be greater than expected. It does have a large root-mean-square amplitude of 0.11 Å. Prepublication calculations by Dewar and Bodor[13] are given in brackets in Figure 7. Agreement for C_3—C_4 and C_2—C_8 is excellent; for C_4—C_5 it is adequate, since the calculated values often are 0.01–0.02 Å short. However, the comparison for C_1—C_5, C_1—C_2, and C_2—C_3 is disturbing, in that their relative orders appear to be inverted. Models in which C_1—C_5 was constrained to be larger than C_2—C_3 were tested extensively but no suitable combination of parameters was found which gave an acceptable R value.

The assignment of classical orbitals to this molecule is not appropriate since these suggest no rationale for the observed rapid interconversion. Note that C_s symmetry provides two A_1 and two A_2 molecular orbitals for the p electrons on C_3, C_4 and C_6, C_7. One each of the A_1 and A_2 MO's serve as two π-bonding orbitals, and the other two provide two π-antibonding orbitals. If these are the only π orbitals in the molecule, to excite them or to break a σ bond would require an energy of the order of 80 kcal. Hence a Walsh-like model[14] must be introduced to describe the bonding situation around C_1, C_2, C_8, which must be modified to show greater overlap at C_1C_2 and C_1C_8 than at C_2C_8. One must allow for a similar description for the anticipatory cyclopropene ring at C_4, C_5, C_6; these would have to contribute (in part) two p orbitals that are not directly involved in the bonding of the hydrogens in the direction perpendicular to the σ-orbital plane. This suggest some π–π overlap for the C_1—C_5 bond, giving it the appearance of the central bond in butadiene.

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[13] Professor M. J. S. Dewar and Dr. Nicholas Bodor; many thanks for private communication.

[14] W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).

Use of a Spectral–Solubility Method in Studies of Molecular Complexes of Iodine

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Abstract: A convenient spectral–solubility method has been developed for inferring thermodynamic constants and spectral band parameters for molecular complexes of iodine; solid mixtures of tetramethylammonium pentaiodide and tetramethylammonium triiodide serve as constant activity sources of iodine. The technique has been used to infer formation constants and extinction coefficients of visible and ultraviolet bands of complexes of iodine with the electron donors benzene, diethyl ether, and pyridine in the solvent heptane. Results are compared with those obtained using conventional spectral methods. The polyiodide solubility method is shown to have several important advantages over purely spectral techniques particularly in the study of relatively weak molecular complexes.

The Benesi–Hildebrand equation and related expressions have been widely used in obtaining spectral and thermodynamic parameters characteristic of 1:1 electron donor–acceptor (EDA) complexes of iodine and other acceptors.[2–4] However, these methods are subject to criticism, particularly regarding their utility in studies of weak molecular complexes.

(1) First of all, in using spectral methods to study complex formation, it is necessary to infer two parameters from a set of spectral measurements at various concentrations—the equilibrium constant for formation of the complex (K_c) and the extinction coefficient (ϵ) of a spectral band having an absorbance which varies in direct proportion to the concentration of the molecular complex. Although the product ϵK_c can be determined from measurements restricted to the dilute region, resolution of the product into separate values of K_c and ϵ requires spectral measurements extending into concentration ranges in which a sizable fraction of the least concentrated reacting solute (usually the acceptor) is in the complexed form.[5] Thus, in studies of complexes for which K_c is considerably less than 1 l. mol^{-1}, it is necessary to use solute concentrations well in excess of 1 M. At such concentration levels, the medium is hardly equivalent to pure solvent; in fact it may be expected that both the spectral and the thermodynamic

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[1] (a) University of Oklahoma; (b) University of Oslo.

[2] (a) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969; (b) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

[3] R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London and New York, 1969.

[4] R. L. Scott and D. V. Fenby, *Annu. Rev. Phys. Chem.*, **20**, 111 (1969).

[5] (a) W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965); (b) D. A. Deranleau, *ibid.*, **91**, 4044 (1969).

properties of the solute species are significantly different from the analogous properties at infinite dilution.[6–8] Attempts have been made to account for the effects of sizable concentrations of dissolved solutes on specific and nonspecific interactions of the solvent with the donor, acceptor, and complex molecules.[8–10] In addition, the possibility has been considered that EDA complexes other than the 1:1 adduct may form at large donor concentrations.[5b,11]

(2) Second, the interpretation of spectra of solutions of donor, acceptor, and complex may be complicated by the presence of numerous orientation isomers of the 1:1 complex[12,13] or by contact charge transfer.[12] The Benesi–Hildebrand method, if it is applicable at all to such systems, yields a value for K_c which is the sum of the formation constants of all the isomers of the 1:1 complex. However, the calculated value of ϵ is a weighted average of the extinction coefficients of the various orientation isomers, and it has been suggested that adducts less stable than the thermodynamically favored one contribute disproportionately to the absorbance.[12] Effects of this sort may explain the unexpected apparent decrease in ϵ with increasing donor strength which occurs with aromatic hydrocarbon–iodine complexes.[12,14] Unfortunately, the force of these arguments is weakened by doubts as to the validity of spectrally determined values of K_c and ϵ, at least in the case of weak complexes (*vide supra*).

