IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI7

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$I_2 + h\nu \rightarrow I + I$

Primary photochemical processes

Reactions	$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$I_2 + h\nu \rightarrow I(^2P_{3/2}) + I(^2P_{3/2})$	151	792

Absorption cross-section data

Wavelength range/nm	Reference	Comment
430-620	Rabinowitch and Wood, 1936a	(a)
420-800	Tellinghuisen, 1973	(b)
280-510	Bauer et al., 1998	(c)
180-750	Saiz-Lopez et al., 2004	(d)

Quantum Yield Data

Measurement	Wavelength/nm	Reference	Comment
$\phi = 1$	370-650	Rabinowitch and Wood, 1936b	(e)
$\phi = 0.93 \pm 0.02$	501.0	Brewer and Tellinghuisen, 1972	(f)
$\phi = 0.70 \pm 0.03$	509.1		
$\phi = 0.62 \pm 0.02$	516.6		
$\phi = 0.66 \pm 0.04$	527.7		
$\phi = 0.72 \pm 0.02$	546.2		
$\phi = 0.67 \pm 0.03$	559.4		
$\phi = 0.59 \pm 0.03$	569.0		
$\phi = 0.33 \pm 0.01$	589.6		
$\phi = 0.35 \pm 0.01$	592.2		
$\phi = 0.54 \pm 0.02$	603.7		
$\phi = 0.67 \pm 0.04$	612.9		
$\phi = 0.88 \pm 0.05$	623.9		

Comments

(a) The visible absorption spectrum was determined from measurements made at a series of wavelengths over the range 430-620 nm, at low resolution (5-10 nm), at room temperature (ca. 293 K). Experiments were carried out using 0.2 mbar pure I_2 either in the absence of a bath gas, or in the presence of 670 mbar of He, air or Ar. Cross sections between 500-570 nm increased in the presence of the bath gases, but showed no dependence on bath gas identity. The cross section reported at the absorption maximum in the absence of a bath gas (i.e., close to 500 nm) was ca. 2.8 x 10^{-18} cm^2 $molecule^{-1}$.

(b) The visible-infrared absorption spectrum was determined from measurements made at 10 nm intervals over the wavelength range 420-800 nm, at a resolution of 0.26 nm. Measurements were made at room temperature (295-300 K) with pressures of purified I_2 of up to ca. 0.15 mbar. The cross section reported at 500nm (the beginning of the $B^3\Pi \leftarrow X^1\Sigma$ continuum) was (2.19±0.07) x 10^{-18} cm^2 $molecule^{-1}$.

(c) The ultraviolet-visible absorption spectrum was recorded over the range 280-510 nm, at a resolution of 1.2 nm, with cross sections reported at 436 nm and 500 nm. Measurements were made at room temperature (295±2 K) with pressures of purified I_2 up to 0.2 mbar. The cross section reported at 500nm was (2.25±0.09) x 10^{-18} cm^2 $molecule^{-1}$.

(d) The ultraviolet-visible-infrared absorption spectrum was recorded using Fourier Transform spectroscopy over the wavelength range 182-750 nm, at a resolution of 0.036 nm in the banded region (500-650 nm) and 1 nm elsewhere. Measurements were made at room temperature (295 K) in 1.013 bar air. The absorption maximum was recorded in the banded region at 533nm, with the cross section reported at 500 nm being 2.29 x 10^{-18} cm^2 $molecule^{-1}$.

(e) Photodissociation quantum yields were determined from the reversible decrease in extinction during steady state illumination of I_2 vapour with a carbon arc or filament lamp. The use of appropriate filters allowed three broad band spectral regions to be considered for the photolysis radiation: ca. 370-502 nm, λ_{max} = 460 nm; ca. 480-590 nm, λ_{max} = 502 nm; ca. 503-650 nm, λ_{max} = 565 nm. The quantum yield in the first region (essentially the $B^3\Pi \leftarrow X^1\Sigma$ continuum) was assumed to be unity. No significant difference in quantum yield for the other regions was observed. Experiments were carried out with 0.2 mbar I_2 in the presence of several hundred mbar of He, Ar, H_2 and N_2.

(f) Photodissociation quantum yields were determined from fluorescence detection of $I(^2P_{3/2})$, during steady state photolysis of I_2 at 12 wavelengths, using a tungsten lamp in conjunction with combinations of interference filters. The transmittance bandwidth varied from 0.3 to 1.4 nm. The yields were determined relative to an assumed value of unity at 492 nm, in the $B^3\Pi \leftarrow X^1\Sigma$ continuum. Low pressure experiments were carried out with I_2 pressures up to ca. 0.01 mbar, to determine the zero pressure limiting quantum yields tabulated above. Experiments with up to 15 mbar N_2 demonstrated that the dissociative yield tends to unity in the presence of higher bath gas pressures.

