

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV PF3

Website: <http://iupac.pole-ether.fr/>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. 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 data sheet last evaluated: June 2015; last change in preferred values: June 2010.

CF₃CHO + hv → products

Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ CHO + hv	→ CF ₃ + HCO	(1) 356.2	336
	→ CF ₃ CO + H	(2) 389.3	307
	→ CHF ₃ + CO	(3) -24.3	----

Absorption cross-section data

Wavelength range/nm	References	Comments
230-360	Meller et al. (1993)	(a)
200-400	Sellevåg et al. (2004)	(b)
200-500	Hashikawa et al. (2004)	(c)
200-400	Chiappero et al. (2006)	(d)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi < 0.02$	290-400	Sellevåg et al. (2004)	(e)
$\Phi_1 = 0.41 \pm 0.07$	254	Chiappero et al. (2006)	(f)
$\Phi_3 = 0.38 \pm 0.07$	254	Chiappero et al. (2006)	(f)
$\Phi_1 = 0.17 \pm 0.03$	308	Chiappero et al. (2006)	(g)

Comments

- (a) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 240-300 K. The UV spectrum of trifluoroacetyldehyde shows a broad band, centered at 305 nm and extending out to 355 nm. Values of σ were given at 5 nm intervals at 298 K.
- (b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 ± 2 K, at a spectral resolution of 2 nm. The UV spectrum of trifluoroacetyldehyde shows a broad band, centered at ~ 300 nm and extending out to ≥ 355 nm. Values of σ were given at 1 nm intervals at 298 K.
- (c) Absolute absorption cross-sections were measured using a diode array spectrometer at 296 K, at a spectral resolution of 1 nm.
- (d) Absolute absorption cross-sections were measured using a diode array spectrometer at 249, 265, 281, and 298 K, at a spectral resolution of 1 nm. There was no discernable effect of temperature on the measured UV absorption spectrum.
- (e) Photolysis of CF_3CHO in pure dry air in the presence of an OH radical tracer (di-*n*-butyl ether) in the $\sim 200 \text{ m}^3$ EUPHORE chamber facility under natural sunlight conditions. The measured first-order loss rate of CF_3CHO during a ~ 3 hr period around solar noon was $7.74 \times 10^{-6} \text{ s}^{-1}$, 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_3CHO ascribed to photolysis during this ~ 3 hr period was $J_{\text{obs}} < 8.5 \times 10^{-7} \text{ s}^{-1}$. This was compared to the maximum photolysis rate of $5.5 \times 10^{-5} \text{ s}^{-1}$ 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 $J_{\text{obs}}/J_{\text{calc}} = 8.5 \times 10^{-7}/5.5 \times 10^{-5}$ gives an upper limit for the photolysis quantum yield of < 0.02 . Solignac et al. (2007) reported quantum yields $J_{\text{obs}}/J_{\text{calc}} = (0.023 \pm 0.012)$, (0.029 ± 0.015) , and (0.046 ± 0.028) for the photodissociation of $\text{C}_3\text{F}_7\text{CHO}$, $\text{C}_4\text{F}_9\text{CHO}$ and $\text{CF}_3(\text{CF}_2)_5\text{CHO}$ in the EUPHORE chamber across the atmospheric range of absorption of the aldehydes. Solignac et al. (2007) suggested that the photolytic loss of CF_3CHO may have been underestimated by Sellevåg et al. (2004). Sellevåg et al. (2005) studied the photolysis of CHF_2CHO in the EUPHORE chamber and reported an effective photolysis quantum yield across the atmospheric range of absorption of the aldehyde of $J_{\text{obs}}/J_{\text{calc}} = 0.30 \pm 0.05$. It is difficult to understand the very different behaviour of CHF_2CHO and CF_3CHO reported by Sellevåg et al. (2004, 2005).
- (f) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of CF_3CHO and NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of CF_3CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of CF_3NO and CF_3H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).
- (g) Photolysis quantum yield measured using CH_3CHO as a chemical actinometer. Mixtures of CF_3CHO and NO (added as radical scavenger) in 700 Torr of N_2 diluent were irradiated using the 308 nm output of an excimer laser. The rate of loss of CF_3CHO was compared to that of CH_3CHO in back-to-back experiments. CF_3NO was observed by IR spectroscopy as a product following the irradiation of $\text{CF}_3\text{CHO}-\text{NO}-\text{N}_2$ mixtures. The molar yield of CF_3NO was indistinguishable from 100%.

Preferred Values

Absorption cross-sections of CF_3CHO at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	0.11	305	3.00
205	0.13	310	2.81

210	0.09	315	2.52
215	0.06	320	2.14
220	0.06	325	1.76
225	0.04	330	1.35
230	0.06	335	0.99
235	0.09	340	0.57
240	0.14	345	0.38
245	0.23	350	0.21
250	0.36	355	0.05
255	0.54	360	0.02
260	0.78	365	0.02
265	1.07	370	0.01
270	1.39		
275	1.76		
280	2.12		
285	2.48		
290	2.78		
295	2.96		
300	3.06		

