

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI8

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 15th December 2000.

CH₃I + hν → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ I + hν → CH ₃ + I(² P _{3/2})	(1)	239	541
→ CH ₃ + I(² P _{1/2})	(2)	330	362
→ CH ₂ + HI	(3)	403	297

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210-360	Jenkin <i>et al.</i> , 1993 ¹	(a)
160-400	Fahr, Nayak, and Kurylo, 1995 ²	(b)
200-380	Roehl <i>et al.</i> , 1997 ³	(c)
235-350	Rattigan, Shallcross, and Cox, 1997 ⁴	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(\text{I}_2)$	254	Christie, 1958 ⁶	(e)
$\Phi\{\text{I}(\text{}^2\text{P}_{1/2}); \text{I}(\text{}^2\text{P}_{3/2})\}$	266	Riley and Wilson, 1972 ⁷	(f)
$\Phi\{\text{I}(\text{}^2\text{P}_{1/2})\}$	248-308	Baughcum and Leone, 1980 ⁸	(g)
$\Phi\{\text{I}(\text{}^2\text{P}_{1/2}); \text{I}(\text{}^2\text{P}_{3/2})\}$	247.5-312.5	Hunter, Lunt, and Kristjansson, 1983 ⁹	(h)

Comments

- (a) The absorption spectrum of CH₃I was recorded by diode array spectroscopy with a resolution of approx. 1 nm using a purified sample. Tabulated cross section values for the indicated range were given, showing a single absorption band extending from 210 to 365 nm. The absolute cross-section at the maximum of absorption at 257.9 nm was $\sigma = 1.22 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$, which was in good agreement with the earlier published spectrum of Porrit and Goodeve⁵.
- (b) Absorption spectrum measured over temperature range 223-333 K at a resolution of 0.1 nm; cross sections at 0.5 nm intervals given. In addition to the gas phase measurements over the wavelength range 160-335 nm, liquid phase measurements over the range 330-400 nm were also reported. A wavelength shift was applied to convert the liquid phase data to accurate gas phase cross sections at the long wavelengths.

- (c) Absorption coefficients for CH₃I were determined by diode array spectrometry with a spectral resolution of 0.6 nm. Tabulated cross section values for the indicated range were given. A single absorption band was observed to extend from <230 nm to 365 nm with a maximum at 260 nm where the absorption cross section was $\sigma = (1.09 \pm 0.08) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ 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 ($\lambda > 290 \text{ nm}$).
- (d) The absorption spectrum of CH₃I (purity > 98%) was recorded by diode array spectrometry with a resolution of 0.3 nm. Tabulated cross section values for the indicated range were given. The absolute cross-section at the maximum of absorption at 260 nm was $\sigma = 1.13 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ with a stated overall uncertainty of $\pm 5\%$. Significant temperature dependence of the absorption cross section was observed over the range 228-298 K, with a decrease in σ with decreasing temperature in the long wavelength tail. A second absorption band is indicated by an increase in σ below 210 nm.
- (e) Photo-oxidation of CH₃I; measurement of loss of CH₃I and yield of I₂ product. $\Phi(-\text{CH}_3\text{I}) = 1.0$; $\Phi(\text{I}_2) = 0.5$.
- (f) Translational energy of the I atoms produced in 266 nm photolysis of CH₃I in a molecular beam. Suggested the following primary processes:
 $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}({}^2\text{P}_{3/2})$
 $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}({}^2\text{P}_{1/2})$
 with I(²P_{3/2}) production at 78% of the primary process.
- (g) Pulsed tunable laser photolysis of CH₃I, with I(²P_{1/2}) detection by infra-red fluorescence at 1.315 μm . $\Phi\{\text{I}({}^2\text{P}_{1/2})\}$ increased from 0.05 to 0.81 over the wavelength range 308-248 nm.
- (h) Branching ratio for I(²P_{1/2})/I(²P_{3/2}) as a function of wavelength determined by an optical acoustic method.

Preferred Values

Absorption cross-sections for CH₃I at 298 K

Wavelength/nm	$10^{20}\sigma/\text{cm}^2$	$10^3\text{B}/\text{K}^{-1}$
205	7.0	
210	3.8	
215	5.2	
220	6.9	
225	9.1	
230	12.6	
235	20.2	0.67
240	37.4	0.61
245	63.6	0.34
250	92.1	0.08
255	111.1	-0.1
260	112.3	-0.12
265	96.6	0.1
270	71.7	0.54
275	47.1	1.33
280	28.0	2.43
285	15.2	3.74
290	7.79	4.98
295	3.92	6.38
300	2.03	6.97
305	1.09	6.82

310	0.619	6.78
315	0.356	6.95
320	0.215	6.94
325	0.124	6.79
330	0.070	7.82
335	0.033	9.34
340	0.023	10.95
345	0.0127	13.58
350	0.0067	16.83
355	0.0026	18.91
360	0.0013	17.28
365	0.0004	23.63

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

Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$ over the range 360-210 nm.

