[Contribution from the Department of Chemistry, Davis Campus of the University of California]

The Interaction of Iodine with Cyclohexene and Vinyl Halides

By L. J. Andrews and R. M. Keefer

Solutions of iodine in cyclohexene and certain vinyl halides display pronounced absorption maxima in the region 260–305 mμ. These maxima are regarded as characteristic of 1:1 molecular complexes. Spectrophotometric measurements have provided data from which the equilibrium constants for formation of certain of these complexes in hexane solution have been calculated.

The spectra of solutions of the halogens in aromatic solvents show high absorption maxima in the region of 300 mμ, which have been interpreted as characteristic of 1:1 halogen–aromatic coördination compounds.[1] From a consideration of the equilibrium constants for formation of a number of such complexes, as evaluated from spectrum measurements, it appears that the aromatic nucleus functions as an electron donor in forming these addition compounds.

Since olefins, as well as aromatic substances, form other types of addition complexes, notably those with silver ion, because of their capacity to function as electron donors,[2] it has seemed of interest to attempt to demonstrate that ethylenic compounds can form halogen coördination complexes. Such an investigation is seriously limited in scope because of the rapidity with which ethylenic compounds in general react to form saturated dihalides. It has now been demonstrated, by procedures used in the aromatic–halogen interaction studies,[1] that several vinyl halides and also cyclohexene undergo interaction with iodine in hexane solution.

Experimental

Materials.—A mixture of hexanes purified for use in spectrophotometric work, as described previously,[2b] was used. Matheson *cis-* and *trans*-dichloroethylenes, of respective b.p. 59.8–60.1° and 48.3–49.0° (762 mm.) were fractionated before use. A sample of Halogen Chemicals *cis-* and *trans*-1-bromo-1-propene was distilled and a cut of b.p. 57.3–62.0° (762 mm.) and $n^{25}\mathrm{D}$ 1.4489 was used in these measurements. Eastman Kodak Co. trichloroethylene, b.p. 85.8–86.0° (761 mm.), cyclohexene, b.p. 82.0–82.1° (761 mm.) and ethylene dichloride, b.p. 82.3–82.7° (762 mm.), were fractionated before use.

The Absorption Spectrum Measurements.—Stock solutions of iodine (0.02 M) in hexane were prepared and standardized at 25°. More dilute solutions of iodine in hexane required for the spectrum measurements were prepared from the stock solutions just prior to use.

The iodine solutions were mixed in known volume ratios with the appropriate unsaturates at 25°, and the spectra of the resultant solutions were measured in glass-stoppered absorption cells against blanks of the same solvent composition on the Beckman spectrophotometer. The cell housing was maintained at 25°. Optical densities as measured are related to the recorded molecular extinction coefficients, ϵ, by the equation $d = \log_{10} I_0/I = \epsilon lc$ where c = total iodine concentration in moles/liter and l = light path length in cm. Other details of the procedures have been described previously.[1]

The vinyl halides showed no tendency to absorb iodine to form diiodides during the course of the measurements as evidenced by the constancy of the light absorption of the solutions in the visible region (*ca.* 500 mμ). When the cyclohexene solutions were allowed to stand in a lighted room, they slowly lost color, presumably because of the formation of cyclohexene diiodide. Solutions kept in an absorption cell within the spectrophotometer cell housing decolorized much more slowly and during the course of the measurements showed extinction coefficients at the visible maximum comparable to those of solutions of iodine in inert solvents. By making rapid measurements of these solutions in the ultraviolet, data were obtained which were reasonably satisfactory for use in calculating equilibrium constants for the complex formation.

Results

The ultraviolet absorption spectra of several solutions prepared by adding iodine in hexane to various ethylenic compounds are compared in Fig. 1 with the spectra of solutions of iodine in saturated solvents. The extinction coefficients recorded are based on total iodine concentration. *trans*-Dichloroethylene–iodine solutions give spectra closely similar to those of *cis*-dichloroethylene solutions. The dichloroethylenes, 1-bromo-1-propene and cyclohexene solutions give major absorption peaks in the region 265–305 mμ in which solutions of iodine in ethylene dichloride and hexane show only very limited absorption. The maximum for the trichloroethylene solution was not obtained, since it occurred outside of the range of the spectrophotometer for this particular solvent. The cyclohexene-iodine spectrum (curve I) is very similar to that of a solution of iodine in benzene[1a] ($\lambda_{\max}$ 297, $\epsilon_{\max}$ 9800).