In developing and testing theories of EDA interactions, it is essential that we acquire accurate values of K_c and ϵ for weak complexes for which conventional spectral methods alone cannot yield reliable results. In order to supplement the spectral results, we believe that it will be fruitful to employ several nonspectral methods (such as solubility, vapor pressure, and colligative property techniques) in studies of the formation of weak complexes. These methods are capable of giving reliable values of K_c for complexes in solutions so dilute that only a small fraction of either the donor or the acceptor molecules is in the complexed form.[15] We have initiated programs of research in our laboratories in which spectral and classical methods are being employed conjunctively to acquire accurate information about both the spectra and energetics of molecular complexes.[7,16] The present communication describes a new spectral–solubility method for studying complexes of iodine in relatively inert solvents and in the vapor phase. Mixtures of solid polyiodides (tetramethylammonium triiodide and tetramethylammonium pentaiodide) are employed as sources of constant iodine activity.[17] In solution studies, the pure solvent and solutions of donor in the solvent are equilibrated with the polyiodide mixture; samples of the equilibrium liquid solution are removed and examined with regard to their absorption spectra and total concentration of dissolved iodine. Values of spectral constants and K_c are reported for complexes of iodine with pyridine, diethyl ether, and benzene in the solvent heptane.

Experimental Section

Heptane (Fisher Spectral Quality) was stored over molecular sieves in a 3-ft glass column. Iodine (Malinckrodt "Resublimed" Reagent Grade) and tetramethylammonium iodide (Matheson, 99+%) were used without further purification. Tetramethylammonium pentaiodide ($TMAI_5$) was prepared using the method of Chattaway and Hoyle.[18] The melting point (128–130°) and available iodine (71.6%), determined by thiosulfate titration, were in good agreement with the expected values.

The liquid donors were distilled through a 30-plate Oldershaw column isolated from water vapor in the atmosphere. Benzene (Matheson Spectroquality) did not discolor sulfuric acid; it was distilled from $CaSO_4$, and the middle portion of the distillate was collected and stored over molecular sieve. Diethyl ether (Malinckrodt, Anhydrous Reagent Grade) was distilled from calcium hydride and used immediately. Pyridine (Baker, ACS) was distilled from BaO and stored over KOH.

Technique. The experimental method for obtaining K_c and ϵ is based upon establishing the equilibrium

$$TMAI_5(s) = TMAI_3(s) + I_2(\text{heptane})$$

and observing changes in the iodine concentration and spectra which occur upon addition of a donor to the heptane solutions. Equilibration of solid $TMAI_5$ with pure heptane or a heptane solution containing dissolved donor induces the dissolution of some iodine, producing an equivalent number of moles of solid $TMAI_3$.[16a] The resulting solid mixture of $TMAI_3$ and $TMAI_5$ is the constant activity source for iodine. In the analysis of data it is assumed that the only iodine species present in solution are free and complexed molecular iodine. In the case of the ether- and pyridine–iodine systems, none of the solutions examined exhibited a significant absorbance around 360 or 290 nm, where I_3^- has been reported to absorb.[19] However, at benzene concentrations in excess of 4 *M*, a broad shoulder appears on the low frequency side of CT band of the benzene·I_2 complex, which may indicate the presence of traces of dissolved I_3^-. Since the analysis of data (*vide infra*) is restricted to the dilute solution region in which there is no evidence that I_3^- or other anionic forms of iodine are soluble, it is unlikely that the results are affected by the solubilization of polyiodide species.

Mixtures of solvent–$TMAI_5$ and (donor + solvent)–$TMAI_5$ were prepared by placing approximately 0.5-g samples of $TMAI_5$ in 150-cc screw cap bottles; donor–solvent mixtures of known concentration were added to the bottles, and the openings were quickly covered with a piece of polyethylene sheet, which formed an air-tight seal when the cap was tightened. All the donor–solvent mixtures except those containing diethyl ether were prepared volumetrically at 25°; concentrations were corrected for volume contraction in the case of systems studied at 15°. In order to minimize losses by evaporation, the ether solutions were prepared in a cold room (0.5°). The bottles containing the equilibrating mixtures were placed in a constant temperature bath (15 or 25°, ± 0.02°) and occasionally shaken to speed equilibration. Equilibrium was normally attained within 4 or 5 days, as indicated by the constancy of total iodine concentration in solution. After equilibration, the polyethylene seals were punctured with the tip of a disposable pipette and solutions were removed and transferred directly to spectral cells for measurement of absorbance. The

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(6) Reference 3, pp 160–165 and 171–173.

