molecular structure by means of an X-ray diffraction study.[2] In order to provide material for a study of the reactions of 1,4-diselenane, a more efficient procedure for its synthesis was sought.

The most promising of several trial procedures involved the direct reaction of aluminum selenide with ethylene bromide. Although the yield based on aluminum selenide is still only 2%, the simplicity of the method, the ready availability of ethylene bromide and the ease of preparation of aluminum selenide permit the preparation of two-gram yields of pure 1,4-diselenane in a matter of 2 or 3 days of laboratory time. The product was identified through: (1) its melting point, (2) a mixed melting point with a portion of the product from the earlier work[1] and (3) the melting point of its tetrabromide.

In the hope of improving the yield still further, magnesium selenide and ferrous selenide were also tried, but in both cases the yield of the desired product was negligible. Also, in order to test the versatility of the reaction, propylene bromide and a mixture of *cis-* and *trans*-2-butene dibromides reacted with aluminum selenide. In both cases the reaction was vigorous and went out of control. Due to this fact and the complexity of the anticipated products, these reactions were not investigated further at this time but were set aside for future study.

It appears that the low yield of the reaction between aluminum selenide and ethylene bromide is due to the formation of an adhering coating of aluminum bromide on the aluminum selenide. It is possible that the yield of 1,4-diselenane could be further improved by avoiding this coating since neither starting material is completely consumed when the reaction stops. Further work in this direction is planned.

Halogens react with 1,4-diselenane to form solids which presumably are 1,1,4,4-diselenane tetrahalides. These latter substances are insoluble in the common organic solvents and are accordingly precipitated quantitatively when solutions of the components are mixed. The extreme insolubility of these halides in carbon disulfide and carbon tetrachloride (in which most dialkyl and diaryl selenium dihalides are quite soluble) makes the determination of their equivalent weights by the method of McCullough, Campbell and Krilanovich[3] practically impossible. The composition of each of these compounds was accordingly determined by weighing the tetrahalide formed when a 5% excess of the halogen was added to a weighed sample of 1,4-diselenane dissolved in carbon tetrachloride. An X-ray diffraction study of the tetrahalides is planned.

Experimental

Aluminum Selenide.—One hundred grams of powdered selenium and forty grams of powdered aluminum were thoroughly mixed and ignited in 20-g. portions in a porcelain crucible. Excess aluminum rose to the surface of the fused mixture and was removed after cooling. The product was ground to a powder and stored in a tightly stoppered bottle.

Ethylene Bromide.—Eastman Kodak Co. white label ethylene bromide was used without further purification.

1,4-Diselenane.—To 100 g. of aluminum selenide in a 1-liter erlenmeyer flask fitted to a reflux condenser was added 200 g. of ethylene bromide. The flask was immersed in a steam-bath until vigorous reaction commenced. It was then removed from the bath and shaken vigorously. The temperature was maintained at 70–80° for two hours during which the sample was shaken vigorously at frequent intervals. A considerable increase in the volume of the aluminum selenide occurred and the solid became black and gummy. Some hydrogen bromide was evolved, presumably due to dehydrobromination of ethylene bromide by aluminum bromide. The reaction mixture was then kept in a bath at approximately 75° for 48 hours with occasional shaking. After cooling, 400 ml. of water was added cautiously to hydrolyze the aluminum bromide and unreacted aluminum selenide. Twenty grams of potassium hydroxide was then added and the mixture was steam distilled. Unreacted ethylene bromide distilled first and was discarded. The 1,4-diselenane, contaminated with small amounts of other selenides and ethylene bromide, then appeared in the condenser and receiver as a pale yellow crystalline solid. The impure product was dissolved in 50 ml. of absolute alcohol and refluxed for 5 minutes with 1 g. of potassium hydroxide to hydrolyze any ethylene bromide or halogenated selenides present. Seventy-five ml. of water was then added and the mixture allowed to stand for one hour. The 1,4-diselenane was filtered out, refluxed with alcoholic KOH, and again precipitated by addition of water. The product was twice recrystallized from ethanol and dried over calcium chloride. The yield was 2 g.

