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Molecular Compounds. V. Solvent Effects on Complexing of 1,3,5-Trinitrobenzene with Aniline and with Naphthalene

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The equilibrium constants for complex formation have been measured for the 1,3,5-trinitrobenzene-naphthalene complex in chloroform-ethanol mixtures and for the 1,3,5-trinitrobenzene-aniline complex in chloroform-ethanol mixtures and in dioxane-water mixtures. The heats, free energies and entropies of formation of the complexes were determined in 75% chloroform-25% ethanol. The structures of the complexes are discussed.

The response of a reaction rate in solution to solvent changes is a useful criterion of mechanism¹ and can, in some cases, be treated quantitatively.² In discussing solvent effects on an equilibrium, the structure of the transition state may be eliminated from consideration, since an equilibrium constant measures the ratio of the rates of two reactions, both of which have the same transition state.

For molecular complex formation, the effect of the solvent will depend on whether the reactants or the complex are preferentially stabilized by solvation.³ Weiss⁴ has predicted that charge-transfer complexing will be favored by increasing the polarity of the medium. This is based on the fact that the reactants are, in most cases, uncharged while the complex has a contributing structure with a charge separation.⁵

This expectation has been fulfilled for the 2,4-dinitrochlorobenzene-aniline complex⁶ but not for the N,N-dimethylaniline-*sym*-trinitrobenzene complex.⁷ This has led us to make a more detailed study of the effect of solvent changes on the equilibrium constant for complex formation, and we have measured the 1,3,5-trinitrobenzene-aniline equilibrium in chloroform-ethanol mixtures and in dioxane-water mixtures and the 1,3,5-trinitrobenzene-naphthalene equilibrium in chloroform-ethanol mixtures.

The heats of formation for the nitrohydrocarbon-hydrocarbon complexes are generally low and usually less than 5 kcal.⁸ However, for complexing between 2,4-dinitrochlorobenzene and substituted anilines, the heats of formation are considerably higher, and in the case of the 2,4-dinitrochlorobenzene-*o*-methoxyaniline complex the heat of forma-

tion in ethanol is 18 kcal.⁹ Also, Abrahams and Robertson¹⁰ have reported a direct observation of a relatively strong bond between an oxygen atom of a nitro group and a carbon atom of an adjacent benzene ring in crystalline *p*-nitroaniline, which forms a self complex. This suggests that the interaction of donor and acceptor may be more specific and more strongly localized in the amine complexes and that earlier views¹¹ of the structure of these complexes should be reconsidered. It was our hope that, if there are structural differences for these two types of complexes, this would manifest itself in a different response to solvent changes.

Experimental

Solvents and Reagents.—J. T. Baker and Adamson Reagent Grade chloroform, which contained 0.75% ethanol as stabilizer, was used without further purification. Absolute ethanol from the U. S. Industrial Chemicals Company was used without further purification. Titration with the Karl Fischer reagent showed that this alcohol contained 0.08% water. For measurements of the 1,3,5-trinitrobenzene-aniline complex in chloroform-ethanol mixtures, the ethanol was purified further by refluxing it over calcium hydride and distilling it from calcium hydride immediately before use. After this treatment the alcohol contained 0.03% water. 1,4-Dioxane was purified by the method of Eigenberger¹²; b.p. 101–102° and stored over sodium. Eastman Kodak Company White Label aniline was distilled from calcium hydride immediately before use, and a middle fraction of b.p. 63° at 8 mm. was used. Naphthalene was crystallized several times from methanol; colorless plates; m.p. 80–81°. 1,3,5-Trinitrobenzene, Eastman Kodak Company White Label, was crystallized from chloroform; almost colorless needles, m.p. 121°.

