IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PF4

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$CF_3C(O)F + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_3C(O)F + h\nu$	$\rightarrow CF_3 + FCO$	(1)		
	$\rightarrow CF_3CO + F$	(2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200-300	Rattigan et al., 1993	(a)
210-265	Meller et al., 1993	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 + \Phi_2 = 1.05 \pm 0.05$	254	Meller et al., 1993	(c)
$\Phi_1 + \Phi_2 = 1.02 \pm 0.05$	240	Bierbrauer et al., 1999	(d)

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 240-300 K. The UV spectrum of trifluoroacetyl fluoride shows a single band extending out to 300 nm, where there is significant temperature dependence. Values of σ were given at 5 nm intervals at 293 K and 238 K as well as temperature coefficients in the long wavelength tail at $\lambda > 270$ nm.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. Cross-sections were averaged over 1, 2 and 5 nm wavelength intervals.

(c) Average of 10 measurements of the overall loss of $CF_3C(O)F$ by photolysis in 1 atm air at 298 K, relative to the loss of $C(O)Cl_2$ for which $\Phi = 1$.

(d) Measurement of the overall loss of $CF_3C(O)F$ in the presence of O_2 (0.67-6.7 mbar) at 298 K.

Preferred Values

Absorption cross-sections of $CF_3C(O)F$ at 293 K and 238 K

λ/nm	10^{20} σ/cm^2		10^3 B/K^{-1} [a]
	293 K	238 K	
200	9.35	9.46	-0.21
205	11.5	11.6	-0.16
210	12.9	13.1	-0.31
215	13.7	13.7	0.03
220	13.4	13.1	0.40
225	11.9	11.4	0.83
230	9.75	9.11	1.23
235	7.26	6.55	1.87
240	4.93	4.18	2.99
245	3.01	2.30	4.91
250	1.67	1.16	6.60
255	0.82	0.49	9.36
260	0.35	0.18	12.4
265	0.13	0.05	18.8
270	0.04	0.01	26.4
275	0.012	0.003	24.7
280	0.004	0.001	23.3
285	0.0016	0.0004	25.2
290	0.0008	0.00	
295	0.0003	0.00	

[a] $\ln \sigma(T) = \ln \sigma(293\ \mathrm{K}) + B(T - 293)$.

Quantum yields for $CF_3C(O)F$ at 298 K

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 200-300 nm.

Comments on Preferred Values

The preferred values for the cross-sections at 293 K are a simple average of the data reported by Rattigan et al. (1993) and Meller et al. (1993). The temperature dependence is based on the 238 K data of Rattigan et al. (1993). The quantum yield of unity is based on the data of Meller et al. (1993) and Bierbrauer et al. (1999), and is assumed to apply over the wavelength region 200-300 nm.

References

Bierbrauer, K. L., Chiappero, M. S., Malanca, F. E. and Argüello, G. A.: J. Photochem. Photobiol. A: Chem., 122, 73, 1999.

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.

Rattigan, O. V., Wild, O., Jones, R. L. and Cox, R. A.: J. Photochem. Photobiol. A: Chem., 73, 1, 1993.