Studies on the Chemistry of Halogens and of Polyhalides. XXX. The Influence of Solvent Properties on the Formation of Pyridine–Iodine Charge-Transfer Complexes

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Abstract: Formation constants of the pyridine–iodine charge-transfer complex have been determined at 25° in 12 solvents with dielectric constants varying from 1.92 to 10.36. The K_X values range from 612 in *n*-hexadecane to 3248 in *o*-dichlorobenzene. The enthalpies and entropies of the complex formation have been determined in five solvents. Comparison of the data with the solvent properties indicates that an increase in the dielectic constant of the reaction medium leads to the stabilization of the pyridine–iodine complex. The phenomenon is complicated, in some cases, by specific solute–solvent interactions, such as solvation of pyridine by chloroform or by the formation of triiodide ion in polar solvents.

During the past two decades, abundant literature has been developed on the subject of molecular charge-transfer complexes.[1] The interest in charge-transfer complexes has been largely stimulated by the rich variety of possible complexes, their importance in biological systems, their importance as reaction intermediates, and, to some extent at least, by the relative ease of experimental studies.

While numerous authors have studied the influence of the structure of the donor and/or acceptor molecules on the complex-forming reaction, the effect of the properties of the reaction medium has not been carefully scrutinized. Merrifield and Phillips[2] studied the complex between tetracyanoethylene (TCNE) and three benzene derivatives. The complexes were examined in three solvents, dichloromethane, diethyl ether, and chloroform. The difference in the equilibrium constants was explained by invoking a solvent competition for the TCNE. Formation constants for the TCNE–solvent interaction were determined relative to an assumed value of zero for the TCNE–chloroform complex. The values for the benzene and substituted-benzene complexes were then corrected for this interaction, and the apparent discrepancy between the equilibrium constants was eliminated within experimental error. Solvent competition for one of the adducts was also used by Foster and Hammick[3] to explain the results they obtained on the N,N-dimethylaniline–*s*-trinitrobenzene system.

Some studies have also been carried out on complexes which are more polar than the π–π type of interaction in the TCNE complexes. In two of these cases, the Lewis acid used was iodine. The bases in these two studies were N,N-dimethylacetamide[4] and triphenylarsine.[5] Dichloromethane, benzene, dioxane, and 3-methysulfolane were used in the first investigation and dichloromethane, carbon tetrachloride, and acetonitrile in the second. In both cases, reactions in solvents with high dielectric constants (3-methylsulfolane and acetonitrile) yielded triiodide ion as a reaction product. While the number of solvents studied was rather small, the results seemed to indicate an increase in the strength of the complex with increasing dielectric constant of the solvent. On the surface, these results would seem to be contrary to Briegleb's[6] prediction that complex formation constants would have an inverse functional dependence on the dielectric constant of the solvent. However, his prediction was based on the formation of a nonpolar complex in which the effect of complexation would be to squeeze out solvent molecules in the solvation sphere of the two reactants. This action should result in a weakening of the complex since the uncomplexed reactants would be more highly solvated than the complex. This effect should increase with increasing dielectric constant of the medium. Bhaskar and Singh[7] previously reported that the formation constant of the pyridine–iodine complex *decreased* with increasing dielectric constant of the reaction medium. These results cannot be regarded as conclusive for several reasons. In the first place, the authors used *n*-hexane, *n*-heptane, cyclohexane, carbon tetrachloride, and chloroform as solvents. The range of dielectric constants, therefore, was very narrow with chloroform having the highest dielectric constant of 4.8, and the values for other solvents hover around 2. Likewise, the differences in the values of the formation constants were very small, and no attempt was made to correct the results obtained in chloroform for the hydrogen-bonding equilibrium between the solvent and pyridine.[8]

Experimental Part

The sources and the purification of the solvents used are given in Table I. Purification procedures for pyridine and iodine were given in a previous publication.[9]

Solutions. Stock solutions of pyridine and iodine were prepared by weighing a quantity of the reactant into a clean, dry volumetric

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[1] (a) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964; (b) G. Briegleb, "Electronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961; (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[2] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[3] R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2685 (1954).

[4] R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **88**, 2717 (1966).

[5] E. Augdahl, J. Grundnes, and P. Klaboe, *Inorg. Chem.*, **4**, 1475 (1965).

[6] G. Briegleb, ref 1b, pp 117–118.