The Absorption Spectra Measurements.—A Beckman model DU spectrophotometer was used throughout. Stopped absorption cells were used, and the cell housing was maintained at constant temperature by means of two Beckman thermospacers, through which water from a constant temperature bath was circulated. Measurements were made at at least six different sets of concentrations of the donor and acceptor. In measuring the 1,3,5-trinitrobenzene-naphthalene complex in chloroform-ethanol mixtures, the trinitrobenzene concentrations were varied from 5×10^{-3} – 9×10^{-2} M, and the naphthalene concentrations were varied from 0.1–0.9 M. For the 1,3,5-trinitrobenzene-aniline complex in chloroform-ethanol mixtures, the trinitrobenzene concentrations were varied from 5×10^{-3} – 1×10^{-2} M and the aniline concentrations were varied from 0.3–1.1 M. In the measurements in dioxane-water mixtures, the trinitrobenzene concentrations were varied from 1×10^{-3} – 7×10^{-3} M and the aniline concentrations

(1) (a) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935); L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 979 (1940); (b) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); (c) E. Grunwald and S. Winstein, *THIS JOURNAL*, **70**, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(2) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1947, chap. VIII. K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, chap. V.

(3) The term "solvation" is used in the general sense of referring to any form of interaction or association of solute with solvent which is accompanied by heat evolution.

(4) J. Weiss, *J. Chem. Soc.*, 245 (1942).

(5) R. S. Mulliken, *THIS JOURNAL*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(6) S. D. Ross and I. Kuntz, *THIS JOURNAL*, **76**, 300 (1954).

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

(8) (a) G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur," Verlag von Ferdinand Enke, Stuttgart, 1937, pp. 114–118; (b) H. v. Halban and E. Zimpelmann, *Z. physik. Chem.*, **117**, 471 (1925); (c) W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1919); (d) S. D. Ross and I. Kuntz, *THIS JOURNAL*, **76**, 74 (1954).

(9) S. D. Ross, M. Bassin and I. Kuntz, *ibid.*, **76**, 4176 (1954). B. R. Hamilton and D. L. Hammick (*J. Chem. Soc.*, 1350 (1938)), on the other hand, have reported low values, comparable with those found with hydrocarbons, for the heats of formation for complexes of 1,3,5-trinitrobenzene with a series of aromatic amines.

(10) S. C. Abrahams and J. M. Robertson, *Acta Cryst.*, **1**, 252 (1948); S. C. Abrahams, *THIS JOURNAL*, **74**, 2692 (1952).

(11) See for example, G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 256 (1929).

(12) E. Eigenberger, *J. prakt. Chem.*, [2] **130**, 75 (1931).

were varied from 0.45–1.4 *M*. The equilibrium constants and extinction coefficients were calculated by methods previously described.¹³ The method of least squares was used in every case.

Results

The equilibrium constants for formation of the 1,3,5-trinitrobenzene–naphthalene complex and the extinction coefficients of the complex at the wave lengths at which the equilibrium constants were calculated for a series of chloroform–ethanol mixtures are given in Table I, and in Fig. 1 the equilibrium constants are plotted against the dielectric constants of the solvent mixtures. It is of interest that in this series of determinations the extinction coefficients are reasonably constant in all the solvent mixtures. This suggests that the structure of the complex is unaltered by these solvent changes.

TABLE I
EQUILIBRIUM CONSTANTS AND EXTINCTION COEFFICIENTS FOR THE 1,3,5-TRINITROBENZENE–NAPHTHALENE COMPLEX IN CHLOROFORM–ETHANOL MIXTURES AT 24.8 ± 0.1°

% by wt. ethanol	Dielectric constant	Wave length, mμ	Extinction coefficient	<i>K</i> , l. mole ⁻¹
0.75	4.8	450	87	1.25
		460	37	1.32
		470	15	1.33
7.0 ^a	6.3	450	92	1.13
		460	43	1.08
		470	18	1.02
7.0 ^b	6.3	450	89	1.14
		460	45	0.99
		470	19	0.94
15.0	8.4	450	84	1.20
		470	17	1.18
		480	7.2	1.03
25.0	11.1	440	169	1.07
		450	88	1.03
		460	42	1.05
50.0	17.3	430	319	0.744
		440	176	.698
		450	85	.716
75.0	22.2	420	504	0.572
		430	284	.549

^a Azeotrope prepared by distillation. ^b Azeotrope prepared by weighing.