Melting points: product from new synthesis, 112.5–113.5°; product from previous work,[1] 113.0–113.5°; mixture (1:1) of products from the two methods, 113.0–113.5.

1,4-Diselenane Tetrachloride.—To 0.5289 g. of 1,4-diselenane in 30 ml. of carbon tetrachloride was added 8.1 ml. of a 0.64 *M* solution of chlorine in that solvent. The precipitate was collected in a sintered glass crucible, washed with 20 ml. of carbon tetrachloride to which 0.5 ml. of the chlorine solution had been added, then air-dried to constant weight; yield of 1,4-diselenane tetrachloride, 0.884 g.; theoretical yield, 0.8794 g.; calculated ratio of moles of chlorine per mole of 1,4-diselenane, 2.02. The white solid melted at 178–181° dec.

1,4-Diselenane Tetrabromide.—The above procedure was used, starting with 0.6595 g. of 1,4-diselenane and 10.5 ml. of 0.62 *M* bromine solution. The yield of tetrabromide was 1.610 g. compared to a theoretical yield of 1.645 g. The calculated ratio of moles of bromine per mole of 1,4-diselenane is 1.93. The pale yellow solid melted at 148–151° dec.

1,4-Diselenane Tetraiodide.—The same procedure was again used, starting with 0.3765 g. of 1,4-diselenane and 32.5 ml. of 0.114 *M* iodine solution. The yield of tetraiodide was 1.264 g., compared to a theoretical yield of 1.270 g. The calculated ratio of moles of iodine per mole of 1,4-diselenane is 1.99. The brick-red solid melted at 150–151° dec.

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[2] R. E. Marsh and J. D. McCullough, THIS JOURNAL, **73**, 1106 (1951).

[3] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

Effect of Temperature on the Absorption Spectrum of Iodine in the Alkyl Iodides[1]

BY DONALD E. SCHULER AND ROBERT H. SCHULER

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There has been in recent years a greatly renewed interest in the general problem of the solvation of iodine, particularly in regard to the resulting effect on the absorption spectrum of iodine solutions.[2,3] Among the solvents in which solvation is pro-

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[1] From the M.S. Dissertation of D. E. Schuler, Canisius College, June, 1952.

[2] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949); see R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952), for a comprehensive summary of electron donor-acceptor interactions.

[3] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

nounced are the alkyl iodides, where iodine gives reddish-brown solutions. Very recently Keefer and Andrews[3] have studied the absorption spectrum of iodine in mixed alkyl iodide–heptane solvents and from observations in the near ultraviolet have determined the equilibrium constant for the formation of the solvate. Earlier work in these laboratories[4] has shown that, in addition to the intense absorption in the ultraviolet, the visible absorption maximum is shifted from that observed in inert solvents, *i.e.*, 520–525 mμ to about 480 mμ in the pure alkyl iodides. This shift is accompanied by an increase in the absorption coefficient at the maximum by a factor of about 1.5. It is the purpose of this contribution to report studies of the temperature dependence of the visible absorption of iodine in the alkyl iodides.

Experimental

The alkyl iodides were thoroughly washed with sodium thiosulfate solution and water, dried and fractionated through a 100-cm. helix packed column. The center cuts, used in these investigations, were characterized as follows: methyl iodide, b.p. 42.5°, $n^{25}\text{D}$ 1.5271; ethyl iodide, b.p. 72.1°, $n^{25}\text{D}$ 1.5102; *n*-propyl iodide, b.p. (at 100 mm.) 44.1°, $n^{25}\text{D}$ 1.5025. Cyclohexane was twice recrystallized, fractionated, and the cut boiling at 79.6° taken. Phillips pure grade *n*-octane was used without further purification.