The visible absorption of iodine in these solvents was also investigated. In general the position and magnitude of the visible absorption peak for the unsaturated solvents are closely similar to those for the saturated solvents (see Table I). It should be noted, as will be apparent from reported equilibrium constants, that with the exception of the cyclohexene solutions only a small fraction of the total dissolved iodine is coördinated with the unsaturates.

If one assumes that the ultraviolet absorption peaks for solutions of iodine in the unsaturated solvents are characteristic of 1:1 complexes as formed by equilibrium (1)

$$I_2 + U = I_2\cdot U \quad K = \frac{(\mathrm{I_2\cdot U})}{(\mathrm{I_2})(U)} \tag{1}$$

then the measured optical densities, d_c, at the absorption maxima (excluding the absorption of free iodine) are related to the complex concentration (C) as follows

$$\log_{10} I_0/I = d_c = (C)\epsilon_c l \tag{2}$$

Using the optical densities measured at these maxima for a series of hexane solutions of iodine and each unsaturate, K and ϵ_c values for the various complexes were evaluated from equation (3)

$$(\mathrm{I_2})_t l/d_c = \frac{1}{K\epsilon_c}\cdot\frac{1}{N_U} + \frac{1}{\epsilon_c} \tag{3}$$

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(1) (a) H. A. Benesi and J. H. Hildebrand, This Journal, **71**, 2703 (1949); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677, 5170 (1950); (c) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951).

(2) (a) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

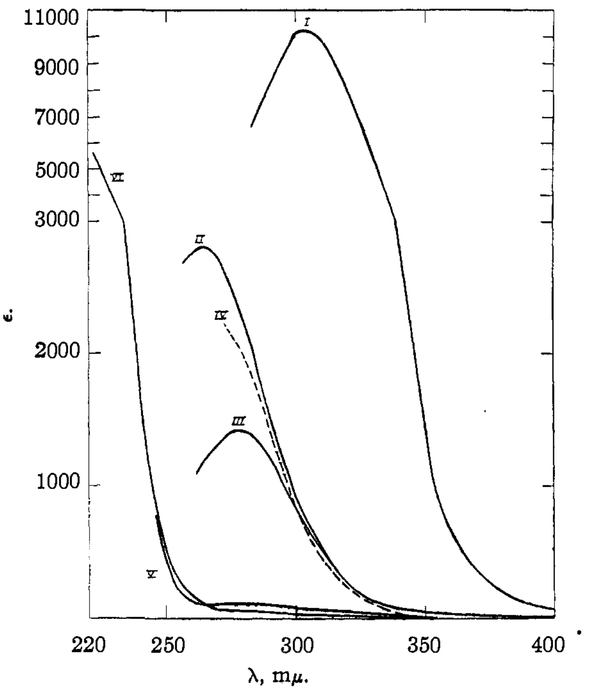


Fig. 1.—The absorption spectrum of iodine in various solvents containing small amounts of hexane: I, cyclohexene N_U = 0.864, 0.520 × 10^{-4} *M* I_2; II, *cis*-dichloroethylene, N_U = 0.944, 1.70 × 10^{-4} *M* I_2; III, 1-bromo-1-propene, N_U = 0.152, 9.35 × 10^{-4} *M* I_2; IV, trichloroethylene, N_U = 0.885, 3.12 × 10^{-4} *M* I_2; V, ethylene dichloride, $N_{C_2H_4Cl_2}$ = 0.944, 1.70 × 10^{-3} *M* I_2; VI, pure hexane (solutions in which the iodine concentrations varied from 0.85 × 10^{-4} – 1.87 × 10^{-3} *M* were used).

in which

$(I_2)_t$ = total molar iodine concentration
N_U = mole fraction of unsaturate in the solvent
ϵ_c = molecular extinction coefficient of the complex at the absorption maximum

This equation is valid under the imposed experimental condition that (U) ≫ $(I_2)_t$.[1]

TABLE I

VISIBLE ADSORPTION OF IODINE IN VARIOUS SOLUTIONS

Solvent[a]	N_{hexane}	$(I_2)_t$, mole/liter × 10^4	λ_{max}	ϵ_{max}[b]
Cyclohexene	0.136	3.12	490	1010
1-Bromo-1-propene	.110	3.12	505	940
cis-Dichloroethylene	.056	1.70	510	900
trans-Dichloroethylene	.056	1.70	515	940
Trichloroethylene	.115	3.12	515	960
Hexane	1.00	9.35	525	940
Ethylene dichloride	0.056	17.0	500	850

[a] In all cases the solutions were prepared for measurement by mixing known volumes of a standard solution of iodine in hexane with the solvent specified. [b] Based on total iodine content of the solution.