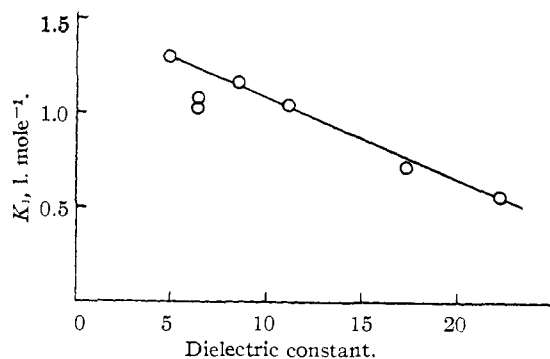


Fig. 1.—The equilibrium constants for formation of the 1,3,5-trinitrobenzene–naphthalene complex vs. the dielectric constants of the solvent in chloroform–ethanol mixtures at 24.8 ± 0.1°.

(13) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **74**, 1891 (1952); S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, *ibid.*, **76**, 69 (1954).

The 7.0% ethanol–93.0% chloroform mixture is an azeotrope boiling at 59.35°. As can be seen from Fig. 1, the equilibrium constant in this solvent mixture deviates from the smooth curve obtained with the other mixtures. This deviation is real and was checked by preparing the azeotrope both by distillation and by mixing the requisite weights of the two pure, anhydrous solvents. The results with the azeotrope prepared by both methods are given in Table I and Fig. 1.

Table II lists data for the 1,3,5-trinitrobenzene–naphthalene complex in 75% chloroform–25% ethanol at three temperatures. From an Arrhenius plot of $\log K$ vs. $1/T$ and using the method of least squares, we can estimate ΔH^0 for this complex, and using the expressions $\Delta F^0 = -RT \ln K$ and $\Delta F^0 = \Delta H^0 - T \Delta S^0$, we obtain the thermodynamic values given in this table. In column 3 we have listed those values of *K* which would exactly fit the least squares straight line.

TABLE II
THE 1,3,5-TRINITROBENZENE–NAPHTHALENE COMPLEX IN 75% CHLOROFORM–25% ETHANOL

Temp., °C.	<i>K</i> (exptl.), l. mole ⁻¹	<i>K</i> (calcd.), ^a l. mole ⁻¹	ΔH^0 , kcal.	ΔF^0 , cal.	ΔS^0 , e.u.
24.8	1.05	1.07	-3.3	-28.3	-10.6
30.4	1.00	0.96	-3.3	2.4	-10.9
39.6	0.81	0.83	-3.3	13.0	-10.5

^a This is the required value for *K* for the point to exactly fit the least squares line of $\log K$ vs $1/T$.

The equilibrium constants and extinction coefficients for the 1,3,5-trinitrobenzene–aniline complex in chloroform–ethanol mixtures at 24.8 ± 0.1° are given in Table III, and the equilibrium constants are plotted against the dielectric constants in Fig. 2. For this complex the extinction coefficients are definitely changed by solvent changes, with the maximum change being greater than 30%. The extinction coefficients decrease regularly as the equilibrium constants increase, and these changes are probably indicative of specific solute–solvent interaction in these systems.¹⁵ The values of the dielectric constants in both Tables I and III are taken from measurements reported by Graffunden and Heymann¹⁶ at 450 m. A plot of dielectric constant vs. wt. % chloroform is a smooth curve over the entire range of solvent compositions.

The equilibrium constant for formation of the 1,3,5-trinitrobenzene–aniline complex in reagent grade chloroform at 22 ± 2° has been reported previously by Landauer and McConnell.¹⁷ They report an equilibrium constant of 5.1 ± 0.7 mole fraction⁻¹. It is not possible to translate exactly their concentration units into ours, since the aniline concentrations involved are as high as 1 *M*, but their value corresponds roughly to 0.41 ± 0.06 l. mole⁻¹,

(14) "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, p. 21.

(15) For a general discussion of solvent effects in absorption spectroscopy see A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1954, p. 263.

(16) W. Graffunden and E. Heymann, *Z. Physik*, **72**, 744 (1931).

(17) J. Landauer and H. McConnell, *THIS JOURNAL*, **74**, 1221 (1952).