Preferred Values

Absorption cross-sections for I_2 at 298 K

λ/nm	10^{18} σ/cm^2	λ/nm	10^{18} σ/cm^2
400	0.029	565	1.54
405	0.038	570	1.28
410	0.043	575	0.955
415	0.053	580	0.912
420	0.058	585	0.729
425	0.081	590	0.644
430	0.133	595	0.588
435	0.153	600	0.466
440	0.199	605	0.422
445	0.253	610	0.400
450	0.327	615	0.336
455	0.432	620	0.300
460	0.560	625	0.276
465	0.709	630	0.274
470	0.880	635	0.220
475	1.07	640	0.233
480	1.29	645	0.222
485	1.52	650	0.212
490	1.75	655	0.203
495	2.00	660	0.186
500	2.24	665	0.170
505	2.45	670	0.174
510	2.62	675	0.156
515	2.76	680	0.146
520	2.78	685	0.137
525	2.85	690	0.126
530	2.82	695	0.106
535	2.75	700	0.101
540	2.60	705	0.074
545	2.41	710	0.063
550	2.25	715	0.059
555	2.02	720	0.054
560	1.74	725	0.031

Quantum Yields

ϕ = 1.0 throughout the wavelength range.

Comments on Preferred Values

Absorption Cross-Sections. The visible-infrared absorption spectrum of I_2 has been the subject of a number of studies and discussions (Rabinowitch and Wood, 1936a; Calvert and Pitts, 1966; Tellinghuisen, 1973; Okabe, 1978; Bauer et al., 1998; Saiz-Lopez et al., 2004). The spectrum is dominated by the transition from the $X^1\Sigma$ ground state into the bound $B^3\Pi$ upper state, which results in rovibrational structure in the wavelength range 650-500 nm, with the dissociative continuum at ≤ 499 nm. There is also a weaker underlying continuum in the structured region, due to the transition to $^1\Pi$ repulsive state.

The shape of the absorption spectrum at wavelengths ≤ 500 nm (i.e. essentially in the continuum), based on a number of studies (Rabinowitch and Wood, 1936a; Tellinghuisen, 1973; Bauer et al., 1998; Saiz-Lopez et al., 2004), is well determined. Measurements in the structured region of the spectrum have been found to be very sensitive to experimental conditions, depending on the absolute concentration of I_2 and on pressure of bath gas, at the spectral resolutions typically employed. Cross sections averaged over a wavelength interval in this region should tend towards the true value when partial saturation of rotational lines is avoided though use of very low I_2 concentrations or at higher bath gas pressures when the lines become sufficiently broadened. The recent measurements of Saiz-Lopez et al. (2004), performed at high resolution and with high bath gas pressures, are therefore used to define the shape of the spectrum, with the preferred values based on their data averaged over 5 nm intervals.

The three most recent studies (Tellinghuisen, 1973; Bauer et al., 1998; Saiz-Lopez et al., 2004) report absorption cross sections in the pressure-independent continuum ($\lambda \leq 500$ nm) which are in excellent agreement, differing by less than 5% at 500 nm. The present recommendation therefore adopts a reference value of $\sigma = 2.24 \times 10^{-18}$ cm^2 $molecule^{-1}$ at 500 nm, which is the average of the values reported in the three investigations.

Quantum Yields. The measurements of Rabinowitch and Wood (1936b) are consistent with a unity quantum yield throughout the visible-infrared spectrum at bath gas pressures greater than about 200 mbar. Brewer and Tellinghuisen (1972) report quantum yields well below unity in the structured region of the spectrum (501-624 nm) at low pressures in the absence of a bath gas, but observed significant increases (to > 0.9) at N_2 pressures of only 15 mbar. The results of these studies are interpreted in terms of collision induced transition from the bound $B^3\Pi$ upper state into the unstable $^1\Pi$ repulsive state, leading to the generation of $I(^2P_{3/2}) + I(^2P_{3/2})$, as does the weaker underlying continuum transition ($^1\Pi \leftarrow X^1\Sigma$). A quantum yield of unity throughout the spectrum is therefore recommended for lower atmospheric conditions. A number of studies have also determined quantum yields for the production of excited state $I(^2P_{1/2})$ atoms, which have been detected at wavelengths below ca. 530 nm (Hunter and Leong, 1987; and references therein). Under atmospheric conditions, collisional quenching of $I(^2P_{1/2})$ to ground state $I(^2P_{3/2})$ occurs rapidly.

References

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