Co.); Calcomine Diazo Brilliant Green 3GD (Calco); Rosanthrene Fast Brown RB (Ciba); 4-(*p*-aminobenzeneazo)-4′-nitrostilbene-2,2′-disulfonic acid (Althouse). 3% dyeings on scoured bleached cotton cloth were prepared by conventional procedures.[5]

Five-g. samples of dyed cloth were stirred at 0–10° for 20 minutes in 400 cc. of water containing 8 g. of sodium nitrite and 24 g. of concentrated hydrochloric acid. It was observed that when these diazotized samples were boiled with water for one hour they would no longer couple with β-naphthol; the boiled samples were then subjected to a second diazotization procedure and would not couple with β-naphthol. This indicated that the original diazotization was quantitative. All work following diazotization was performed in darkness to avoid possible photo effects.

Diazotized samples were immersed for three minutes in a solution of the cupro-ammonia reducing agent used in our earlier work.[6] After rinsing with dilute acid the sample would no longer couple with alkaline β-naphthol. Its color was slightly duller than the original dyeing. After rediazotizing, however, coupling with β-naphthol occurred to produce a color almost identical with a standard prepared by coupling an unreduced sample with β-naphthol. Control experiments showed that the effect produced by the reducing agent was not produced by the reducing solution when cupro-ammonia ion was omitted. Since it was demonstrated above that the original diazotization was complete, we cannot escape the conclusion that cupro-ammonia ion converted the diazo compound to the orginal amine.

Crude designs were printed on a sample of diazotized dyed cloth with the cupro-ammonia reducing reagent. When the sample was developed with β-naphthol in the usual way the printed portion failed to couple. These same portions could then be rediazotized and coupled with another developer such as phenylmethylpyrazolone. A variety of printing effects were obtained in this way.

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[5] Trotman and Trotman, "The Bleaching, Dyeing and Chemical Technology of Textile Fibers," 2nd ed., Griffin, London, 1946, p. 386.

[6] E. R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball and E. R. Read, This Journal, **63**, 730 (1941) Method 2.

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The Absorption Spectra of I_2, I_3^-, I^-, IO_3^-, $S_4O_6^=$ and $S_2O_3^=$. Heat of the Reaction $I_3^- = I_2 + I^-$

By Alice D. Awtrey and Robert E. Connick

In connection with rate studies in the thiosulfate–iodine–triiodide system[1] it was necessary to determine the molar extinction coefficients of these and other species in aqueous solution.

In Fig. 1 are given the spectra of I_2 and I_3^- in the visible and ultraviolet regions. The molar extinction coefficients, ε, at the maxima are listed in Table I. In Fig. 2 are shown the spectra of I^-, IO_3^-, $S_4O_6^=$ and $S_2O_3^=$.

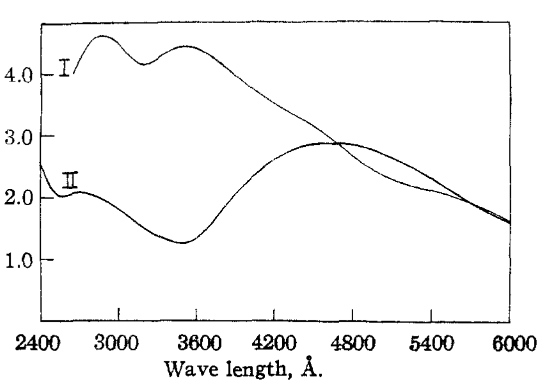

Fig. 1.—Molar extinction coefficients of triiodide ion and iodine in water: I, triiodide ion; II, iodine.

Table I

Molar Extinction Coefficients of I_3^- and I_2 at the Maxima

	Wave length, Å.	$\epsilon_{I_3^-}$	ϵ_{I_2}
I_3^-	3530	26,400	18
	2875	40,000	95
I_2	4600	975	746
	2700	17,200	121

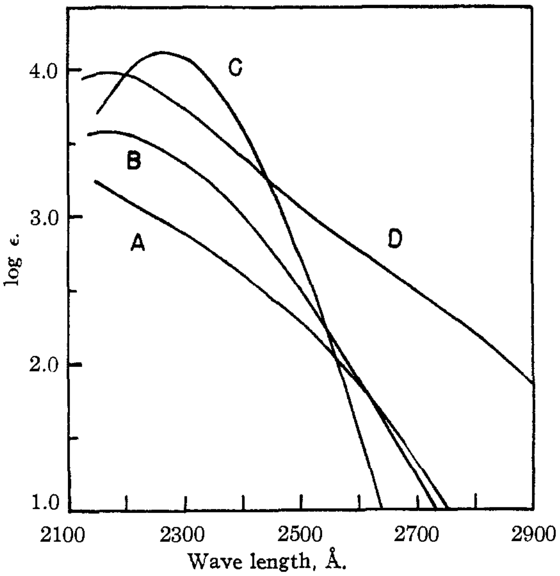

Fig. 2.—Molar extinction coefficients in water: A, IO_3^-; B, $S_2O_3^=$; C, I^-; D, $S_4O_6^=$.