[7] K. R. Bhaskar and S. Singh, *Spectrochim. Acta*, **23A**, 1155 (1967).

[8] P. J. Berkely, Jr., and M. W. Hanna, *J. Phys. Chem.*, **67**, 846 (1963).

[9] W. J. McKinney, M. K. Wong, and A. I. Popov, *Inorg. Chem.*, **7**, 1001 (1968).

Table I. Source and Purity of the Solvents Used in This Research

Solvent	Source	Purification
Dichloromethane	Fisher "Certified"	Distilled from BaO, bp 39.9° (760 mm)
n-Heptane	Aldrich Chemical Co.	Stirred with several portions of concd H_2SO_4 until acid no longer became colored, washed with H_2O, and distilled from BaO, bp 98.3° (760 mm)
Chloroform	Malinckrodt, N. F.	Washed seven times with 50% its volume of H_2O and dried over $CaSO_4$, water content <2m*M*, bp 61.1° (760 mm)
o-Dichlorobenzene	Eastman "99 + %"	Stirred for 24 hr with concd H_2SO_4, washed three times with H_2O, and distilled from BaO, bp 181° (760 mm)
m-Dichlorobenzene	Aldrich Chemical Co.	Distilled from BaO, bp 173° (760 mm)
n-Hexadecane	Aldrich Chemical Co.	Stirred with concd H_2SO_4, washed with H_2O, and vacuum distilled from BaO, fp 18.2°
1,1,2-Trifluorotrichloroethane	Matheson Coleman and Bell "Spectroquality"	Distilled from BaO, bp 46.8°
Benzene	Fisher "99% Mole Pure"	Stirred with concd H_2SO_4; washed with H_2O, dilute KOH, and twice more with H_2O; and distilled from BaO, bp 80.0° (760 mm)
Toluene	Eastman "Sulphur Free"	Same as benzene, bp 110.3° (760 mm)
p-Xylene	Aldrich Chemical Co.	Fractional freezing, fp 13.2°
Carbon tetrachloride	Fisher "Technical"	See A. I. Popov and W. A. Deskin, *J. Am. Chem. Soc.*, **80**, 2976 (1958)
1,2-Dichloroethane	Fisher "Certified"	See A. I. Vogel, *J. Chem. Soc.*, 644 (1948)
Nitromethane	Commercial Solvents Corp.	See G. A. Clarke and S. Sandler, *Chemist-Analyst*, **50**, 79 (1961)

flask. They were then diluted to volume with the appropriate solvent in a water bath thermostated at 25.0°. The proper aliquots of these solutions were then pipetted into another volumetric flask which was brought to volume in a thermostated bath kept at the same temperature at which the final absorption measurements were made.

Solutions of iodine and pyridine were prepared just before each measurement. Contact of solutions with the atmosphere was kept to a minimum, but no attempt was made to do all of the transfers in an inert atmosphere. The results indicate that the brief contacts of the solutions with air did not alter significantly the experimental data. It was found that pyridine slowly catalyzed the dehydrochlorination of chloroform and 1,2-dichloroethane. In these cases, special care was taken to use solutions as soon as possible after their preparation. A study of absorbance *vs.* time for a pyridine–iodine solution in the above solvents showed that the decomposition was inconsequential during the time required to complete the measurements. An attempt to obtain the formation constant of the complex in nitromethane was unsuccessful due to a rapid decomposition of pyridine–iodine solutions.

Measurements of the absorption maximum of the blue-shifted iodine band of the complex were made in a series of mixed solvents obtained by adding varying amounts of nitromethane to carbon tetrachloride. The dielectric constants of these mixed solvents were calculated by use of the principle of additivity (*i.e.*, $D_{\text{calcd}} = X_{CCl_4}D_{CCl_4} + X_{CH_3NO_2}D_{CH_3NO_2}$). The value of the dielectric constant of nitromethane used in the aforementioned calculations was 35.9. The results of these measurements are contained in Figure 2.

Spectral Measurements. Spectral measurements were made on a Beckman DU spectrophotometer with a thermostated cell compartment. The wavelength scale of the instrument was calibrated using a holmium oxide filter. The accuracy of the absorbance scale was checked by the method of additive absorbances and by the method of Haupt[10] using standard alkaline chromate solutions. The temperature of the cell compartment was determined by inserting a calibrated thermometer into the compartment through a styrofoam cover and allowing the system to come to equilibrium. The temperature could be controlled to ±0.1°.