Absorption spectra were taken with a Beckman DU quartz spectrophotometer equipped with a thermostated cell compartment. Optical densities ($-\log I/I_0 = \epsilon lc$) were measured against an air blank and the densities of the solutions obtained by subtraction of the values for the pure solvent. The absorption cell consisted of 1 cm. square Pyrex tubing into which the solution was sealed after the sample had been degassed. This precluded any appreciable increase in iodine concentration due to loss of solvent or oxidation of the iodide. The sample could be returned to room temperature after a run at high temperature, and thus it could be ascertained that there had been no change in iodine concentration.

The solutions were made up by weighing the iodine (approximately 7 mg. weighed to ±0.02 mg.) in a capsule and introducing this into a 50-ml. volumetric flask. The solvent was then added to the flask thermostated at 20°. The coefficients of volume expansion ($1/v\ \mathrm{d}v/\mathrm{d}t$) were determined dilatometrically and found to be at room temperature 0.00120 for methyl and ethyl iodide, 0.00119 for propyl iodide, and 0.00122 for the hydrocarbon solvents. The concentrations of the solutions were then calculated at each temperature taking into account the volume change due to expansion of the solvent.

Results and Discussion

In Fig. 1, the spectrum of the visible absorption of iodine in *n*-propyl iodide is given for temperatures between 5 and 99°. As the temperature of the sample increases it is seen that there is an asymmetric broadening of the spectrum, accompanied by a shift of the maximum toward the red and a decrease in the intensity of the absorption at the maximum. For comparison purposes, the spectrum of iodine in *n*-octane is also given. It is seen here that although there is a general temperature broadening, that there is little shift in the wave length of the maximum.

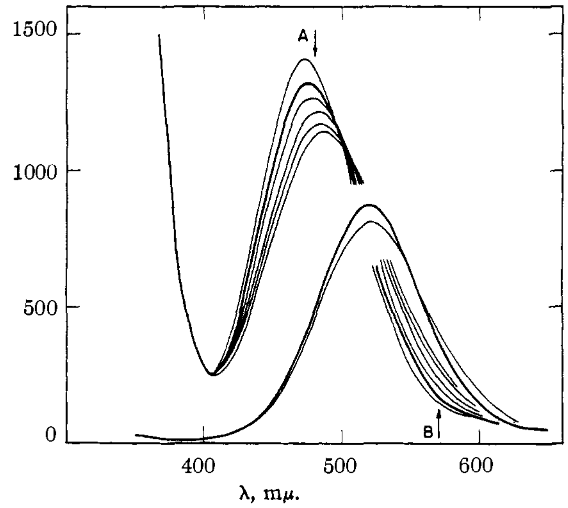

Fig. 1.—Absorption spectrum of solutions of iodine in propyl iodide at (reading down at A and up at B) 5, 25 (heavy curve), 45, 65, 85 and 99° and of solutions of iodine in octane at 25 (heavy curve) and 80°.

The behavior of methyl and ethyl iodides as solvents is very similar to that described above. Figure 2 illustrates the dependence of the wave length maximum upon temperature. This maximum is seen to be displaced toward the red approximately 1 Å./°C. In a solvent consisting of 20 wt. % ethyl iodide in octane, where the maximum occurs at approximately 500 mμ at 25°, similar effects are observed, the shift maximum being somewhat greater. In general the spectrum at the higher temperatures appears to be approaching that observed in inert solvents. The intense absorption of iodine in the alkyl iodides below 400 mμ, which is difficult to study because of the absorption of the solvent, appears to show a slight but not pronounced increase with increase in temperature. In the mixed solvent, ethyl iodide–octane, the effect is reversed, a somewhat greater decrease being ob-