Quantum Yields of CF₃CHO

$$\Phi_1 = 0.41 \text{ at } 254 \text{ nm}$$

$$\Phi_3 = 0.38 \text{ at } 254 \text{ nm}$$

$$\Phi_1 = 0.17 \text{ at } 308 \text{ nm}$$

Reliability

$$\Delta\Phi_1 = \pm 0.14 \text{ at } 254 \text{ nm.}$$

$$\Delta\Phi_3 = \pm 0.14 \text{ at } 254 \text{ nm.}$$

$$\Delta\Phi_1 = \pm 0.06 \text{ at } 308 \text{ nm.}$$

Comments on Preferred Values

The preferred values for the cross-sections are an average of the data reported by Sellevåg et al. (2004), Hashikawa et al. (2005), and Chiappero et al. (2006) which are in good agreement (see figure below) with the data of Borkowski and Ausloos (1962), Francisco and Williams (1992) and Meller et al. (1993). The preferred values for the quantum yields are taken from the work of Chiappero et al. (2006) which is more direct than the study by Sellevåg et al. (2004) in which a substantial correction was necessary to account for loss of CF₃CHO via leaks from the chamber. The results from Solignac et al. (2007) for longer chain perfluoroaldehydes suggest that the photolytic loss of CF₃CHO was underestimated by Sellevåg et al. (2004). Omitting the dilution correction, the data from Sellevåg et al. (2004) provide an upper limit of $\Phi_1 < 0.14$ which is consistent with the result of Chiappero et al. (2006) accounting for the expected decrease of Φ_1 with wavelength over the range 308 to 335 nm.

The products of photolysis of CF₃CHO have been investigated by Dodd and Smith (1957), Richer et al. (1993), and Chiappero et al. (2006). Dodd and Smith used 313 nm photolysis light and estimated quantum yields of 0.021 for the CHF₃ + CO channel and 0.12 for the CF₃ + HCO channel. Richer et al. (1993) studied the 254 nm photolysis of CF₃CHO in air and observed CHF₃ (14%), CF₂O (80%), CO (60%), and CO₂ (45%). The observation of CHF₃ product shows that the CF₃H + CO channel (3) is important in the 253.7 nm photolysis. Considering the likely contribution of reaction with CF₃O radicals to the CF₃CHO loss, the observed 14% CF₃H yield provides a lower limit for $\phi_3 > 0.14$. Chiappero et al. (2006) studied the products of CF₃CHO photolysis 254 and 308 nm in the presence of large amounts of NO

as a radical scavenger to prevent secondary loss of CF₃CHO. In experiments using 254 nm light CHF₃ and CF₃NO were observed as products whereas only CF₃NO (in a yield indistinguishable from 100%) was observed using 308 nm light. As shown in the figure below, the quantum yield derived by Chiappero et al. (2006) at 308 nm is consistent with the total quantum yield determination of Dodd and Smith (1957) at 313 nm.

Assuming that Φ_1 decreases linearly from 0.17±0.03 at 308 nm (Chiappero et al. (2006)) to zero at 335 nm ($\sim\lambda_{\text{threshold}}$) and using spectral actinic flux calculated with the 4-stream Tropospheric Ultraviolet Visible (TUV) model version 4.1 (Madronich and Flocke (1998)) for a solar zenith angle of 40° gives a photolysis rate of CF₃CHO which corresponds to an effective average quantum yield for the entire 295-370 nm region of $\Phi_1 = 0.06\pm 0.02$ which provides a convenient parameter to use in atmospheric models to assess the photolysis of CF₃CHO. This is consistent with the upper limit of $\Phi_1 < 0.14$ derived from Sellevåg et al. (2004) omitting the dilution correction ($7.76 \times 10^{-6}/5.5 \times 10^{-5} = 0.14$), with the measurement of $\Phi_1 = 0.12$ at 313 nm by Dodd and Smith (1957), and with the measurement of photolysis quantum yields in the range 0.02-0.30 for other fluorinated aldehydes (CHF₂CHO, C₃F₇CHO, C₄F₉CHO and CF₃(CF₂)₅CHO) by Sellevåg et al. (2004) and Solignac et al. (2007). Calvert et al. (2010) assumed a wavelength independent quantum yield of 0.17 and estimated a photolysis lifetime for CF₃CHO of 19 hours for overhead sun at 40°N latitude at 500 m altitude. Further work would be useful to better understand the wavelength dependence of Φ_1 .

References

- Borkowski, R. P., and Ausloos, P.: J. Am. Chem. Soc. 84, 4044, 1962.
- 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.
- 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.
- Dodd, R. E. and Smith, J. W.: J. Chem. Soc., 1465, 1957.
- Francisco, J. S., and Williams, I. H.: Mol. Phys. 6, 1433, 1992.
- Hashikawa, Y., Kawasaki, M., Waterland, R. L., Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M. D., Ball, J. C., and Wallington, T. J.: J. Fluorine Chem., 125, 1925 (2004).
- Madronich, S., and Flocke, S. J. : In Handbook of Environmental Chemistry, Vol. II, Part L., Reactions and Processes, edited by P. Boule, pp. 1-26, Springer-Verlag, Heidelberg, (1998).
- Meller, R., Boglu, D. and Moortgat, G. K.: "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23-25, pp. 130-138, 1993.
- Richer, H., Sodeau, J. R. and Barnes, I.: "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23-25, pp. 182-188, 1993.
- Sellevåg, S. R., Kelly, T., Sidebottom, H. and Nielsen, C. J.: Phys. Chem. Chem. Phys., 6, 1243, 2004.
- Sellevåg, S. R., Stenstrom, Y., Helgaker, T., Nielsen, C. J.: J. Phys. Chem. A 109, 3652, 2005,
- Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., Sidebottom, H.: Phys. Chem. Chem. Phys. 9, 4200, 2007.