(7) S. D. Christian and E. E. Tucker, *J. Phys. Chem.*, **74**, 214 (1970).

(8) Reference 2a, pp 92–100.

(9) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965).

(10) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Amer. Chem. Soc.*, **88**, 2717 (1966).

(11) Reference 3, pp 167–170.

(12) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).

(13) (a) D. Atack and O. K. Rice, *J. Phys. Chem.*, **58**, 1017 (1954); (b) O. K. Rice, *Int. J. Quantum Chem.*, **2S**, 219 (1968).

(14) Reference 3, pp 72–76.

(15) (a) S. D. Christian, E. E. Tucker, and H. E. Affsprung, *Spectrochim. Acta, Part A*, **23**, 1185 (1967); (b) S. D. Christian, A. A. Taha, and B. W. Gash, *Quart. Rev., Chem. Soc.*, **24**, 20 (1970).

(16) (a) J. D. Childs, S. D. Christian, J. Grundnes, and S. R. Roach, *Acta Chem. Scand.*, **25**, 1679 (1969); (b) J. Grundnes, S. D. Christian, V. Cheam, and S. B. Farnham, *J. Amer. Chem. Soc.*, **93**, 20 (1971).

(17) A related solubility method, using solid iodine as a source of constant iodine activity, has been employed by Kortüm and coworkers [G. Kortüm and M. Kortüm-Seiler, *Z. Naturforsch. A*, **5**, 544 (1950); G. Kortüm and W. M. Vogel, *Z. Electrochem.*, **59**, 16 (1955)] in thermodynamic studies of molecular complexes of iodine.

(18) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, 654 (1923).

(19) A. I. Popov and R. F. Swensen, *J. Amer. Chem. Soc.*, **77**, 3724 (1955).

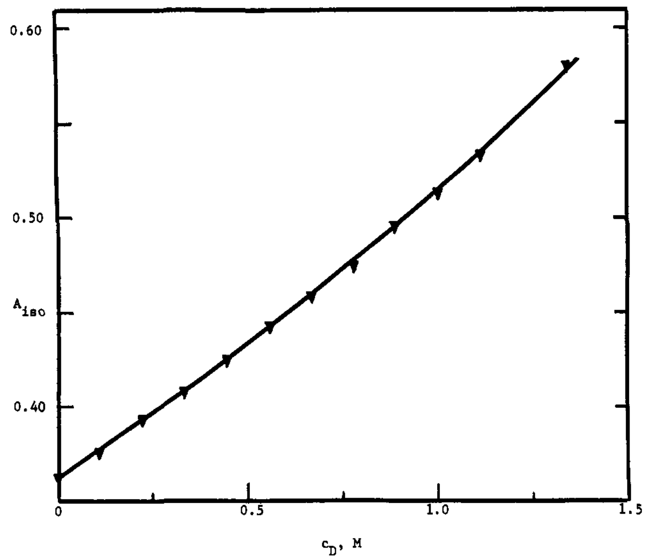

Figure 1. Absorbance at the isosbestic wavelength (520 nm) of solutions of benzene (at molar concentration C_D) and iodine in heptane, at constant iodine activity at 25°; curve represents least-squares quadratic fit of absorbance data for a path length of 2 cm. The limiting concentration of I_2 in heptane, at zero donor concentration, is 1.97×10^{-4} *M.*

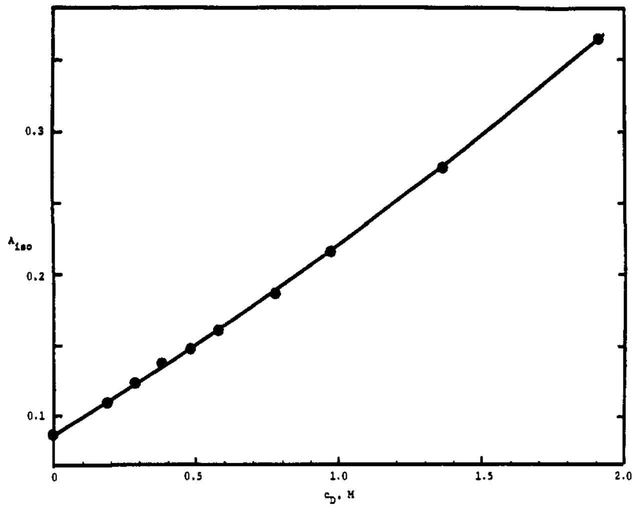

Figure 2. Absorbance at the isosbestic wavelength (494 nm) of solutions of diethyl ether (at molar concentration C_D) and iodine in heptane, at constant iodine activity at 15°; curve represents least-squares quadratic fit of absorbance data for a path length of 2 cm. The limiting concentration of I_2 in heptane, at zero donor concentration, is 1.22×10^{-4} *M.*