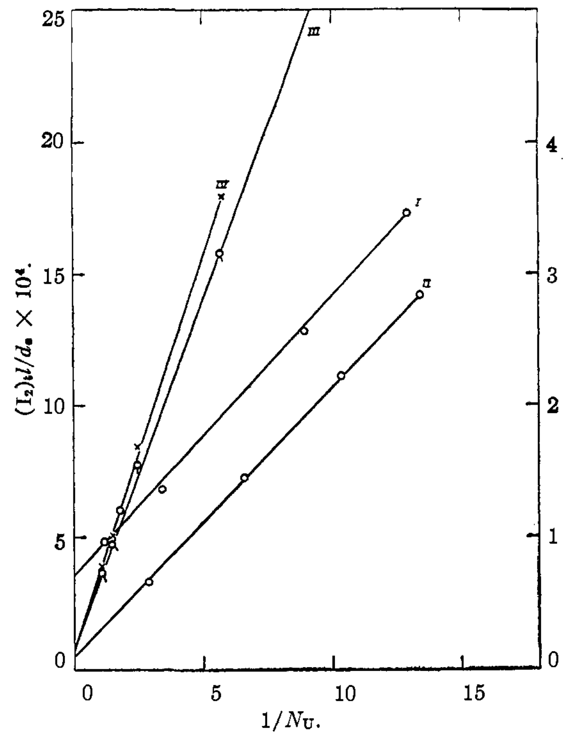


Fig. 2.—The evaluation of ϵ_c and *K*: I–IV, respectively, give data for cyclohexene, 1-bromo-1-propene, *cis*-dichloroethylene and *trans*-dichloroethylene; for line I use right-hand ordinate; for lines II–IV use left-hand ordinate.

In Fig. 2 the experimental data are treated graphically according to equation (3), and the *K* and ϵ_c values determined from the resultant straight lines[1a] are recorded in Table II. In making these calculations the measured d_c values were corrected for the absorption of free iodine by approximation procedures described previously.[1b,c] These corrections were based on spectrum measurements of solutions of iodine in hexane of iodine concentration comparable to those of the unsaturates under investigation.

TABLE II

EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS (25°) FOR THE IODINE COMPLEXES OF THE UNSATURATES IN HEXANE SOLUTIONS

	λ_{max}[a]	$\epsilon_{c\,max}$	*K*
Cyclohexene	302	14000	3.4
1-Bromo-1-propene	278	18500	0.53
cis-Dichloroethylene	262	12000	.32
trans-Dichloroethylene	262	14000	.24

[a] The wave length of maximum absorption varies slightly with the hexane content of the solution.

The results on trichloroethylene, for which data at the complex maximum were not available, could not be interpreted satisfactorily, presumably because of marked variations in the extinction coefficient of the complex with changes in N_U at wave lengths away from the absorption maximum. A similar situation was encountered in studies of bromine–aromatic complexes.[1b]

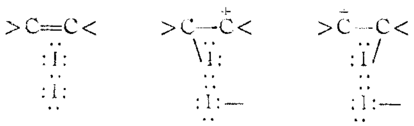
The *K* values for this type of complex formation diminish with increasing halogen substitution at the double bond. As noted in previous work on silver ion complexes[3] this may be attributed to the inductive effect of halogen on the π electrons of the double bond. The small differences in *K* values for the *cis*- and *trans*-dichloroethylenes must be regarded as insignificant, since for these compounds

(3) L. J. Andrews and R. M. Keefer, THIS JOURNAL, 73, 5733 (1951).

the error in estimating ϵ_c values from the ordinate intercepts in the plot of equation (3), *cf.* Fig. 2, is large.

It is interesting to note that the K value for the iodine–cyclohexene complex is higher than that measured by Benesi and Hildebrand for the iodine benzene complex in n-heptane (1.18), and the maximum extinction coefficients of the cyclohexene and benzene complexes are of the same order of magnitude.