Calculations. The formation constants were calculated using a modified Ketelaar equation. The procedure has been described in a previous publication.[9] The values were changed from M^{-1} to mole fraction units by use of the following relationship

$$K_X = \frac{K_M}{V_S + X_{py}(V_{py} - V_S)} \qquad (1)$$

where K_X and K_M are the mole fraction and the molar equilibrium constants, X_{py} is the mole fraction of pyridine, and V_{py} and V_S are the molar volumes of pyridine and of the solvents. The above equation is based on the assumption that no volume change occurs on mixing. In the present study the concentration of pyridine was always kept below 0.03 *M*, and the concentration of iodine was 10^{-4} *M*. Therefore, $X_{py} < 0.01$, and under these conditions, eq 1 can be reduced to

$$K_X = K_M S^0 \qquad (2)$$

where S^0 is the concentration of pure solvent in moles/liter. Likewise with these low solute concentrations, it seems reasonable to assume that the activity correction would be a constant over the range of donor concentrations used in these studies.

Whenever possible, corrections were made for the solvent–solute interaction. It has been shown that chloroform forms a hydrogen-bonded complex with pyridine[8] with $K_X = 0.69$. Likewise, it is well known that aromatic compounds form charge-transfer complexes with iodine. In fact, the formation constants of benzene, toluene, and xylene complexes with iodine have been reported to be 0.15, 0.16, and 0.31 l. mole^{-1}, respectively.[11]

In order to allow for the solvent–solute interaction in the case of the four solvents mentioned above, the corrected values of the formation constants were calculated from the expression[4,12]

$$K_{\text{cor}} = K_{\text{obsd}}(1 + K_S S^0) \qquad (3)$$

where K_S is the equilibrium constant (M^{-1}) for the solute–solvent interaction, K_{obsd} is the experimental value for pyridine–iodine complex in the given solvent, and S^0 is the concentration of the pure solvent in moles/l.

Results and Discussion

Formation constants of the pyridine–iodine complex in 12 different solvents are presented in Table II. Comparison of these values with various physical properties of the respective solvents indicates a possible correlation only with the dielectric constant of the medium. A plot of *D vs.* K_X is shown in Figure 1. While the points do not fall on a smooth curve, there seems to be little doubt that, other factors being equal, an increase in the dielectric constant of the solvent results in an increase

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(10) G. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(11) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

(12) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

Table II. Formation Constants of the Pyridine–Iodine Complex in Different Solvents

Solvent	K_{fM}[a]	K_{fx}	K_S	$K_{fx,cor}$	D	λ_{max}, mμ
p-Xylene	91.6 ± 0.9	739 ± 7.3	0.31[b]	2588	2.27	402
Toluene	87.8 ± 1.8	822 ± 17	0.16[b]	2053	2.38	405
Benzene	82.9 ± 0.5	928 ± 5.6	0.15[b]	2486	2.28	404
Chloroform	77.7 ± 0.6	963 ± 7.4	0.69[c,d]	1627	4.81	400
n-Heptane	157 ± 1.2	1064 ± 8.1			1.92	424
Carbon tetrachloride	105 ± 0.7	1082 ± 7.2			2.24	416
1,1,2-Trifluorotrichloroethane	159 ± 0.9	1328 ± 7.5			2.41	414
Dichloromethane	151 ± 0.6	2341 ± 9.3			9.08	395
1,2-Dichloroethane	189 ± 2.2	2351 ± 27			10.36	395
m-Dichlorobenzene	225 ± 2.9	1964 ± 25			5.04	404
o-Dichlorobenzene	367 ± 2.1	3248 ± 19			9.93	400
n-Hexadecane	211 ± 2.1	612 ± 6.1			2.05	419

[a] For a compilation of other values of the formation constant of the pyridine–iodine complex in various solvents, see ref 9 and H. D. Bist and W. B. Person, *J. Phys. Chem.*, **71**, 2750 (1967). [b] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952). [c] P. J. Berkeley, Jr., and M. W. Hanna, *J. Phys. Chem.*, **67**, 846 (1963). [d] The value of K_S is given in mole fraction untis. The value of K_S in moles is approximately equal to K_S in molar units times the concentration of pure solvent.

in the stability of the complex. The observed scatter, in all likelihood, is the result of specific solvent–solute interactions.