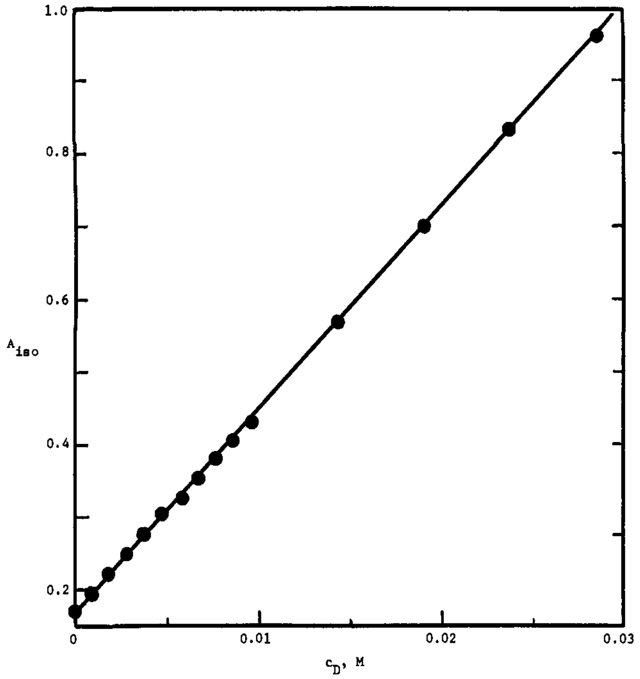

Figure 3. Absorbance at the isosbestic wavelength (477 nm) of solutions of pyridine (at molar concentration C_D of uncomplexed pyridine) and iodine in heptane, at constant iodine activity at 25°; curve represents least-squares linear fit of absorbance data for 2-cm path length. The limiting concentration of I_2 in heptane, at zero concentration, is 1.97×10^{-4} *M.*

bottles were recapped and the samples were preserved for use in subsequent experiments at the same or a different temperature.

Spectral measurements were made with a Beckman DU-2 spectrometer equipped with a variable-temperature cell compartment. The temperature of the solutions could be controlled to ±0.2°. Except for the diethyl ether solutions, all spectral measurements were made at 25°. In determining the total iodine concentration, it was only necessary to measure absorbance at the isosbestic wavelength, λ_{iso}; in fact, once a solution had been removed from the equilibration vessel at either temperature, analysis for total iodine could be completed without regard for the influence of temperature on the complex-formation equilibrium. To avoid problems of evaporation of ether from the cell, all measurements of the ether system were conducted at a cell temperature of 15°.

In order to obtain spectral data from which equilibrium constants and extinction coefficients could be calculated, it was necessary to determine accurate values of the isosbestic wavelength for each system; the following procedure was used in determining λ_{iso}. Equal aliquots of a standard I_2 solution and varying amounts of donor were added to heptane and diluted to a final constant volume with heptane. Spectral measurements made through a range of wavelengths in the vicinity of λ_{iso} (at 1-nm increments) yielded absorbance data at constant total concentration of iodine, from which λ_{iso} could be determined to within ±1 nm. The values of λ_{iso} obtained for the various systems were: benzene, 520; diethyl ether, 494; and pyridine, 477 nm; in good agreement with literature results. A slight error in determination of λ_{iso} will not lead to sizable errors in the determination of iodine concentration in the case of the benzene system, inasmuch as λ_{iso} falls in a relatively flat region of the spectral curve. Errors in λ_{iso} are somewhat more important in the ether and pyridine systems, since the extinction coefficient varies more rapidly with λ in the vicinity of the isosbestic point.

One important parameter which can be inferred directly from spectral measurements on the equilibrated solutions is ϵ_{CT}, the extinction coefficient of the EDA complex at the CT-band maximum. Liquid samples from the equilibrator vessels were introduced into spectrometer cells, thermostatted at the same temperature as that used in the equilibration. Simultaneous measurements were made of the absorbances at the isosbestic wavelength and at the wavelength corresponding to the maximum intensity of the CT band (A_{iso} and A_{CT}, respectively). In the dilute concentration region, ΔA_{CT} (the change in A_{CT}, corrected for the absorbance of free iodine and donor) varies linearly with ΔA_{iso} (the change in absorbance at λ_{iso}). If one attributes the total enhancement of iodine solubility to formation of the complex (*vide infra*), the limiting slope of a plot of ΔA_{CT} against ΔA_{iso} may be equated to the ratio $\epsilon_{CT}/\epsilon_{iso}$. Since ϵ_{iso} is simply equal to the known extinction coefficient of iodine in pure heptane at λ_{iso}, ϵ_{CT} may be calculated directly. A prime advantage of the present experimental procedure over previous spectral methods is that ϵ_{CT} can be determined independent of K_c from measurements at two wavelengths in the very dilute solution region.

