

# LASER PHOTOLYSIS OF IODIDE IONS: SPECTROSCOPIC EVIDENCE FOR IODINE ATOMS AND KINETICS OF THEIR REACTION WITH IODIDE IN VARIOUS SOLVENTS

A. TREININ\* and E. HAYON†

Pioneering Research Laboratory, U.S. Army Natick Laboratories,  
Natick, Mass. 01760, U.S.A.

(Received 27 May 1974)

TECHNICAL LIBRARY  
U. S. ARMY  
NATICK LABORATORIES  
NATICK, MASS. 01760

## INTRODUCTION

PLATZMAN made a major contribution to the understanding of the electronic spectra of inorganic ions in solution in a model proposed by him and Franck<sup>(1)</sup> for the optically excited states of the halide ions in solution, i.e. their charge-transfer-to-solvent (CTTS) states. This model was later modified and extended to account for other CTTS spectra and for their environmental effects<sup>(2)</sup>. The doublet splitting shown by the spectra of I<sup>-</sup> and Br<sup>-</sup> was interpreted by Franck and Scheibe<sup>(3)</sup> as due to complete detachment of the excited electron. In their model, Platzman and Frank retained the picture of effectively free halogen atoms (keeping the solvation structure of the parent ions) but considered the electron to be bound in the field of the polarized medium, with the charge mainly concentrated on the solvation layer.

A recent refined analysis<sup>(4)</sup> of the halide spectra in various solvents has provided evidence for additional CTTS bands, which have been interpreted in terms of different binding states of the electron. However, there is no experimental evidence for the presence of "free" halogen atoms in the CTTS states. Considerable charge expansion, as in Rydberg transitions<sup>(5)</sup>, may account for the properties of these spectra. Similar doublet splitting is shown by spectra of various iodine compounds, which are due to internal transitions<sup>(6)</sup>. Moreover, even if complete electron detachment is achieved, the state of the halogen atom should be different from that in equilibrium, where charge-transfer interactions are established between the atoms and solvent molecules<sup>(7,8)</sup>. The lifetime of the CTTS state is probably determined by diffusion of the atom from excitation site or relaxation of solvation layer. Therefore, photochemical experiments with a resolution in the picosecond time scale may shed light on its nature.

In the microsecond time scale, the fate of excited halide ions in solution is well known from flash photolysis experiments. These and steady-state photochemistry experiments have provided ample evidence that chemical annihilation of the CTTS state occurs by reaction (1):

The solvated electron was identified by its spectrum<sup>(9)</sup> and by its chemical effects<sup>(10)</sup>. But the halogen atoms could not be observed owing to their fast conversion to the dihalide ions



which were identified in solution<sup>(11)</sup>. Only by using the matrix isolation technique, could iodine atoms produced from  $I^-$  in boric acid glasses be identified by their atomic spectrum in the vacuum U.V.<sup>(12)</sup>.

Here we wish to describe a first study of the photolysis of  $I^-$  in the nanosecond time scale, using the laser technique. The iodine atoms were identified in various solvents not by their atomic absorption, which is masked by that of  $I^-$  and the solvent, but by the absorption of the  $I$ -solvent complexes. From these experiments and from others involving the laser photolysis of  $I_3^-$ , new information on reaction (2) is provided.

#### EXPERIMENTAL

Irradiation was conducted at 265 nm with a frequency quadrupled neodymium laser (Holobeam) delivering single pulses of  $\approx 15$  ns duration. The transient spectra were measured at right angles to the laser beam, using the light output from a pulsed 250 W Osram xenon lamp. The reaction cell, with an  $\approx 8$  mm effective optical path, was enclosed in a temperature-controlled jacket.

Ethyl and propyl nitriles (both Eastman) were redistilled from Drierite. Fresh 1,2-dimethoxyethane (Eastman) was used without further purification, and all the other reagents were of the highest purity available commercially. Tetraheptylammonium iodide (Eastman) was used for preparing iodide solutions in ethyl and propyl nitriles and in dimethoxyethane. All iodide solutions were freed from air by bubbling argon, but not the  $I_3^-$  solutions in order to avoid evaporation of  $I_2$ . However,  $O_2$  was found to have no effect on the results.

The hydrolysis of iodine in water at pH  $\sim 6.0$  cannot have a significant effect on the results reported below. At the concentrations of  $I_2$  used less than  $5 \times 10^{-6}$  mol dm<sup>-3</sup> of  $I^-$  was observed (determined from the absorption of  $I_3^-$  at 287 nm). This  $[I^-]$  was less than 10 per cent that of the iodide initially added to the iodine solution. With  $I_2$  alone the solutions produced very faint transient absorption. Also, no transient absorptions were observed from the organic solvents in the absence of  $I^-$ .