It seems reasonable to expect that the increase in the bulk dielectric constant of the reaction medium will result in greater stability of the pyridine–iodine complex. The dipole moments of iodine, pyridine, and of the complex are 0.0, 2.20, and 4.90 D, respectively.[13] It appears, therefore, that with increasing polarity of the solvents they will tend to solvate more strongly the highly polar complex and thus contribute to its stability. Kobinata and Nagakura,[14a] as well as Boule,[14b] recently reported a study of the dipole moments of iodine complexes with aliphatic amines in benzene and in dioxane solutions. All of the values obtained were in the 6.0–7.2-D range. The authors noted that the dipole moments of the complexes increased with increasing concentration of the amines in the solvent mixtures. Since the dielectric constant of the medium likewise increased with the amine concentration, the authors interpreted the results by postulating an increase in the stabilization of the charge-transfer structure. These results agree with our observation that in solvents with $D > 15$, the charge separation in the complex increases to the extent where clear-cut separation of the charges occurs with the resulting formation of triiodide ion.

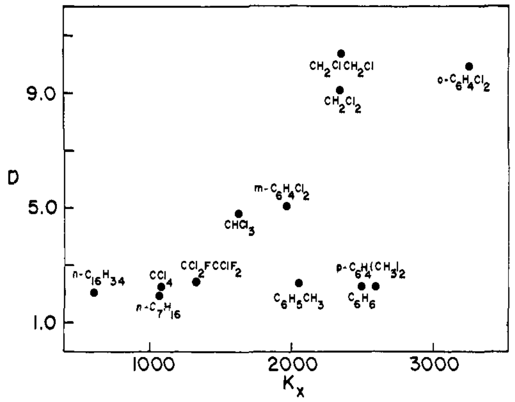

Figure 1. Relationship between the formation constant expressed in mole fraction units of the pyridine–iodine complex and the dielectric constant of the solvent in which it was measured.

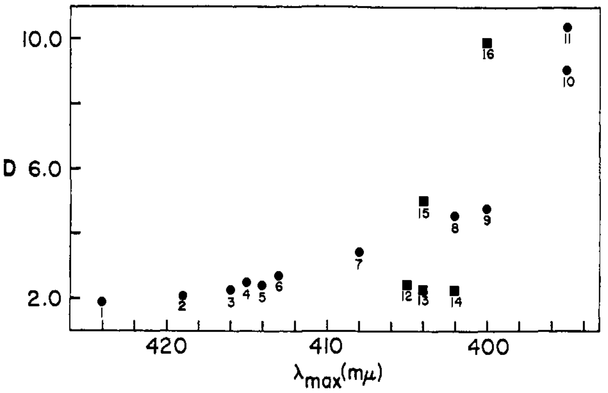

Figure 2. Relationship between the wavelength of maximum absorption of the blue-shifted iodine band of the complex and the dielectric constant of the solvent in which it was measured. Solvents: (1) *n*-heptane; (2) *n*-hexadecane; (3) carbon tetrachloride; (4) $X_{CCl_4} = 0.99284$ and $X_{CH_3NO_2} = 0.00716$, $D_{calcd} = 2.48$; (5) 1,1,2-trifluorotrichloroethane; (6) $X_{CCl_4} = 0.9857$ and $X_{CH_3NO_2} = 0.0143$, $D_{calcd} = 2.72$; (7) $X_{CCl_4} = 0.9646$ and $X_{CH_3NO_2} = 0.0345$, $D_{calcd} = 3.43$; (8) $C_{CCl_4} = 0.9304$ and $X_{CH_3NO_2} = 0.696$, $D_{calcd} = 4.58$; (9) chloroform; (10) dichloromethane; (11) 1,2-dichloroethane; (12) toluene; (13) benzene; (14) *p*-xylene; (15) *m*-dichlorobenzene; (16) *o*-dichlorobenzene.