The equilibrium constant for the dissociation of triiodide ion was determined spectrophotometrically at different temperatures, and Δ*H* was calculated to be −5100 cal.

Experimental

Absorption Spectra.—The molar extinction coefficient, ε, of triiodide ion was determined by measuring the optical density of solutions containing 0.049 *M* potassium iodide and 10^{-3} or 10^{-4} *M* perchloric acid; the total iodine concentrations were 1.03×10^{-5} and 6.76×10^{-5} *M*. A thermostated cell holder, used with the Beckman spectrophotometer, kept the temperature at 25.0°. The absorption cells were 10 and 2 cm. in length. Corrections were made for absorption due to free I_2 and to I^-; that due to perchlorate is negligible at these wave lengths and concentrations. The extinction coefficient at wave lengths lower than 2600 Å. was not obtained because of absorption due to iodide in these solutions.

For determining the spectrum of I_2, a solution was made up containing approximately 5×10^{-4} *M* iodine and 1.5×10^{-6} *M* potassium iodate, and having 0.10 *M* perchloric acid; the flask was sealed and put in a thermostat at 25° for ten days, to come to equilibrium. From the equilibrium constants[2]

$$\frac{(I^-)^5(IO_3^-)(H^+)^6}{(I_2)^3} = 2.7 \times 10^{-48} \text{ and } \frac{(I^-)(HOI)(H^+)}{(I_2)} = 2.58 \times 10^{-13}$$

are calculated approximate concentrations: $(I^-) = 10^{-6}$ *M*; $(I_3^-) = 4 \times 10^{-10}$ *M*; $(HOI) = 10^{-6}$ *M*. The maximum optical density due to triiodide, at 2875 Å., is 0.001;

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[1] A. D. Awtrey and R. E. Connick, This Journal, **73**, 1341 (1951).

[2] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

the absorption due to iodide, iodate and undissociated iodic acid is negligible, even at 2400 Å. Correction was made for the absorption of perchloric acid.

The accuracy of the maximum molar extinction coefficients given in Table I is 1%; that of the curves in Fig. 1 is somewhat less.

The spectra of I^-, IO_3^-, $S_4O_6^=$ and $S_2O_3^=$ were measured by dissolving the sodium or potassium salt in doubly distilled water and measuring the optical density of the solutions with a Cary recording spectrophotometer. The accuracy of the molar extinction coefficients shown in Fig. 2 is about 10%. The values for tetrathionate are in agreement with those in the literature,[3] but for thiosulfate there is a discrepancy of the order of a factor of 1.5 between these data and those reported elsewhere.[3,4]

The Heat of Dissociation of Triiodide Ion.—The triiodide ion concentration in a solution containing 2.00×10^{-3} *M* potassium iodide and 10^{-4} *M* perchloric acid was measured spectrophotometrically at different temperatures. The total iodine concentration was determined from the known equilibrium constant[5] at 25.0°, and the equilibrium constant at the other temperatures then calculated. The data are given in Table II.

TABLE II

THE TRIIODIDE EQUILIBRIUM CONSTANT AT DIFFERENT TEMPERATURES

Temp., °C.	log (I_0/I) at 3530 Å.	(I_3^-) $\times 10^6$ *M*	(I_2) $\times 10^6$ *M*	$K \times 10^3$ *M*	$1/T_{abs.}$ $\times 10^3$
1.0	0.538	2.038	0.667	0.654	3.648
16.1	.460	1.743	0.962	1.10	3.458
25.0	.420	1.591	(1.114)	(1.40)	3.356
25.0	.418	1.583	(1.109)	(1.40)	3.356
33.4	.379	1.436	1.256	1.75	3.264
39.2	.350	1.321	1.371	2.08	3.202

Allowing a 1% error in each spectrophotometer reading, the error in the equilibrium constants calculated in this way is about 5%. An experiment at high iodide ion concentration showed that the extinction coefficient of triiodide ion at 3530 Å. does not change with temperature.