#### RESULTS AND DISCUSSIONS

To reduce the rate of reaction (2), the concentration of  $I^-$  had to be kept below  $\approx 10^{-3}$  mol dm<sup>-3</sup>. The extinction coefficient of  $I^-$  in water at 265 nm, at room temperature, is  $\approx 14$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> (1.4 m<sup>2</sup>/mol) and, therefore, under these conditions the system could not be studied. Two methods were used to enhance light absorption: (a) the temperature and solvent sensitivities of the iodide spectrum<sup>(2,4)</sup> were utilized to shift the band of  $I^-$  to longer wavelengths, (b) some  $I^-$  was transformed to  $I_3^-$ , which absorbs strongly in this region.

the organic solvents another transient absorption was observed, and its build-up was complete within the duration of the pulse. These two types of transients are similar to those observed with  $I_2$  in hydroxylic solvents<sup>(7)</sup>, and they are similarly interpreted.

Figure 1 shows the transient absorption bands produced from  $10^{-4}$  mol dm<sup>-3</sup> solutions of  $I^-$ , 20–40 ns after the pulse, and Table I summarizes the spectral data. We assign these bands, which are completely developed within the duration of the pulse, to charge transfer (CT) complexes of iodine atoms with solvent molecules.

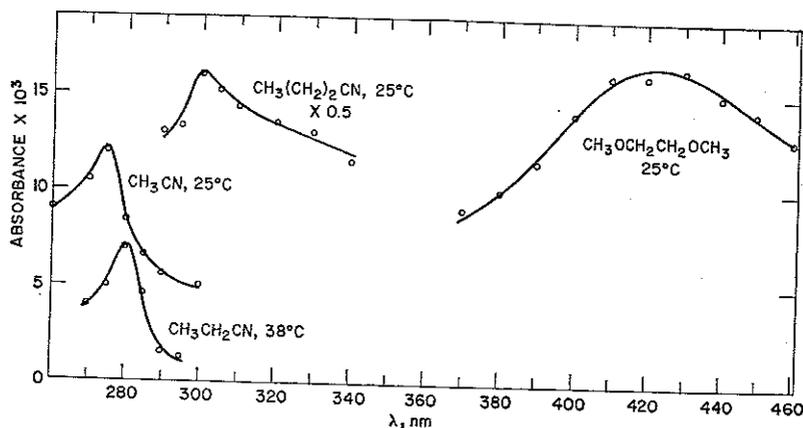


FIG. 1. Transient absorption spectra produced from the laser photolysis of  $10^{-4}$  mol dm<sup>-3</sup>  $I^-$  in various solvents. Absorbance read 20–40 ns after the pulse.

TABLE I. SPECTRAL PROPERTIES AND QUANTUM YIELDS OF IODINE ATOMS PRODUCED IN THE PHOTOLYSIS OF IODIDE IN VARIOUS SOLVENTS (25°C)

Solvent	$I_D^*$ (eV)	$\phi(I)^\dagger$	$h\nu_{exp}$ (eV)	$h\nu_{calc}^\ddagger$ (eV)	$\epsilon_{max}(I)$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )
H <sub>2</sub> O§	12.60	0.36	4.87	5.15	1040
CH <sub>3</sub> CN	12.20	0.7, 0.75	4.53	4.80	2300
C <sub>2</sub> H <sub>5</sub> CN	11.84	0.4	4.43	4.48	1800
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CN	11.67	0.3	4.14	4.35	8500
CH <sub>3</sub> OH§	10.85	0.60	3.77	3.97	1350
(CH <sub>3</sub> ) <sub>2</sub> CHOH§	10.15	0.70	3.26	3.16	1550
CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	9.65¶	0.6	2.96	2.90	4000

\* From Ref. (14).

† Present work: optical excitation at 265 nm; other data at 254 nm. Quantum yield based on  $\epsilon_{max}(I_2^-) = 1.4 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

‡ From expression (3).

§ The spectral data for hydroxylic solvents is from Ref. (13).

|| From Ref. (15).

¶ Assumed to equal  $I_D$  of (CH<sub>3</sub>O)<sub>2</sub>CHCH<sub>3</sub><sup>(14)</sup>; Ref. (16) gives  $I_D \approx 9.7$  eV.