Conventional spectral experiments of the Benesi-Hildebrand type[3] were performed to obtain data for comparison with previous literature results. Spectral data were analyzed using a computer method described previously.[20]

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(20) J. Grundnes and S. D. Christian, *J. Amer. Chem. Soc.*, **90**, 2239 (1968).

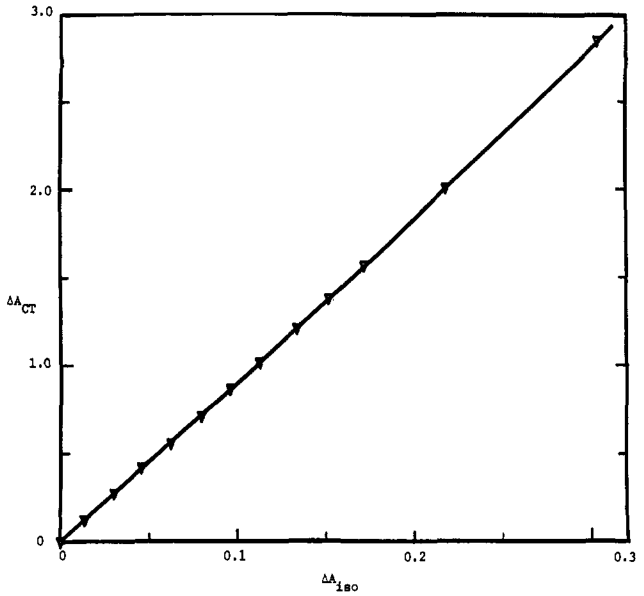

Figure 4. Change in absorbance at the wavelength of the CT band maximum (288 nm) as a function of change in absorbance at the isosbestic wavelength (520 nm) for solutions of benzene and iodine in heptane at constant iodine activity; curve represents least-squares quadratic fit of data. ΔA_{CT} is normalized to 2-cm path length.

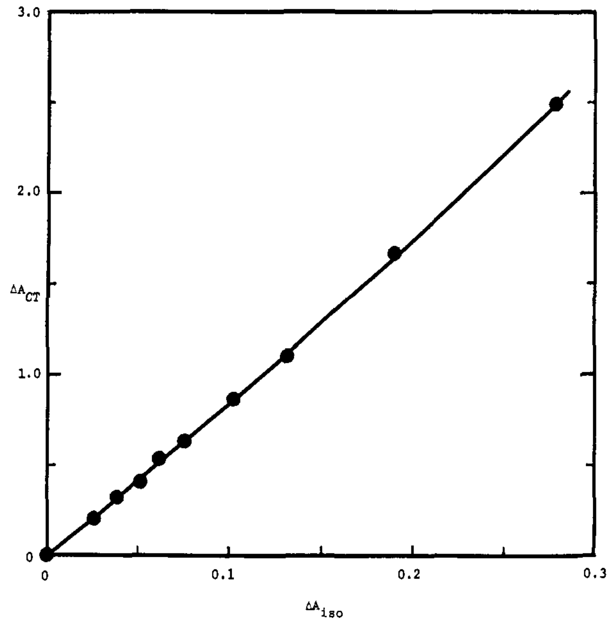

Figure 5. Change in absorbance at the wavelength of the CT band maximum (250 nm) as a function of change in absorbance at the isosbestic wavelength (494 nm) for solutions of diethyl ether and iodine in heptane at constant iodine activity; curve represents least-squares quadratic fit of data. ΔA_{CT} is normalized to 2-cm path length.

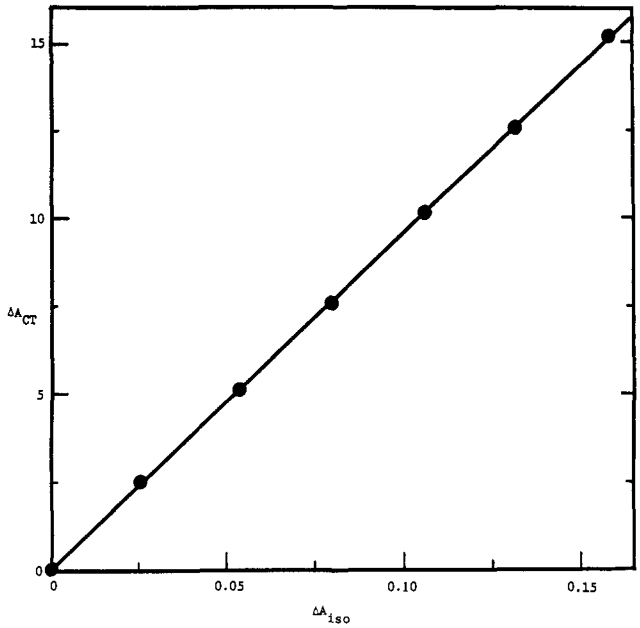

Figure 6. Change in absorbance at the wavelength of the CT band maximum (250 nm) as a function of change in absorbance at the isosbestic wavelength (477 nm) for solutions of pyridine and iodine in heptane at constant iodine activity; curve represents least-squares linear fit of data. ΔA_{CT} is normalized to 2-cm path length.