A semi-logarithmic plot of *K* against the reciprocal of the absolute temperature gives a straight line, within experimental error. The value of ΔH calculated from the slope of this line is −5100 cal., with a maximum uncertainty of ±400 cal. A value of −4300 is obtained from the data of Jones and Kaplan[5] at 0° and 25°.

[3] L. Lorenz and R. Samuel, *Z. physik. Chem.*, **B14**, 219 (1931).

[4] H. Ley and E. König, *ibid.*, **B41**, 365 (1938).

[5] (a) G. Jones and B. B. Kaplan, THIS JOURNAL, **50**, 1845 (1928); (b) W. C. Bray and G. M. J. Mackey, *ibid.*, **32**, 914 (1910).

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The *cis* and *trans* Isomers of 1,2-Dichloro-1-propene

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The *cis* and *trans* isomers of 1,2-dichloropropene have been prepared recently[2] and have boiling points of 76 and 93°. The assignment of *cis* and *trans* configurations had not been made but by analogy with the dichloroethylenes the low boiling isomer might be expected to have the *trans* configuration. The configuration of these isomers was then more fully investigated by King and Smith[3] who measured the electric moment of the molecules in the vapor phase. Since they found that the high boiling isomer had a moment of 2.2 debye units and the low boiling isomer had a moment of 0.8 debye unit the configurations were identified as *cis* and *trans*, respectively.

The investigation of the structure as a problem in spectroscopy was undertaken before the results of King and Smith were available and our results are in agreement with the finding of these authors.

The *cis*- and *trans*-dichloropropenes and their completely deuterated analogs were prepared by Dr. L. Leitch.[4] The spectra were obtained with a

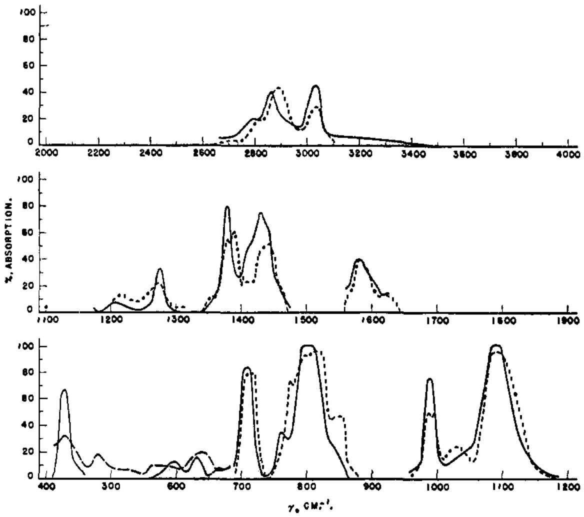

Fig. 1.—Infrared spectrum of $CH_3CCl{=}CHCl$ low boiling, *trans* isomer: ——, liquid, 0.025 mm.; - - -, gas, 65 mm.; — — —, gas, 65 mm.

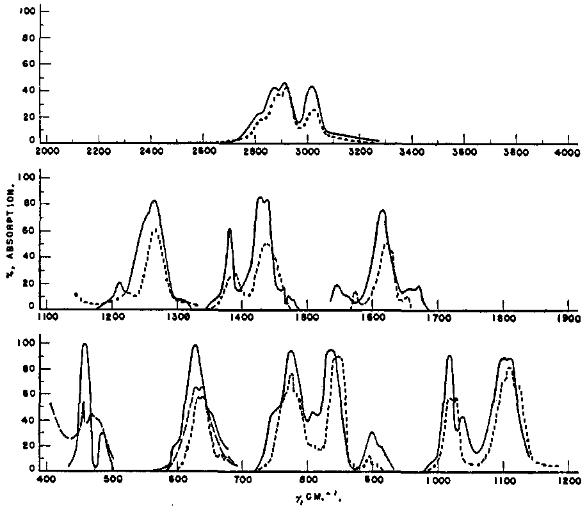

Fig. 2.—Infrared spectrum of $CH_3CCl{=}CHCl$ high boiling *cis* isomer: ——, liquid, 0.025 mm.; - - -, gas, 45 mm.; — — —, gas, 36 mm.

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[1] National Research Laboratories Postdoctorate Fellow 1948–1950.

[2] Huntress and Sanchez-Nieva, THIS JOURNAL, **70**, 2813 (1948).

[3] W. H. King and H. A. Smith, *ibid.*, **72**, 3459 (1950).

[4] L. Leitch, *Can. J. Chem.*, in press.