Since no data are available with these particular solvents, the assignment is supported by comparing the transition energies with theory.  $h\nu$  was calculated by using the

where  $I_D$  is the ionization potential of solvent. Relation (3) was found to apply to iodine atoms in hydroxylic solvents. The agreement is good although nitrile complexes are expected to display some  $\pi$ -character (see Table I, where data for hydroxylic solvents were also included).

In all our experiments the CT spectra of iodine atoms were overlapped by the absorption of  $I_2^-$ , and in no case could we observe their decay kinetics. After the pulse, the absorption continued to grow in relatively slowly, which indicates that at all wavelengths studied the extinction coefficients of "I-solvent" radicals were lower than that of  $I_2^-$ . However, owing to their decay the growth in absorption was particularly slow at wavelengths close to their absorption maxima.

In water iodine atoms absorb at 255 nm<sup>(13)</sup>, which is strongly overlapped by the absorption of  $I^-$ . Therefore, it was not possible to detect them in aqueous solutions of iodide. This overlap had to be considered also in the case of methyl and ethyl nitriles. The corresponding spectra were corrected for depletion of  $I^-$  at the end of the pulse. This depletion was taken as equal to the amount of  $I_2^-$  finally produced and before it appreciably decayed. (Under the conditions employed, I atoms were completely converted to  $I_2^-$ ; see below.) The latter was determined by assuming  $\epsilon_{\max}(I_2^-) = 1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (140 m<sup>2</sup>/mol), the same value as in water<sup>(17)</sup>.  $\lambda_{\max}$  of  $I_2^-$  is little affected by solvent (compared to water,  $\Delta\lambda \leq +10 \text{ nm}$  was observed) and, as in the case of  $I_3^-$ <sup>(18)</sup>,  $\epsilon_{\max}$  is not likely to be appreciably sensitive to solvent. More direct support for this assumption was provided by evaluating the quantum yield of reaction (1),  $\phi_I$ , from the amounts of light energy absorbed by  $I^-$  at 265 nm and of  $I_2^-$  produced. For  $\text{CH}_3\text{CN}$  the value thus derived shows excellent agreement with available data obtained from steady photochemistry experiments<sup>(15)</sup> (Table I). This is important to note, since for  $\text{CH}_3\text{CN}$  the correction for depletion of  $I^-$  was most pronounced and could affect the determination of  $\lambda_{\max}$ .

On the basis of the same assumption,  $\epsilon_{\max}$  of the I-complexes was evaluated:  $\epsilon_{\max}(I) = 1.4 \times 10^4 [D_{\max}(I)/D_{\max}(I_2^-)]$ ,  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , where  $D$  is optical density. The values (Table I) lie in the range covered by other iodine-solvent complexes<sup>(8)</sup>, but compared to other nitriles the value for propyl nitrile appears to be exceptionally high. The  $I_2^-$ -solvent CT bands also display marked solvent sensitivity for  $\epsilon_{\max}$ <sup>(19)</sup>.

### Kinetics

The growth kinetics of  $I_2^-$  was studied at 380–390 nm. All solutions contained a large excess of  $I^-$  ( $[I^-]/[I] \geq 100$ ), therefore only reaction (2) should be considered for I atoms. The same applies for  $I_2^-$ , since its decay was relatively slow. Under these conditions the growth of  $I_2^-$  should follow a first-order kinetics with

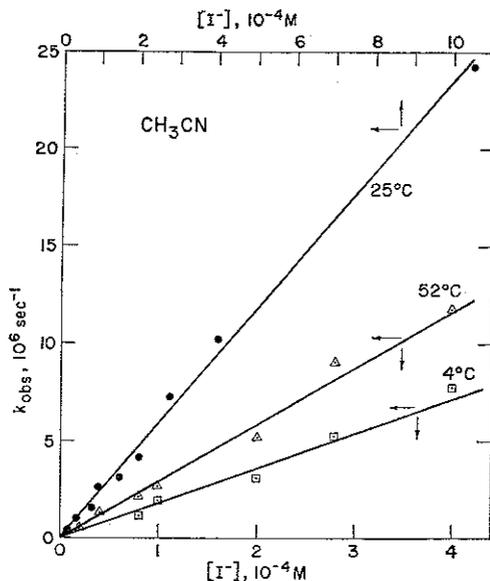
$$(4) \quad k_{\text{obs}} = k_2[I^-] + k_{-2},$$

where  $k_0$  and  $k_{-0}$  are the rate constants of reaction (2), in the forward and backward