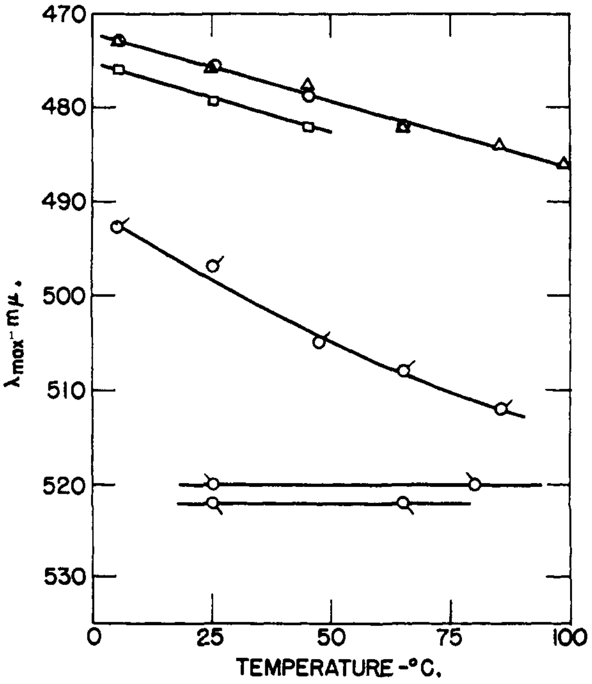

Fig. 2.—Variation of the wave length of maximum absorption with temperature for solutions of iodine in methyl iodide, □; ethyl iodide, O; *n*-propyl iodide, △; 20 wt. % ethyl iodide in octane, ơ ; *n*-octane, ò ; and cyclohexane, ọ.

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(4) J. Graham, M.S. Dissertation, Canisius College, 1949.

served. Cromwell and Scott,[5] in spectrophotometric measurements of the heat of formation of the benzene–iodine complex, report no measurable temperature broadening of the ultraviolet absorption in benzene.

As the temperature is lowered below 0°, the coloration of the solutions of iodine in the alkyl iodides is observed visually to become deep brown and finally straw yellow in color in the solid state at liquid nitrogen temperature. Freed and Sancier[6] have observed a similar temperature shift at 77°K. for the propylene–iodine complex together with pronounced intensification of the absorption in the ultraviolet.

In the case of the pure alkyl iodides as solvents, an increase in temperature generally results in a decrease in the extinction coefficients in the region from 400 to 500 mμ and an increase in the region above 500 mμ. This increase for the long wave length region is quite pronounced, *e.g.*, at 550 mμ the molar extinction coefficient in propyl iodide increases from 250 at 5° to 500 at 99°.

The relative oscillator strength (taken here to be $f = \int_{400\ \text{m}\mu}^{625\ \text{m}\mu} \epsilon\, d\nu$; ν in cm.$^{-1}$) shows a surprisingly small temperature coefficient in spite of the fact that the absorption is much more intense in the propyl iodide solutions ($f'/f = 1.92$ at 25°). The coefficient corresponds to a change of 7.9% in going from 5 to 99° in the propyl iodide and 4.1% (extrapolated) for an equivalent temperature interval in the octane solution.

These observations might perhaps be adequately explained in terms of a shift in a solvation equilibrium (of the form $RI + I_2 \rightleftarrows RI \cdot I_2$) toward the left with increasing temperature. However this system seems to be somewhat more complicated, particularly in that the behavior of the extinction coefficient (and oscillator strength) does not more than qualitatively parallel the shift in maximum. Also the effect of temperature is unexpectedly low for the relatively large displacement of the maximum in these solutions. An alternate explanation along the lines suggested by Bayliss and Rees[7] seems worthy of consideration in this regard, *i.e.*, that the change in spectrum in the alkyl iodide solvents is due to a generalized solvation resulting in a perturbation of the normal iodine absorption.

[5] T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3826 (1950).

[6] S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952).

[7] N. S. Bayliss and A. L. G. Rees, *J. Chem. Phys.*, **8**, 377 (1940); N. S. Bayliss, *Nature*, **163**, 764 (1949).