These iodine complexes at the double bond may be structurally similar to the cyclic halonium ion so often discussed as an intermediate in the addition of halogen to the double bond. Certainly a structure of the type, as represented by the resonance forms



is in keeping with the accepted structures for the olefin–silver ion complexes.[2a] It seems likely that the characteristic absorption peaks of these complexes may be interpreted in terms of an intermolecular charge-transfer process, as has been done previously for the aromatic–halogen complexes.[4]

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[4] R. S. Mulliken, THIS JOURNAL, **72**, 605 (1950); **74**, Feb. (1952).

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Experimental Investigation of Fractionation in the Electrophoresis–Convection Apparatus

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A study has been made of the fractionation by electrophoresis–convection of systems containing two protein components. The experimental separation factors are in excellent agreement with the theoretical separation factors and as in the case of single protein systems the experimental rate of transport is in moderately good agreement with the theory. The experimental times of transport correspond to effective field strengths bearing ratios of between unity and one-fifth to the nominal applied field strength.

Introduction

In view of the increasing importance of electrophoresis–convection as a simple convenient method of fractionating aqueous solutions of protein mixtures a systematic experimental study of the conditions determining the rate of transport and the degree of fractionation of proteins by electrophoresis–convection has been undertaken. The results of the investigation of transport in systems containing a single mobile protein component have been presented in a previous article.[2] The results of a study of the fractionation by electrophoresis–convection of systems containing two non-isoelectric protein components is reported in the present paper.

The electrophoresis–convection apparatus as described by Cann, Kirkwood, Brown and Plescia[3] consists of two reservoirs connected by a narrow, vertical, semipermeable channel formed between two sheets of Visking Corporation sausage casing. The top of the upper reservoir is open so that the reservoirs and channel may be filled with a solution of the proteins to be fractionated. In operation the apparatus is filled and immersed in a suitable buffer solution between two flat platinum electrodes arranged to provide a homogeneous electric field across the channel upon the passage of a direct current between them. The field effects a horizontal transport of the protein components establishing horizontal density gradients in the channel, which, under the action of gravity, result in differential migration of the proteins into the lower reservoir. In the case of a single protein system the protein is simply concentrated in the bottom reservoir. External circulation of the buffer is maintained to prevent accumulation of electrolysis products.

The theory of electrophoresis–convection developed by Kirkwood and co-workers[4] predicts that for the general multi-component system $(C_i/C_i^\circ)^{\mu_j} = (C_j/C_j^\circ)^{\mu_i}$ at the time of sampling for any two components i and j of the system, where C_i/C_i° is the ratio of the concentration of component i in the top reservoir to its initial concentration and μ_i is the electrophoretic mobility of component i. From this relation the separation factor, f_2, in the top reservoir for the general two component system can be shown to satisfy

$$\begin{aligned} (1 + X_2^\circ(f_2 - 1))^\beta / f_2 &= \gamma^\beta \\ f_2 &= (C_2/C_2^\circ)/(C_1/C_1^\circ) \qquad (1) \\ \beta &= 1 - \mu_2/\mu_1 \end{aligned}$$

where $\gamma = (C_1 + C_2)/(C_1^\circ + C_2^\circ)$ is the weight fraction of total protein remaining in the top reservoir, and $X_2^\circ = C_2^\circ/(C_1^\circ + C_2^\circ)$ is the initial weight fraction of component 2. Table I presents f_2 as a function of X_2°, β and γ, as calculated from Eq. (1).

The time required to transport a specified fraction of protein from the top to the bottom reservoir of the apparatus can be calculated from the theory. However, in the case of two components, the integrals involved depend upon too many parameters characteristic of the particular pair of proteins to make a systematic tabulation practical.

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[1] U. S. Public Health Service postdoctoral fellow of the National Institutes of Health.

[2] R. A. Brown, J. B. Shumaker, J. R. Cann and J. G. Kirkwood, THIS JOURNAL, **73**, 4420 (1951).

[3] J. R. Cann, J. G. Kirkwood, R. A. Brown and O. J. Plescia, *ibid.*, **71**, 1603 (1949).

[4] J. G. Kirkwood, J. R. Cann and R. A. Brown, *Biochim. et Biophys. Acta*, **5**, 301 (1950); **6**, 606 (1951).