IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI9

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$CF_3I + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{3/2})$	(1)	230	521
$\rightarrow CF_3 + I(^2P_{1/2})$	(2)	320	374

Absorption cross-section data

Wavelength range/nm	Reference	Comments
216-370	Solomon *et al.,* 1994[1]	(a)
160-340	Fahr *et al.,* 1995[2]	(b)
235-400	Rattigan *et al.*, 1997[3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	266	Riley and Wilson, 1972[7]	(d)
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	304	Kang *et al.*, 1996[5]	(e)
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	275-303	Furlan, Gejo, and Huber, 1996[6]	(f)

Comments

(a) Absorption coefficients for purified CF_3I determined by diode array spectrometry, over temperature range 200-298 K. A single absorption band was observed to extend from 370-210 nm with a maximum at 267 nm where the absorption coefficient was $\sigma = 6.0 \times 10^{-18}$ cm^2 molecule^{-1}.

(b) The absorption spectrum of CF_3I was recorded by diode array spectormetry with a resolution of appr. 1 nm using a purified sample. The absolute cross-section at the maximum of absorption at 267 nm was $\sigma = 6.8 \times 10^{-18}$ cm^2 molecule^{-1}. A second band extends into the vacuum UV. The temperature dependence over the wavelength range 160-240 nm was determined at 240, 295 and 355 K; and over the range 240-350 nm for 218-333 K.

(c) The absorption spectrum of CF_3I was recorded by diode array spectormetry with a resolution of appr. 0.6 nm using a purified sample. The absolute cross-section at the maximum of absorption

at 267 nm was $\sigma = (6.0 \pm 0.1) \times 10^{-18}$ cm^2 molecule^{-1}. A second band extends into the vacuum UV. The temperature dependence was determined for 243-333K.

(d) Translational energy of the I atoms produced in 266 nm photolysis of CF_3I in a molecular beam. Suggested the following primary processes:

$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{3/2})$

$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{1/2})$

with $I(^2P_{3/2})$ production at 78% of the primary process.

(e) Relative yield of $I(^2P_{1/2})/I(^2P_{3/2})$ determined by (2+1) REMPI and pulsed field TOF-MS following laser photodissociation of CF_3I. $\phi\{I(^2P_{1/2}) = 0.69$.

(f) Relative yield of $I(^2P_{1/2})/I(^2P_{3/2})$ obtained by high resolution photofragment translational spectrometry using pulsed laser photolysis and TOF-MS. $\phi\{I(^2P_{1/2})$ increased from 0.38 at 303 nm to 0.92 at 275 nm.

Preferred Values

Absorption cross-sections for CF_3I at 298 K

Wavelength/nm	$10^{20}\sigma$/cm^2	10^3B/K^{-1}
235	7.5	0.155
240	13.4	0.21
245	21.4	-0.121
250	32.5	-0.45
255	45.5	-0.766
260	57.3	-0.992
265	64.2	-1.07
270	63.9	-0.936
275	56.9	-0.554
280	45.6	-0.0505
285	33.8	1.02
290	23.0	2.18
295	14.6	3.34
300	8.81	4.56
305	5.13	5.81
310	2.88	6.82
315	1.59	7.49
320	0.907	7.89
325	0.49	8.22
330	0.263	8.57
335	0.144	9.06
340	0.0771	9.98
345	0.0393	10.9
350	0.0208	12.5
355	0.0115	13.3
360	0.0064	14.6
365	0.0036	14.6
370	0.002	15.5
375	0.0011	17.1
380	0.0007	17.7
385	0.0004	19.7
390	0.0001	22.6

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

There is excellent agreement between all three reported data sets for the cross section and its temperature dependence. The maximum of the first absorption band is lower and red-shifted compared with methyl iodide. The band narrowed with decreasing temperature leading to a significant decrease in the cross section in the long wavelength tail; at 320 nm the value decreases by nearly 50% at 200 K. The recommended values for σ and its temperature dependence are the mean of all three studies.[1-3]

Photolysis is expeceted to occur with unit quantum efficiency by breaking of the C-I bond to yield CF_3 + I. State-selected photofragment spectroscopy has shown that I atms are produced predominantly in the excited state $I(^2P_{1/2})$, following photodissociation of CF_3I near the band maximum. The branching ratio for: $I(^2P_{1/2})/I(^2P_{3/2})$ production decreases at longer wavelengths but there is some disagreement in the actual values.[4-6]

References

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