IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI10

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$CH_2ClI + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_2ClI + h\nu \rightarrow CH_2Cl + I$	(1)	217	551
$\rightarrow CH_2I + Cl$	(2)	344	347

Absorption cross-section data

Wavelength range/nm	Reference	Comments
235-390	Rattigan *et al.,* 1997[1]	(a)
200-380	Roehl *et al.*, 1997[3]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(I_2)$	266	Schmitt and Comes, 1987[3]	(c)

Comments

(a) Absorption coefficients for CH_2ClI (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. A single absorption band was observed to extend from 230 -400 nm with a maximum at 270 nm where the absorption cross section was $\sigma = (1.21 \pm 0.07) \times 10^{-18}$ cm^2 molecule^{-1} at 298 K. The temperature dependence of the absorption cross section was determined over the range 243-333 K; broadening of the band was observed giving a significant decline in σ with decreasing temperature in the tropospheric photolysis region (λ>290 nm).

(b) The absorption spectrum of CH_2ClI (purity 97%) was recorded by diode array spectrometry with a resolution of 0.3 nm. The absolute cross-section at the maximum of absorption at 270 nm was $\sigma = 1.35 \times 10^{-18}$ cm^2 molecule^{-1} with a stated overall uncertainty of±5%. Significant temperature dependence of the absorption cross section was observed over the range 228-298K, with a decrease in σ with a decrease in temperature in the long wavelength tail. A second absorption band is indicated by an increase in σ below 220 nm.

(c) Laser photolysis of CH_2ClI; measurement of yield of I_2 by time resolved laser absorption spectroscopy at 514.5 nm.

Preferred Values

Absorption cross-sections for CH_2ClI at 298 K

Wavelength/nm	$10^{20}\sigma/cm^2$	$10^3B/K^{-1}$
205	122	
210	39.1	
215	10.3	
220	7.0	
225	9.06	
230	13.8	
235	21.2	0.24
240	31.8	0.122
245	45.6	-0.018
250	62.9	-0.114
255	84	-0.283
260	105	-0.444
265	121	-0.547
270	127	-0.587
275	120	-0.47
280	103	-0.18
285	80.7	0.317
290	58.1	0.985
295	39.8	1.73
300	25.9	2.56
305	16.7	3.08
310	10.9	3.5
315	7.16	3.56
320	4.79	3.46
325	3.23	3.44
330	2.14	3.72
335	1.4	4.09
340	0.905	4.87
345	0.569	5.69
350	0.35	6.88
355	0.225	8.16
360	0.138	9.01
365	0.081	11.1
370	0.048	11.5
375	0.027	12.8
380	0.017	15.1
385	0.008	19.1
390	0.006	20.5

Temperature dependence given by: $\ln \sigma = \ln \sigma(298) + B(T-298/K)$

Quantum Yield

$\Phi_1 = 1.0$ over the range 230-390 nm.

Comments on Preferred Values

The data of Rattigan *et al.*[1] and Roehl *et al.*[2] are in excellent agreement both in terms of the absolute absorption cross sections, and their temperature dependence as a function of wavelength. The earlier data of Schmitt and Comes[3] also showed a maximum at 270 nm but the absolute cross section was higher (1.5×10^{-18} cm^2 molecule^{-1}). The preferred values for the cross-sections are a simple mean of data of Rattigan *et al.*[1] and Roehl *et al.*[2], and the temperature dependence, expressed in terms of a single parameter B in the equation: $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$ from the work of Rattigan *et al.*[1] is adopted.

The photodecomposition of CH_2ClI studied by Schmitt and Comes[3] indicated dissociation via reaction (1), in line with other alkyl iodides, occurring with a quantum yield of unity. Reaction (2) may be important following absorption in the band at $\lambda<220$ nm.

References

1. O. V. Rattigan, D. E. Shallcross, and R. A. Cox, J. Chem. Soc. Farad. Trans. **93**, 2839 (1997).
2. C. M. Roehl, J. B. Burkholder, G. K. Moortgat, A. R. Ravishankara, and P. J. Crutzen, J. Geophys. Res. **102**, 12819 (1997).
3. G. Schmitt and F. J. Comes, J. Photochem. Photobiol. A **41**, 13 (1987).