Results and Discussion

The interpretation of results from the $TMAI_5$–$TMAI_3$ solubility experiments is remarkably simple, provided one is willing to assume that each of the solute species individually obeys Henry's law in the limiting region of concentration[21] and that nonspecific donor–iodine interactions are either negligible or accounted for as part of the derived value of the equilibrium constant.[22] Thus, in very dilute solutions of donor dissolved in heptane, the increase in solubility of iodine (at fixed iodine activity) is equated to the concentration of complex. However, at the isosbestic point the extinction coefficient of uncomplexed iodine (ϵ_{iso}) is known and equal to that of the complex; therefore, measurement of the increase in absorbance at the isosbestic wavelength indicates directly the concentration of the 1:1 complex at a known, constant concentration of uncomplexed I_2. And, as was noted in the previous section, the limiting ratio of the increase in absorbance at the CT-band maximum to that at the isosbestic point may be set equal to $\epsilon_{CT}/\epsilon_{iso}$.

Figures 1–3 are plots of A_{iso} against molar concentrations of the free donor (c_D) for the systems benzene–, diethyl ether–, and pyridine–iodine.[24] From the limiting slopes of these curves, values of K_c corresponding to the infinitely dilute solution can be calculated (K_c = slope/intercept).[25] An interesting feature of the curves

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(21) This assumption is also required in the Benesi–Hildebrand and related analyses of spectral data, although users of the spectral methods have frequently assumed that variations in the activity coefficients of the solute species will fortuitously cancel in the expressions derived for equilibrium constants. With the present method, it is not difficult to obtain unambiguous values of the limiting slopes of plots such as those in Figures 1–3, corresponding to extrapolation into the infinitely dilute region.

(22) Attempts have been made to divide changes in the activity of a solute in the presence of dissolved donor into a part owing to specific donor–solute interactions and a part arising from nonspecific effects which can be accounted for by using solubility parameter theory.[8,17] However, there is no unambiguous way to separate these effects, and we prefer to report equilibrium constants accounting for the entire enhancement of solubility of iodine. Childs[23] has recently discussed the contribution of nonspecific interactions to values of molecular complex formation constants derived from solubility data.

(23) J. D. Childs, Ph.D. Dissertation, The University of Oklahoma, 1971.

(24) In the benzene and ether systems, c_D is considerably greater than the concentration of the complex, so that the total donor concentration is virtually equal to c_D. In the case of the pyridine system, c_D is calculated by correcting the total pyridine concentration for the concentration of pyridine in the complexed form.

(25) In the limiting linear regions of plots such as those in Figures 1 and 2 the observed absorbance at the isosbestic wavelength may be

Table I. Formation Constants and Spectral Results for Complexes of Iodine with Benzene, Diethyl Ether, and Pyridine in Heptane

		Solubility method			Spectral method			
Donor	Temp, °C	K_c, l./mol	ϵ_{CT}, cm^{-1} l. mol^{-1}	$\epsilon_{CT}K_c$	K_c, l./mol	ϵ_{CT}, cm^{-1} l. mol^{-1}	$\epsilon_{CT}K_c$	Ref
Benzene	25	0.356 ± 0.008	8,080 ± 80	2880 ± 85	0.150	18,000	2700	*a*
					0.211 ± 0.012	14,200 ± 500	2950 ± 270	*b*
Diethyl ether	15	1.44 ± 0.06	5,720 ± 70	8233 ± 361	1.23 ± 0.05	5,560 ± 90	6840 ± 280	*b*
					1.3	5,480	7124	*c*
Pyridine	25	163 ± 2	41,400 ± 1000	$(6.7 \pm 0.1) \times 10^6$	185	50,000	1×10^7	*d*
					137 ± 5	51,730	7.1×10^6	*e*
					142 ± 8			*f*
					157 ± 1			*g*

[a] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949). [b] This work. [c] S. M. Brandon, M. Tamres, and S. Searles, *J. Amer. Chem. Soc.*, **82**, 2129 (1960). [d] C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954). [e] H. D. Bist and W. B. Person, *J. Phys. Chem.*, **71**, 2750 (1967). [f] P. V. Huong, N. Platzer, and M. L. Josien, *J. Amer. Chem. Soc.*, **91**, 13 (1969). [g] W. J. McKinney and A. I. Popov, *ibid.*, **91**, 5215 (1969).