TABLE II. RATE CONSTANT OF THE REACTION  $I + I^- \rightarrow I_2^-$  IN VARIOUS SOLVENTS

Solvent	$t$ °C	$\eta^*$ ( $10^{-3}$ poise)	$k_2(\text{exp})$ ( $10^{10}$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$k_2(\text{calc})^\dagger$ ( $10^{10}$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
H <sub>2</sub> O	25	8.90	$1.3 \pm 0.2$	0.74
	75	3.79	2.6	2.03
CH <sub>3</sub> CN	4	4.20	1.7	1.45
	25	3.45	2.3	1.90
	52	2.82	2.9	2.55
C <sub>2</sub> H <sub>5</sub> CN	25	4.13	2.1	1.60
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CN	25	5.51	1.4	1.20
CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	25	4.55	1.2	1.45

\* From Ref. (20).

† From Debye's expression:  $k = 8RT/3000\eta$ .FIG. 2. The dependence upon  $[I^-]$  of the observed first-order rate constant for the formation of  $I_2^-$  in  $CH_3CN$ , as monitored at 385 nm.

absorbed all the light to yield I atoms by reaction (5)<sup>(11)</sup>:



The formation kinetics of  $I_2^-$  was still considered to be determined only by reaction (2), since (a)  $I^-$  was in excess and (b) varying the concentration of  $I_2^-$  was shown to have no effect on the kinetics. The general solution of the kinetics of reaction (2) is

$$(6) \quad t = \frac{1}{k_2[I^-] + k_{-2}} \ln \frac{[I_2^-]_{\text{eq}} - [I_2^-]_0}{[I_2^-]_{\text{eq}} - [I_2^-]},$$

where  $[I_2^-]_0$  and  $[I_2^-]_{\text{eq}}$  are the initial and equilibrium concentrations of  $I_2^-$ , respec-

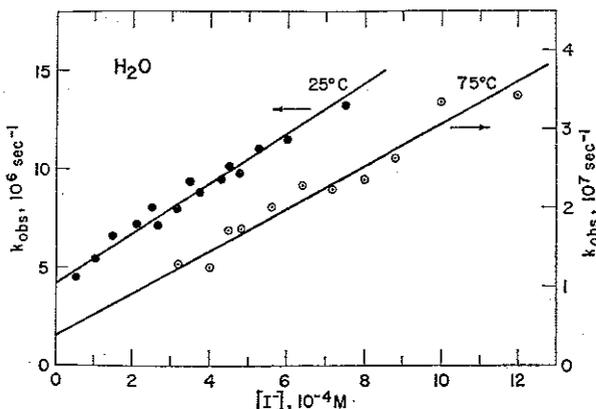


FIG. 3. The dependence upon  $[I^-]$  of the observed rate constant for the formation of  $I_2^-$  in water. Lower line:  $I^-$  alone; upper line:  $I^-$  in presence of  $6 \times 10^{-5} \text{ mol dm}^{-3} I_2$ . Kinetics monitored at 385 nm.

became apparent that for organic solvents, within the limits of error,  $k_{\text{obs}}$  is proportional to  $[I^-]$ , i.e.  $k_{-2}$  is relatively low.

The previous values for  $k_2$  in water at room temperature are  $7.6 \times 10^9$  (21) and  $9.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (13). The lowest value was obtained from pulse radiolysis experiments (21) where the formation of  $\text{IOH}^-$  as a precursor might complicate the kinetics (22).

The high values of  $k_2$  imply a diffusion-controlled mechanism, and this is verified by comparing them with values calculated from Debye's expression

$$(7) \quad k_{\text{diff}} = \frac{8RT}{3000\eta}$$

Apart from water at 25°C, where the iodine species are probably small compared to the  $\text{H}_2\text{O}$  aggregates, the agreement is within 20–30 per cent.

The line intercepts in Figs 2 and 3 give  $k_{-2}$ , the rate constant of the back reaction. However, as seen from the figures, considerable error may be involved in their determination; in the organic solvents they are too low to be estimated. The value for water at 25°C,  $k_{-2} = (4 \pm 2) \times 10^6 \text{ s}^{-1}$ , is much higher than the value recently determined,  $k_{-2} = 7 \times 10^5 \text{ s}^{-1}$  (23). The latter was obtained from laser photolysis of  $I_2$  solutions, under conditions where  $[I] \gg [I^-]$ , so that recombination of iodine atoms could be a major process.

