

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI12

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CH₂I₂ + hv → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₂ I ₂ + hv → CH ₂ I + I	(1)	219	547
→ CH ₂ + I ₂	(2)	335	357

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220-360	Schmitt and Comes, 1980 ¹	(a)
265-340	Koffend and Leone, 1981 ²	(b)
200-380	Roehl <i>et al.</i> , 1997 ³	(c)
200-380	Mossinger <i>et al.</i> , 1998 ⁴	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(\text{I}_2)$	300	Schmitt and Comes, 1980 ¹	(e)
$\Phi\{1(^2\text{P}_{1/2}); \text{I}(^2\text{P}_{3/2})\}$	254	Baughcum and Leone, 1980 ⁵	(f)
$\Phi\{1(^2\text{P}_{1/2})\}$	248-340	Koffend and Leone, 1981 ²	(g)

Comments

- (a) Conventional UV absorption spectrometry. The spectrum consisted of two asymmetrical peaks at 288 nm and 248 nm, suggesting several overlapping bands, and a third band below 220 nm. The absolute cross-section at the first maximum of absorption at 290 nm was $\sigma = 4.07 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (b) The absorption spectrum of CH₂I₂ was recorded by conventional UV absorption spectrometry. The absolute cross-section at the first maximum of absorption at 286 nm was $\sigma = 3.92 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (c) The absorption spectrum of CH₂I₂ (purity 97%) was recorded by diode array spectrometry with a resolution of 0.3 nm. The third absorption maximum occurred at 210 nm. The absolute cross-section at the first maximum of absorption at 290 nm was $\sigma = 3.84 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ with a stated overall uncertainty of $\pm 5\%$. This was within 6% of the value of Schmitt and Comes¹

and 2% of the Koffend and Leone data². Significant temperature dependence of the absorption cross section was observed over the range 273-298K, with a decrease in σ with decreasing temperature in the long wavelength tail.

- (d) Absorption coefficients for CH₂I₂ (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. Tabulated cross section values for the indicated range were given. The absolute cross-sections at absorption maxima of 248nm and 288 nm were $\sigma = (1.62 \pm 0.10) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma = (3.78 \pm 0.23) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ respectively at 298 K. The temperature dependence of the absorption cross section was determined over the range 278-348K; the temperature dependence was complex reflecting the presence of several overlapping bands but there was a significant decline in σ with decreasing temperature in the tropospheric photolysis region ($\lambda > 290 \text{ nm}$).
- (e) Pulsed laser photolysis of CH₂I₂; measurement of yield of I₂ by absorption spectrometry. Primary products deduced to be I atoms, partially in the excited state.
- (f) Pulsed tunable laser photolysis of CH₂I₂, with I(²P_{1/2}) and excited CH₂I₂ detection by infra red emission.
- (g) Pulsed tunable laser photolysis of CH₂I₂, with I(²P_{1/2}) detection by infra red fluorescence at 1.315 μm . $\Phi\{I(²P_{1/2})\}$ increased from zero to 0.46 over the wavelength range 340 - 248 nm.

Preferred Values

Absorption cross-sections for CH₂I₂ at 298 K

Wavelength/nm	$10^{20}\sigma/\text{cm}^2$	$10^3\text{B}/\text{K}^{-1}$
205	407	
210	404	
215	322	0.1515
220	260	0.14
225	198	0.19
230	132	0.51
235	109	0.56
240	123	0.15
245	150	0.18
250	157	0.67
255	140	1.58
260	120	2.04
265	130	1.30
270	179	0
275	255	-0.71
280	328	-1.24
285	373	-1.21
290	381	-0.94
295	372	-0.58
300	357	-0.37
305	338	0
310	314	0.07
315	280	0.15
320	244	0.27
325	203	0.27
330	161	0.51
335	120	0.55
340	83.3	1.36
345	53.7	1.99
350	32.6	3.19

355	19.2	4.09
360	10.9	5.39
365	6.05	6.77
370	3.4	8.25
375	1.93	11.3
380	1.16	
385	0.77	

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

Quantum Yield

$\Phi_1 = 1.0$ over the range 230-380 nm.

Comments on Preferred Values

There is good agreement between all the reported absorption spectra of CH_2I_2 . The cross section data of Roehl *et al.*² and Mossinger *et al.*⁴ are in excellent agreement both in terms of the absolute absorption cross sections, and its temperature dependence as a function of wavelength, expressed in terms of a single parameter B in the equation $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$. The preferred values for the cross-sections are a simple mean from both data sets, and the temperature dependence of Mossinger *et al.*⁴ is adopted since it is based on a wider range of temperature.

The study of the photodecomposition of CH_2I_2 by Schmitt and Comes¹ 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 centered at $\lambda = 215$ nm. Significant fraction of I atoms are formed in the excited state in the tropospheric photolysis region.

References

- ¹ G. Schmitt and F. J. Comes, *J. Photochem.* **14**, 107 (1980).
- ² J. B. Koffend and S. R. Leone, *Chem. Phys. Lett.* **81**, 136 (1981).
- ³ C. M. Roehl, J. B. Burkholder, G. K. Moortgat, A. R. Ravishankara, and P. J. Crutzen, *J. Geophys. Res.* **102**, 12819 (1997).
- ⁴ J. C. Mossinger, D. E. Shallcross, and R. A. Cox, *J. Chem. Soc. Farad. Trans.* **94**, 1391 (1998).
- ⁵ S. L. Baughcum and S. R. Leone, *J. Chem. Phys.* **72**, 6531 (1980).