Comments on Preferred Values

Porret and Goodeve⁵ measured the absolute absorption cross-sections of methyl iodide in the range 200-360 nm in their pioneering work on the quantitative investigation of electronic spectra of simple molecules. The first absorption band extends from 360 nm to ~ 210 nm and is attributed to a $\sigma \rightarrow n$ transition. The recently reported cross sections of Jenkin *et al.*¹, Rattigan *et al.*³ and Roehl *et al.*⁴ are in good agreement with each other and with those in the earlier published study⁵. The results of Fahr *et al.*² agree well with the other measurements at $\lambda > 300$ nm, but are significantly higher by ~20% at the maximum of absorption. The preferred values for the cross-sections at 298 K are based on the data for the absolute absorption cross-sections reported by Jenkin *et al.*¹, Rattigan *et al.*³ and Roehl *et al.*⁴ The listed values are actual values at 1 nm intervals.

The effect of temperature on the absorption cross-section has been studied by Fahr *et al.*², Rattigan *et al.*³ and Roehl *et al.*⁴ All studies show excellent agreement for the temperature dependence and reveal an apparent narrowing of the band as temperature decreases, leading to an increase in σ at the band head and a decrease in σ in the long wavelength tail of absorption. The temperature dependence of CH₃I absorption has also been investigated by Waschewsky *et al.*¹⁰ who argue that the temperature-dependent cross section measurements are complicated by the presence of dimers and therefore do not apply to atmospheric spectra. Analysis by Rattigan *et al.*³ and Roehl *et al.*⁴ of their measurements taken over an extensive range of pressures and temperatures shows that the effect of dimers must be completely negligible for their experimental conditions. The recommended 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.*³ is adopted.

The photochemistry of alkyl iodides has been extensively studied since the early investigations of photolytic reactions and has been reviewed by Majer and Simons (1964)¹¹, Calvert and Pitts (1966)¹² and Okabe (1978)¹³. For methyl iodide the primary process is dissociation into a methyl radical and an iodine atom, processes (1) and (2), occurring with a quantum yield of unity. Reaction (3) may be important following absorption in the vacuum uv.⁷

More recently the primary photodissociation processes have been studied extensively in conjunction with the laser emission: $I(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + hv$, observed at 1.315 μm in the near-UV flash photolysis of CH₃I¹⁴. State-selected photofragment spectroscopy has shown that I atoms are produced in both the ground $I(^2P_{3/2})$ and the electronically excited $I(^2P_{1/2})$ state. There is some disagreement in the observed wavelength dependence of the branching ratio for: $I(^2P_{1/2})/I(^2P_{3/2})$ ^{8,9}.

References

- ¹ M. E. Jenkin, T. P. Murrells, S. J. Shalliker, and G. D. Hayman, *J. Chem. Soc. Farad. Soc.* **89**, 433 (1993).
- ² A. Fahr, A. K. Nayak, and M. J. Kurylo, *Chem. Phys.* **197**, 195 (1995).
- ³ O. V. Rattigan, D. E. Shallcross and R. A. Cox, *J. Chem. Soc. Farad. Trans.* **93**, 690 (1997).
- ⁴ C. M. Roehl, J. B. Burkholder, G. K. Moortgat, A. R. Ravishankara, and P. J. Crutzen, *J. Geophys. Res.* **102**, 12819 (1997).
- ⁵ D. Porret and C. F. Goodeve, *Trans. Farad. Soc.* **33**, 690 (1937).
- ⁶ M. I. Christie, *Proc. Roy. Soc. (London) A* **244**, 411 (1958).
- ⁷ S. J. Riley and K. R. Wilson, *Disc. Farad. Soc.* **53**, 132 (1972).
- ⁸ S. L. Baughcum and S. R. Leone, *J. Chem. Phys.* **72**, 6531 (1980).
- ⁹ T. F. Hunter, S. Lunt, and K. S. Kristjansson, *J. Chem. Soc. Farad. Soc.* **79**, 303 (1983).
- ¹⁰ G. C. Waschewsky, R. Horansky, and V. Vaida, *J. Phys. Chem.* **100**, 11559 (1996)
- ¹¹ J. R. Majer and J. P. Simons, *Adv. Photochem.* **2**, 137 (1964).
- ¹² J. G. Calvert and J. N. Pitts, Jr., 'Photochemistry' J. Wiley New York 1966.
- ¹³ H. Okabe, "Photochemistry of Small Molecules", Wiley Interscience, 1978.
- ¹⁴ J. V. V. Kasper and G. C. Pimentel, *Appl. Physics Lett.* **5**, 231 (1964).