TABLE III
EQUILIBRIUM CONSTANTS AND EXTINCTION COEFFICIENTS
FOR THE 1,3,5-TRINITROBENZENE-ANILINE COMPLEX IN
CHLOROFORM-ETHANOL MIXTURES AT $24.8 \pm 0.1^\circ$

% by wt. ethanol	Dielectric constant	Wave length, $m\mu$	Extinction coefficient	K , $l. \times \text{mole}^{-1}$
0.75	4.8	460	1231	0.258
		470	1021	.252
		480	790	.261
7.0	6.3	460	1110	0.293
		464	1002	.303
		470	970	.301
25.0	11.1	450	997	0.373
		460	997	.359
		470	862	.352
		490	547	.391
50.0	17.3	460	977	0.418
		470	820	.432
		480	686	.442
		490	580	.423
60.0	19.4	460	976	0.442
		464	884	.464
		470	776	.488
65.0	20.4	460	840	0.544
		464	770	.567
		470	702	.565
70.0	21.4	460	1108	0.382
		464	1041	.389
		470	1031	.348
75.0	22.2	460	1188	0.355
		470	1013	.359
		480	973	.310
		490	759	.333
85.0	23.5	456	1101	0.405
		460	1131	.370
		464	1085	.368
		470	904	.410
100	24.6	440	1300	0.389
		450	1181	.389
		460	1015	.403
		470	875	.405

which is higher than our value of $0.257 \pm 0.005 l. \text{mole}^{-1}$.¹⁸

The 1,3,5-trinitrobenzene-aniline complex in 75% chloroform-25% ethanol was also studied at three temperatures, and the resultant values of the equilibrium constants and the thermodynamic quantities are given in Table IV.

TABLE IV
THE 1,3,5-TRINITROBENZENE-ANILINE COMPLEX IN 75%
CHLOROFORM-25% ETHANOL

Temp., $^\circ\text{C}.$	K (exptl.), $l. \text{mole}^{-1}$	K (calcd.), ^a $l. \text{mole}^{-1}$	ΔH° , kcal.	ΔF° , cal.	ΔS° , e.u.
24.8	0.369	0.368	-5.1	590	-19.1
30.4	.296	.308	-5.1	734	-19.2
39.6	.244	.244	-5.1	876	-19.1

^a This is the required value for K for the point to exactly fit the least squares line of $\log K$ vs. $1/T$.

Table V lists the equilibrium constants and extinction coefficients for the 1,3,5-trinitrobenzene-

(18) We cannot account satisfactorily for this discrepancy. In part, it may be due to differences in temperature (see Table IV) and differences in the solvent, since reagent grade chloroform varies in the amount of alcohol added as stabilizer.

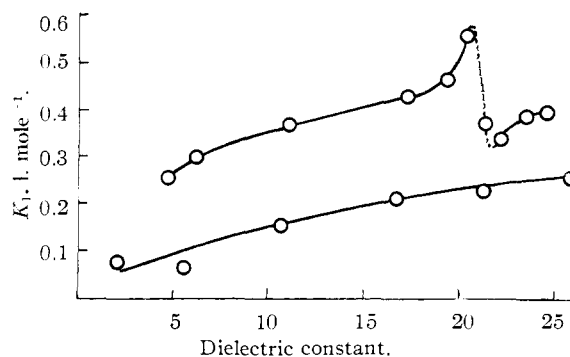


Fig. 2.—The equilibrium constants for formation of the 1,3,5-trinitrobenzene-aniline complex vs. the dielectric constants of the solvent at $24.8 \pm 0.1^\circ$: upper curve, chloroform-ethanol mixtures; lower curve, dioxane-water mixtures.

aniline complex in dioxane-water mixtures at $24.8 \pm 0.1^\circ$. The solvent composition was varied so as to cover the same range of dielectric constants as was covered with the chloroform-ethanol mixtures. The values of the dielectric constants are taken from the measurements of Akerlof and Short,¹⁹ and the equilibrium constants are plotted against the dielectric constants in Fig. 2. The low equilibrium constants obtained in 100 and 90% by wt. dioxane are close to the limit of measurement with the particular absorption cells we used. In this case, too, the extinction coefficients vary but in a more random manner.