in Figures 1 and 2 is the significant positive curvature which is observed even at donor concentrations less than 1 *M*. Clearly, at least in the case of the benzene system, the laws of dilute solution do not apply up to the higher donor concentrations which have been employed in inferring K_c and ϵ_{CT} with the Benesi–Hildebrand technique. However, for all the systems represented here, it is easy to obtain a value of the limiting slope and to calculate the single unknown parameter, K_c, from the A_{iso} *vs.* c_D data.[23,25] It should be emphasized that the concentration of iodine does not exceed 10^{-3} *M* in any of the solutions used in obtaining the data for Figures 1–3; in previous applications of the solubility method, in which pure iodine was used as a source of constant iodine activity, the levels of iodine concentration were several hundred times greater.[17]

Figures 4–6 show plots of ΔA_{CT} against ΔA_{iso}, from which it is possible to infer values of ϵ_{CT} for the donor·I_2 complexes (see Experimental Section). In the case of the benzene complex, the ΔA_{CT} *vs.* ΔA_{iso} plot is linear throughout a wider range of concentration than the plot of A_{iso} *vs.* c_D. This suggests the possibility that Beer's law is obeyed by the individual species (complex and I_2) beyond the range in which Henry's law applies.

Table I summarizes spectral parameters and K_c values obtained with the polyiodide solubility technique; it also includes results from the literature and from the present research inferred solely from spectral data. Reported values of the product $K_c\epsilon_{CT}$ are fairly consistent for a given complex, whether determined by the solubility method or from spectral measurements alone. However, for the weakest of the three complexes (benzene·I_2) the solubility method yields a much larger value of K_c and a correspondingly reduced value of ϵ_{CT}. Results for the ether system show less discrepancy, although K_c determined by the solubility method is somewhat greater than the spectral value. In the case of the moderately strong pyridine·I_2 complex, both K_c and ϵ_{CT} agree reasonably well from one method to the other.

We suggest that the polyiodide solubility method presented here deserves consideration as a convenient alternative to purely spectral methods for determining K_c and ϵ_{CT} for weak molecular complexes of iodine. The method combines the advantages of previous solubility and spectral procedures, while avoiding several weaknesses in the earlier methods. Both K_c and ϵ_{CT} are obtained from spectral measurements in the very dilute solution region on the same set of solutions; extrapolations of spectral data from unreasonably high concentration regions are unnecessary. A criticism directed at Kortüm's solubility method[26]—that the I_2 concentrations are too large compared to those employed in the spectral experiments to allow a direct comparison of the two methods—is avoided, inasmuch as the iodine concentrations fall in the same ranges as those commonly employed in spectral experiments. Adherence to the dilute solution laws, in the limiting regions of concentration for which accurate data are obtained with the present method, is much more likely. In these limiting regions, complexes of stoichiometry other than 1:1 should not ordinarily be present in concentrations sufficient to complicate the interpretation of data. However, it should be noted that if several forms of the 1:1 complex do exist, the present method and the Benesi–Hildebrand method both will yield K_c values which are sums of the formation constants for the individual orientation isomers (see introduction, subparagraph 2).

Childs, *et al.*, have recently used the polyiodide solubility method to redetermine values of K_c and ϵ_{CT} for several alkyl benzene–iodine complexes,[23] for which it has been reported that ϵ_{CT} decreases as the donor strength increases. The new results yield K_c values which are larger and ϵ_{CT} values which are correspondingly smaller than those previously reported. There is relatively little variation in ϵ_{CT} for iodine complexes

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written $A_{iso} = A^0_{iso} + l\epsilon c_{DI_2}$ where A^0_{iso} is the absorbance of the iodine solution obtained by equilibrating pure heptane with $TMAI_3(s)/TMAI_5(s)$, and where it is assumed that the total increase in solubility of iodine owes to formation of the complex, DI_2. Then, $c_{DI_2} = \Delta A_{iso}/(l\epsilon_{iso})$ and $K_c = c_{DI_2}/(c_D c_{I_2}) = [\Delta A_{iso}/(l\epsilon_{iso})]/(c_D A^0_{iso}/l\epsilon_{iso})] = (\Delta A_{iso}/c_D)/A^0_{iso}$, where the numerator $(\Delta A_{iso}/c_D)$ is the limiting slope of a plot of A_{iso} *vs.* c_D, and the denominator (A^0_{iso}) is the intercept of such a plot at $c_D = 0$. In fitting data for systems exhibiting curvature in the A_{iso}–c_D plots, it is convenient to use a numerical least-squares technique to obtain A_{iso} as a quadratic function of c_D and to identify the limiting slope $(dA_{iso}/dc_D)_{c_D=0}$ as the coefficient of the linear term in the expression $A_{iso} = A^0_{iso} + \alpha c_D + \beta c_D{}^2$. This procedure yields values of α with small error limits for data such as those depicted here.[23] Alternatively, an apparent value of K_c may be calculated point by point from the relation $K_c{}^{app} = \Delta A_{iso}/(c_D A^0_{iso})$ and the values plotted against c_D. A linear plot results, with an intercept at $c_D = 0$ equal to K_c.