Using our values of  $k_2$  and  $k_{-2}$ , the equilibrium constant of reaction (2)  $K_{\text{eq}}(25^\circ) = (3 \pm 2) \times 10^3 \text{ mol dm}^{-3}$  was derived. Previous values were  $1.13 \times 10^5$  (21),  $1.2 \times 10^4$  (11) and  $1.4 \times 10^4 \text{ mol dm}^{-3}$  (13). In the organic solvents  $k_{-2} \leq 10^5 \text{ s}^{-1}$  (Fig. 2) and  $K_{\text{eq}}$  is at least 100 times higher than that in water. A similar increase in stability constants on replacing water by organic solvents is shown by polyhalide ions, e.g. the log  $K$  values of  $I_2^-$  in water and acetonitrile are 2.9 and 6.6 respectively. Solvation

## REFERENCES

1. R. PLATZMAN and J. FRANCK, in *Farkas Memorial Volume*, Jerusalem, 1952, p. 21; *Z. Phys.* 1954, **138**, 411.
2. G. STEIN and A. TREININ, *Trans. Faraday Soc.* 1959, **55**, 1087, 1091; 1960, **56**, 1393; I. BURAK and A. TREININ, *ibid.* 1963, **59**, 1790; A. TREININ, *J. phys. Chem.* 1964, **68**, 893.
3. J. FRANCK and G. SCHEIBE, *Z. phys. Chem.* 1928, **A139**, 22.
4. M. FOX and E. HAYON, *Chem. Phys. Lett.* 1972, **14**, 442; *J. Am. chem. Soc.*, to be published.
5. C. K. JØRGENSEN, in *Halogen Chemistry*, edited by V. GUTMANN, Academic Press, New York, 1967, Vol. 1, p. 265.
6. L. I. KATZIN, *J. chem. Phys.* 1955, **23**, 2055.
7. P. FORNIER DE VIOLET, R. BONNEAU and J. JOUSSOT-DUBIEN, *Chem. Phys. Lett.* 1973, **19**, 251.
8. R. E. BUHLER, *J. phys. Chem.* 1972, **76**, 3220; *Radiat. Res. Rev.* 1972, **4**, 233.
9. M. S. MATHESON, W. A. MULAC and J. RABANI, *J. phys. Chem.* 1963, **67**, 2613.
10. (a) E. HAYON, *J. phys. Chem.* 1961, **65**, 1937; (b) J. JORTNER, M. OTTOLENGHI and G. STEIN, *J. phys. Chem.* 1962, **66**, 2029, 2042; (c) *ibid.* 1963, **67**, 1271; (d) *ibid.* 1964, **68**, 247.
11. L. I. GROSSWEINER and M. S. MATHESON, *J. phys. Chem.* 1957, **61**, 1089.
12. A. ZALIOUK-GITTER and A. TREININ, *J. chem. Phys.* 1965, **42**, 2019.
13. P. FORNIER DE VIOLET, R. BONNEAU and J. JOUSSOT-DUBIEN, *J. Chim. phys.* 1973, **70**, 1404.
14. *Ionization Potentials, Appearance Potentials, and Heat of Formation of Gaseous Positive Ions*, NSRDS-Natl Bur. Stand. 26, Washington, 1969.
15. M. FOX, *Quart. Rev.* 1970, **24**, 565.
16. E. M. VOIGT, *J. phys. Chem.* 1968, **72**, 3300.
17. J. K. THOMAS, *Trans. Faraday Soc.* 1965, **61**, 702.
18. A. I. POPOV, in *Halogen Chemistry*, edited by V. GUTMANN, Academic Press, New York, 1967, Vol. 1, p. 225.
19. H. TSUBOMURA and R. P. LANG, *J. Am. chem. Soc.* 1961, **83**, 2085.
20. LANDOLT-BÖRNSTEIN, 6. Auflage, II. Band, 5 Teil, 1969.
21. J. H. BAXENDALE and P. L. T. BEVAN, *Trans. Faraday Soc.* 1968, **64**, 2389.
22. D. ZEHAVI and J. RABANI, *J. phys. Chem.* 1972, **76**, 312; D. BEHAR, P. L. T. BEVAN and G. SCHOLES, *J. phys. Chem.* 1972, **76**, 1537; G. G. JAYSON, B. J. PARSONS and A. J. SWALLOW, *J. chem. Soc., Faraday Trans. I.* 1973, **9**, 1597.
23. P. FORNIER DE VIOLET, R. BONNEAU and J. JOUSSOT-DUBIEN, *Mol. Photochem.* 1973, **5**, 61.