IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl34

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

Primary photochemical transitions

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

Absorption cross-section data

Wavelength range/nm	References	Comments
200-330	Meller and Moortgat, 1997	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 + \Phi_2 = 0.95 \pm 0.05$	254	Meller and Moortgat, 1997	(b)
$\Phi_1 + \Phi_2 = 1.01 \pm 0.11$	193	Maricq and Szente, 1995	(c)
$\Phi_1 + \Phi_2 = 1.01 \pm 0.11$	248		
$\Phi_1 + \Phi_2 = 0.98 \pm 0.13$	254-280	Weibel et al., 1995	(d)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 223-298 K. The UV spectrum of trifluoroacetyl chloride shows two overlapping bands, the first having a maximum at 255 nm ($\sigma = 6.87 \times 10^{-19}$ cm^2 molecule^{-1}), and the second at λ <200 nm. There is significant absorption at wavelengths >300 nm, where the cross-sections become increasingly temperature dependent. The estimated overall errors in the values of σ were ±3% over the wavelength range 200-310 nm, increasing to ±20% for longer wavelengths where the cross-sections (and hence absorptions) are low. Values of σ were presented at 2 nm intervals at 223 K, 248 K, 273 K and 298 K. The measured absorption cross-sections were fit to the equation $\ln\sigma(\lambda, T) = A_o + A_1\lambda + A_2\lambda^2 + A_3\lambda^3 + A_4\lambda^4 + (B_o + B_1\lambda + B_2\lambda^2 + B_3\lambda^3 + B_4\lambda^4)(T - 273)$, with the following values which fit the measurements to within 3% throughout most of the

spectrum, but with larger errors in the range 220-230 nm (up to 6% error) and at >300 nm (up to 20% error at 330 nm):

	λ = 200-220 nm	λ = 218-330 nm
A_0	-2.0111750×10^{4}	-8.8912918×10^{1}
A_1	3.1757333×10^{2}	9.6418661×10^{-1}
A_2	-2.5671017	$-5.4370794 \times 10^{-3}$
A_3	7.8520098×10^{-3}	1.4975946×10^{-5}
A_4	$-8.9707718 \times 10^{-6}$	$-1.6768324 \times 10^{-7}$
B_o	3.0306320×10^{2}	3.7950580
B_1	-5.8082356	$-5.9114731 \times 10^{-2}$
B_2	4.1715164×10^{-2}	3.4406419×10^{-4}
B_3	$-1.3306565 \times 10^{-4}$	$-8.8699856 \times 10^{-7}$
B_4	1.5906451×10^{-7}	$8.5483894 \times 10^{-10}$

(b) Average of measurements of the overall loss of $CF_3C(O)Cl$ during photolysis in N_2. Measurements of the photodissociation quantum yield of $CF_3C(O)Cl$ in air at total pressures of 67-1013 mbar showed no effect of total pressure or of the presence of O_2.

(b) Pulsed laser photolysis of $CF_3C(O)Cl$-C_2H_6-O_2-N_2 mixtures at a total pressure of 160 mbar, with detection of CF_3O_2 radicals by time-resolved UV spectroscopy and of HCl by IR spectroscopy. CF_3O_2 radicals were formed from CF_3 radicals and HCl was formed from $Cl + C_2H_6 \rightarrow HCl + C_2H_5$. The system was calibrated by photolysis of CH_3Cl at 193 nm and of Cl_2 at 248 nm instead of $CF_3C(O)Cl$, with the assumption that the photodissociation quantum yields of CH_3Cl and Cl_2 are unity.

(d) Quantum yields derived from the amounts of C_2F_6 and CF_3Cl formed from irradiating $CF_3C(O)Cl$ at 254 and 280 nm (high pressure mercury arc-monochromator combination). Actinometry was performed with potassium ferrioxalate solution. It was observed that $(2[C_2F_6] + [CF_3Cl])/[CO] = 0.99 \pm 0.05$, consistent with formation of CF_3 radicals, Cl atoms and CO followed by the combination reactions $CF_3 + CF_3 \rightarrow C_2F_6$ and $CF_3 + Cl \rightarrow CF_3Cl$. Hence $\Phi(-CF_3Cl(O)Cl) = 2\Phi(C_2F_6) + \Phi(CF_3Cl)$.

