO products was reported. There was no observable formation of CH_2F_2 consistent with the photolysis occuring via channel (1) to give CHF_2 and HCO radicals.

Calvert et al. (2010) assumed a wavelength independent quantum yield of 0.30 and estimated a photolysis lifetime for CHF_2CHO of 6 hours for overhead sun at 40^{o}N latitude at 500 m altitude with an ozone column of 350 DU.

References

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, in press, 2010.

Sellevåg, S. R., Stenstrom, Y., Helgaker, T., Nielsen, C. J.: J. Phys. Chem. A 109, 3652, 2005,


Sellevag et al. (2005)
CHF2CHO
Cross-section (10-20 cm2 molecule-1, base e)
Wavelength (nm)
0
1
2
3
4
5
200
250
300
350
400