

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCI13

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CH₃OCl + hν → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ OCl + hν → CH ₃ O + Cl	(1)	202.9	589
→ CH ₃ + ClO	(2)	312.4	383
→ CH ₂ OCl + H	(3)	417.4	287

Absorption cross-section data

Wavelength/nm	Reference	Comments
200-460	Crowley et al., 1994	(a)
230-394	Jungkamp et al., 1995	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength region/nm	Reference	Comments
$\phi_1 = 0.95 \pm 0.05$	308	Schindler et al., 1997	(c)
$\phi_1 = 1$	248	Krisch et al., 2004	(d)

Comments

- Monochromator/diode array set up with spectral resolution of 0.4 nm. The spectrum measured at 295 K showed no dependence on resolution between 0.3 and 1.2 nm. Correction applied for small Cl₂ impurities which were quantified by MS.
- Monochromator / double diode array set up (temperature and resolution not quoted). Impurities (CH₃OH and Cl₂) quantified by MS.
- Pulsed laser photolysis (excimer at 308 nm, dye laser at 235 nm) with REMPI–TOF mass spectrometric detection of Cl photofragments in both ²P_{1/2} and ²P_{3/2} states. The overall quantum yield of Cl atom generation at 308 nm was measured relative to Cl₂. The ratio of Cl (²P_{1/2}) / Cl (²P_{3/2}) was found to be 0.31 ± 0.02 at 308 nm and 1.45 ± 0.05 at 235 nm.
- Crossed laser-molecular beam scattering experiment with detection of photofragments by VUV photoionisation-TOFMS (Cl detected as Cl⁺ and CH₃O as CHO⁺). No other photofragments were observed.

Preferred Values
Absorption cross sections for CH₃OCl at 295 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	6.61	340	0.908
210	5.41	350	0.649
220	10.0	360	0.441
230	16.1	370	0.296
240	16.6	380	0.203
250	11.5	390	0.144
260	6.00	400	0.108
270	2.75	410	0.082
280	1.56	420	0.064
290	1.35	430	0.048
300	1.44	440	0.037
310	1.49	450	0.027
320	1.39	460	0.020
330	1.18		

Quantum yields

$\phi_1 = 1.0$ throughout the absorption spectrum

Comments on Preferred Values

There is very good agreement between the cross sections presented in both studies for $\lambda > 260$ nm, (Crowley et al., 1994; Jungkamp et al., 1995) though some differences are observed at the short wavelength end of the spectra. The data of Crowley et al. (1994), which cover a larger wavelength range and extend further into the actinic region are preferred. The preferred overall quantum yield of 1.0 is based on the work of Schindler et al. (1997), which is consistent with the observations of Krisch et al. (2004) and with quantum yields measured for other hypohalites such as HOCl.

References

- Crowley, J. N., Helleis, F., Müller, R., Moortgat, G. K. and Crutzen, P. J.: J. Geophys. Res. 99, 20683, 1994.
- Jungkamp, T. P. W., Kirchner, U., Schmidt, M. and Schindler, R. N.: J. Photochem. Photobiol. A 91, 1, 1995.
- Krisch, M. J., McCunn, L. R., Takematsu, K., Butler, L. J., Blasé, F. R. and Shu, J.: J. Phys. Chem. A 108, 1650, 2004.
- Schindler, R. N., Liesner, M., Schmidt, S., Kirchner, U. and Benter, Th.: J. Photochem. Photobiol. A 107, 9, 1997.