Preferred Values

Absorption cross-sections for $CF_3C(O)Cl$ at 298 K and 223 K

λ/nm	$10^{20}\ \sigma/cm^2$	
	298 K	223 K
200	50.16	45.83
202	30.47	26.56
204	17.70	14.63
206	9.960	7.830
208	5.567	4.197
210	3.274	2.461
212	2.102	1.662
214	1.620	1.361
216	1.442	1.343
218	1.484	1.421
220	1.665	1.641
222	1.896	1.845

224	2.201	2.184
226	2.544	2.538
228	2.904	2.901
230	3.278	3.261
232	3.685	3.646
234	4.080	4.025
236	4.505	4.456
238	4.902	4.852
240	5.283	5.223
242	5.629	5.553
244	5.957	5.900
246	6.271	6.177
248	6.503	6.411
250	6.694	6.577
252	6.799	6.679
254	6.863	6.712
256	6.858	6.674
258	6.786	6.586
260	6.599	6.383
262	6.393	6.148
264	6.159	5.875
266	5.859	5.567
268	5.510	5.219
270	5.120	4.814
272	4.726	4.396
274	4.306	3.965
276	3.876	3.564
278	3.444	3.133
280	3.035	2.724
282	2.630	2.304
284	2.253	1.931
286	1.907	1.619
288	1.593	1.334
290	1.324	1.090
292	1.082	0.8672
294	0.8670	0.6739
296	0.6811	0.5117
298	0.5282	0.3977
300	0.4038	0.2978
302	0.3035	0.2178
304	0.2214	0.1520
306	0.1580	0.1018
308	0.1087	0.0642
310	0.0722	0.0376
312	0.0472	0.0211
314	0.0301	0.0115
316	0.0189	0.0061
318	0.0123	0.0033
320	0.0084	0.0019
322	0.0057	
324	0.0037	
326	0.0025	
328	0.0017	

Quantum yields for CF_3COCl

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 200-325 nm.

Comments on Preferred Values

The data of Meller and Moortgat (1997) are in good agreement with the earlier results of Rattigan et al. (1993) and Jemi-Alade et al. (1991), except in the region of minimum absorption near 220 nm. The preferred values for the cross-sections are those reported by Meller and Moortgat (1997). The quantum yield is based on the measurements of Meller and Moortgat (1997), Marciq and Szente (1995) and Weibel et al. (1995). Maricq and Szente (1995) concluded that at 193 and 248 nm photolysis proceeds via channel (1), with the CF_3CO radical dissociating totally at 193 nm and ~ 86% of the time at 248 nm. This interpretation (Maricq and Szente, 1995) is reasonably consistent with the product data of Weibel et al. (1995) for the wavelength range 254-280 nm and of Malanca et al. (1997, 1998) at 254 nm.

References

Jemi-Alade, A. A., Lightfoot, P. D. and Lesclaux, R.: Chem. Phys. Lett., 179, 119, 1991.

Malanca, F. E., Argüello, G. A. and Staricco, E. H.: J. Photochem. Photobiol. A: Chem., 103, 19, 1997.

Malanca, F. E., Argüello, G. A., Staricco, E. H. and Wayne, R. P.: J. Photochem. Photobiol. A: Chem., 117, 163, 1998.

Maricq, M. M. and Szente, J. J.: J. Phys. Chem., 99, 4554, 1995.

Meller, R. and Moortgat, G. K.: J. Photochem. Photobiol. A: Chem., 108, 105, 1997.

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

Weibel, D. E., Arguello, G. A., de Staricco, E. R. and Staricco, E. H.: J. Photochem. Photobiol. A: Chem., 86, 27, 1995.