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Physical Properties of *cis*-1-Cyano-1,3-butadiene

BY K. V. WISE

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A recent literature survey at this Laboratory revealed a scarcity of physical property data on *cis*-1-cyano-1,3-butadiene. Several physical properties of high purity *cis*-1-cyano-1,3-butadiene (99.80 ± 0.08 mole %) were measured; the experimentally determined values are given in Table I together with conservative estimates of uncertainties wherever possible.

TABLE I

MEASURED PHYSICAL PROPERTIES OF *cis*-1-CYANO-1,3-BUTADIENE

F.p. for zero impurity, $T_{f0} \pm 0.04°$		−62.58
Heat of fusion, ΔH_F ±250 cal./mole		3028
Refractive index, $n^{25}{}_D$ ±0.0001		1.4835[a]
dn_D/dt (25°)		−0.0005
Density, $d^{25}{}_4$ ±0.0002 g./ml.		.8578[b,c]
dd_4/dt (25°)		− .00087
Viscosity, η^{25} ±0.006 millipoise		5.973
$d\eta/dt$ (25°)		−0.061
Flash point (Tag Closed Tester), °F.		95
Vapor pressure constants in Antoine eq.[d] for temp. range 45–110°	A	7.376
	B	1639
	C	230

Solubility: 1.5 wt. % soluble in water at 25°, and completely miscible with all common organic solvents

[a] H. R. Synder, *et al.*, THIS JOURNAL, **75**, 4742 (1953), report $n^{20}{}_D$ 1.4855. [b] *Ibid.*, report $d^{26}{}_4$ 0.8541 and $d^{t}{}_4$ 0.866. [c] D. D. Coffman, THIS JOURNAL, **57**, 1982 (1935), reports $d^{20}{}_4$ 0.8644. [d] The Antoine equation is written as $\log_{10} P_{mm} = A - (B/C + t)$.

The purity of the *cis*-1-cyano-1,3-butadiene used in this work was determined cryoscopically by the methods described by Taylor and Rossini.[1] The infrared spectrum (Baird double beam infrared spectrophotometer) of high purity *cis*-1-cyano-1,3-butadiene was also obtained; the spectrum was identical with the one published by Snyder, *et al.*, reference (*a*). The density value which Snyder, *et al.*, report for the density of the *trans* isomer of 1-cyano-1,3-butadiene is identical to the density value obtained in this work for the *cis* compound. Snyder also obtained higher density and refractive index values for the *trans* isomer than for the *cis*. This order is contrary to the usual order (*cis* higher than *trans*) for several other pairs of *cis* and *trans* compounds.

Experimental

Purification.—*cis*-1-Cyano-1,3-butadiene was purified by fractionation in a Smith column at 56 mm. The column was packed with glass helices and had 10–15 theoretical plates. A reflux ratio of 5:1 was maintained during the take-off of the high purity fraction boiling at 61°.

Freezing Points.—The freezing point for zero impurity (T_{f0}) and the actual freezing points (T_f) for several distillate cuts of *cis*-1-cyano-1,3-butadiene were ascertained from time–temperature cooling curves; these freezing curves were obtained with either equipment similar to the NBS freezing point apparatus[2] or with a Leeds and Northrup Automatic Stull Recorder.[3-5] The readability of the former is better than 0.001°, and the uncertainty of temperature measurements with the Automatic Stull Recorder is ±0.03°. In ascertaining the freezing points, liquid nitrogen was used as a constant temperature cooling medium, and the rate of cooling near the freezing point was approximately one degree per minute. A spiral Nichrome-wire stirrer which moved up and down in the freezing tube ensured equilibrium during freezing. It was never necessary to induce crystalliza-

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[1] W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944).

[2] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *ibid.*, **35**, 355 (1945).

[3] D. R. Stull, *Rev. Sci. Instruments*, **16**, 318 (1945).

[4] Brochure, "Speedomax High-Precision Resistance Thermometer Recorder with Automatic Range Extension," Leeds and Northrup Company, Philadelphia, Pa.

[5] D. R. Stull, *Ind. Eng. Chem., Anal. Ed.*, **18**, 234 (1946).