(26) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *Recl. Trav.Chim. Pays-Bas*, 71, 1104 (1952). A reviewer has commented that this is probably not a fair criticism of the Kortüm method, and in fact where direct comparisons can be made, the Kortüm technique and the polyiodide solubility method yield quite similar results.

of the various aromatic hydrocarbon donors, although K_c increases with donor strength as expected. A discussion of these results, including correlations of K_c and of λ and ϵ of the blue-shifted band with donor strength, is given elsewhere.[23,27]

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(27) J. D. Childs, S. D. Christian, and J. Grundnes, unpublished results.

Modes of Rearrangement in Phosphoranes

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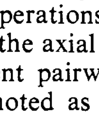
Abstract: The types or modes of rearrangement that a trigonal bipyramid molecule can undergo are presented. The limited experimental evidence on phosphorane rearrangements, pertinent to distinguishing among these modes, is analyzed.

In 1950 Gutowsky and Hoffman[1] observed the ^{19}F nmr spectrum of PF_5 to be a doublet which implied[2] an intramolecular rearrangement equilibrating the equatorial and axial sites of the trigonal bipyramid (TBP) determined by electron diffraction. It has been generally accepted[3] that the rearrangement observed in PF_5 and in other phosphoranes takes place *via* the pseudorotation mechanism proposed by Berry in 1960.[4] There has, however, been no presentation of the simple problem in combinatorics which provides a description of all the experimentally distinguishable kinds of rearrangement or "modes of rearrangement" that a TBP molecule can undergo, without which a meaningful analysis of the experimental data cannot be made.

The question of mode of rearrangement is an unfamiliar one since in organic chemistry all rearrangements about an atom involve only one observable consequence: racemization among the two distinguishable isomers as in amines, sulfoxides, phosphine oxides, and substituted methanes. The TBP geometry of phosphoranes with its two axial and three equatorial sites for ligands is such that there are five different modes of rearrangement or types of possible stereochemical change, and these are discussed here along with the limited experimental evidence which might serve to distinguish among them. These modes describe all the basic stereochemical modifications of a TBP so that every TBP rearrangement can be classified according to which one or more of these modes is attained by the rearrangement mechanism involved. The arguments presented here could equally well be applied to rearrangements in all other TBP molecules.

Theory and Discussion

We consider the number of ways that the labeled ligands of a phosphorane **1** can be rearranged among



1

themselves while preserving the explicit location on the TBP of three, two, one, and none of the ligands, respectively. At the same time we must group together all permutations among the indices or *apparent* rearrangements which give *indistinguishable* TBP's differing only by one of the six operations of the point group C_{3v}.

If a and e symbolize the axial and equatorial ligands, respectively, the different pairwise or two-ligand rearrangements can be denoted as the symbolic permutations, ae, aa, and ee, the three-ligand rearrangements as aae, aee, and eee, the four-ligand rearrangements as aaxee, aexee, and aexae, which are concerted pairs of pairwise rearrangements, and eeea, eeaa, and eaea, and the five-ligand rearrangements as aaxeee, aexaee, eexaae, aaeee, and aeaee. The ordering of the letters is in the permutational sense so that, for example, eaea means that an equatorial ligand goes to an axial site, that axial ligand goes to the next equatorial site, that equatorial ligand goes to the next axial site, and that axial ligand goes to the original equatorial site. The operations of the point group are such that each stereoisomer can be obtained by more than one of the permutation operations, so that there are only six distinct *types* of rearrangements which we call "modes" and specify as

$$\mathrm{M}_0(1) = \mathrm{I},\ \mathrm{eee},^2\ \mathrm{aaxee}^3$$
$$\mathrm{M}_1(3) = \mathrm{eaea}^2\ (\mathrm{BPR}),\ \mathrm{aexaee}^4\ (\mathrm{TR})$$
$$\mathrm{M}_2(6) = \mathrm{ae},\ \mathrm{eeea},^2\ \mathrm{eeaa},^2\ \mathrm{eexaae}\ (\mathrm{TR}')$$
$$\mathrm{M}_3(1) = \mathrm{aa},\ \mathrm{ee},^3\ \mathrm{aaxeee}^2$$
$$\mathrm{M}_4(6) = \mathrm{aee}^2\ (\mathrm{R}_3),\ \mathrm{aae}\ (\mathrm{R}_3'),\ \mathrm{aexee},\ \mathrm{aaeee}^2$$
$$\mathrm{M}_5(3) = \mathrm{aexae}^2\ (\mathrm{DPR}),\ \mathrm{aeaee}^4$$

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(1) H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, 80, 110 (1950); *J. Chem. Phys.*, 19, 1259 (1951).

(2) This interpretation, of course, rests on the assumption that this is not due to an accidental near magnetic equivalence of the TBP fluorine atoms.

(3) See, for example, the review of R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 4, 496 (1965).

(4) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).