The above phenomena would be expected from an examination of the theoretical behavior of polarizable dipoles in a changing dielectric medium.[15] Indeed, other ramifications of this behavior would be expected. According to Mulliken's theory[16] of charge-transfer complexes, the spectrum of the complex would be altered by the dielectric constant of the medium. In particular, the energy of the charge-transfer band would be shifted. The direction of this shift would depend upon the relative importance of two factors, if one assumes that the energy of the no-bond wave function remains constant. One effect would be due to the increase in energy of the dative wave function as a result of the increased charge separation, and the other effect would be due to the decrease in energy of the dative wave function as a result of the solvation of the polar

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(13) K. Toyoda and W. B. Person, *J. Am. Chem. Soc.*, **88**, 1629 (1966); value determined in *n*-heptane.

(14) (a) S. Kobinata and S. Nagakura, *ibid.*, **88**, 3905 (1966); (b) P. Boule, *ibid.*, **90**, 517 (1968).

(15) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., New York, N. Y., 1952, p 138.

(16) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3689 (1954).

species. Because of the absorption of pyridine and of the solvents in the ultraviolet region, the charge-transfer band cannot be observed. Lacking this information it is nevertheless informative to examine the relationship between the dielectric constant of the solvent and the wavelength of maximum absorption of the blue-shifted iodine band of the complex shown in Figure 2. The blue-shifted iodine band has been explained by Mulliken.[17] This explanation is based on the assumption that in the excited state of the complex an electron has been transferred from the donor to the iodine molecule. This electron goes into an antibonding orbital of the iodine which is diffuse and increases the effective size of the iodine molecule. When light is absorbed by the complexed iodine molecule, the excitation energy is supplemented by an energy of repulsion between the donor and the abnormally large iodine molecule. The blue shift should become larger with increasingly close contact between the donor and iodine which is related to the bond strength of the complex. Thus the fact that the frequency shift of the iodine band is related to the dielectric constant of the medium is another indication of the influence of the dielectric constant on the complexation reaction. It is also interesting to note the deviation of the points (12–16) in cases where aromatic solvents were used. This can easily be understood in terms of the known specific solute–solvent interactions which have already been mentioned.

Thermodynamic data obtained by measuring the formation constant of the complex as a function of temperature are given in Table III. As can be seen by examining the values, the differences are not significant within experimental error and, therefore, do not, at this time, contribute to our understanding of the role of the solvent in the complexation reaction.

Table III. Enthalpy and Entropy Values for the Pyridine–Iodine Complexation in Different Solvents

Solvent	$-\Delta H$, kcal/mole	$-\Delta S$, eu
n-Heptane	8.16 ± 0.22	17.3 ± 0.8
Carbon tetrachloride	7.47 ± 0.06	15.8 ± 0.2
Dichloromethane	8.59 ± 0.31	18.9 ± 1.1
1,2-Dichloroethane	7.77 ± 0.16	15.6 ± 0.6
Chloroform	7.82 ± 0.19	17.5 ± 0.6

On the basis of the above results it seems reasonable to conclude that the reports on the *decrease* in the stability of iodine complexes with increasing dielectric constant of the medium[7] cannot be correct.

It is clear, however, that it would be naive to expect a monotonic correlation between a given physical property of a series of solvents and the stability of the pyridine–iodine complex since this approach neglects specific solvent–solute interactions. While we endeavored to correct for this in the case of aromatic solvents and chloroform, the correction is tenuous at best and it only takes into account the interaction of iodine with the solvent in the first three cases and of pyridine with the solvent in the last. There is little doubt that weak interactions exist between other solvents and pyridine as well as iodine and that these interactions influence the over-all stability of the complex. In fact, it has been shown recently that there is a significant interaction between pyridine and carbon tetrachloride (as well as other aromatic compounds).[18] In the calculation of formation constants, however, it is a common practive to arbitrarily treat the solvent as an inert dispersing medium regardless of the magnitude of the concentrations of the solutes. In certain cases it may be possible to find systems where such assumptions may be justifiable,[19] but such cases must be rather exceptional. In general, it seems safe to conclude that if we wish to understand the role of the solvent in molecular complex formation, we should know the nature and the extent of solute–solvent interactions with both reactants and products to the maximum accuracy attainable.

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[17] R. S. Mulliken, *Rec. Trav. Chim.*, 75, 845 (1956).

[18] D. A. Bahnick and W. B. Person, *J. Chem. Phys.*, **48**, 1251 (1968).

[19] I. D. Kuntz, Jr., F. P. Gasparo, M. D. Johnston, Jr., and R. P. Taylor, *J. Am. Chem. Soc.*, **90**, 4778 (1968).