TABLE V
EQUILIBRIUM CONSTANTS AND EXTINCTION COEFFICIENTS
FOR THE 1,3,5-TRINITROBENZENE-ANILINE COMPLEX IN
DIOXANE-WATER MIXTURES AT $24.8 \pm 0.1^\circ$

% by wt. ethanol	Dielectric constant	Wave length, $m\mu$	Extinction coefficient	K , $l. \text{mole}^{-1}$
100	2.1	460	2677	0.079
		464	2909	.068
		470	2177	.083
		470	2177	.083
90	5.6	460	3427	0.060
		464	3139	.062
		470	2802	.063
80	10.7	460	1567	0.155
		464	1454	.158
		470	1401	.150
70	17.7	460	1260	0.234
		464	1284	.213
		470	1279	.193
65	21.3	456	1556	0.236
		460	1584	.218
		464	1471	.225
		470	1303	.235
60	25.9	460	1355	0.258
		464	1366	.242
		470	1262	.242

Discussion

The solvating ability²⁰ of a solvent is not a precise concept, in spite of the fact that solvation is essen-

(19) G. Akerlof and O. A. Short, *THIS JOURNAL*, **68**, 1241 (1936).

(20) For a more detailed discussion of solvation, see J. H. Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1936, chaps. IV-VI. See also, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345-350.

tially an electrostatic phenomenon, and we can precisely measure the polarity of an individual molecule by its dipole moment in the gas phase and can relate the polarity of a liquid to its dielectric constant, which is, however, both temperature and frequency dependent. The reason for this is that the requirements for effective solvation in a given case are highly specific and have some of the characteristics of a lock and key relationship. If we consider the case of a dipolar molecule being solvated by a dipolar solvent, the ease of interaction will depend on the extent to which the magnitudes of the dipoles and the separation and dispersal of the charges making up the dipoles are matched for solute and solvent. The importance of this element of spacing and steric orientation has been clearly demonstrated by Swain and Brown²¹ in the case of catalysis.

The results of our measurements in chloroform-ethanol mixtures (Tables I and III) are clearly not explainable as simply responses of the systems to variations in the dielectric constants of the medium. The results with the 1,3,5-trinitrobenzene-aniline complex, in particular, suggest that highly specific interactions between the solutes and solvent are involved in certain ranges of solvent composition. Fortunately, the results of Hirobe²² and the very complete study of Scatchard and Raymond²³ make it possible to discuss our results in terms of the chemical species present as the compositions of chloroform-ethanol mixtures are varied.

Scatchard and Raymond have calculated the excess chemical potentials, free energy, heat content and entropy of mixing for this system. The excess heat content passes through a maximum when the mole fraction of ethanol is 0.2 and a minimum when the mole fraction of ethanol is 0.8. The temperature entropy product, $-TS_x^E$, goes through a minimum when the alcohol mole fraction is 0.1 and a maximum at an alcohol mole fraction of 0.8. The entropy of vaporization of ethanol is large indicating association, while that of chloroform is normal. When a small amount of ethanol is first added to chloroform, the excess entropy of mixing is positive indicating destruction of this association. At the other end of the concentration scale when chloroform is first added to ethanol, the excess entropy of mixing is negative. This corresponds to an increase in association with the formation of larger alcohol clusters which now also contain a chloroform molecule. The chloroform molecules may, in a sense, be looked upon as cross-linking agents, since they bind together alcohol clusters into larger clusters, but in these latter clusters, each molecule is less tightly held. In the concentration region between the minimum and maximum in excess entropy, large clusters are being broken up into smaller clusters, first, perhaps, into clusters involving several alcohol molecules per chloroform molecule, and finally into clusters involving one ethanol molecule and one chloroform molecule, $H_3C-Cl \dots$ HOR.

(21) C. G. Swain and J. F. Brown, Jr., *THIS JOURNAL*, **74**, 2538 (1952).

(22) H. Hirobe, *J. Fac. Sci. Tokyo*, [1] **1**, 155 (1925).

(23) G. Scatchard and C. L. Raymond, *THIS JOURNAL*, **60**, 1278 (1938).

In the light of the preceding discussion, it is possible to offer a qualitative explanation of the results reported in Tables I, III and V. A striking feature of the results reported in Table I is the fact that the extinction coefficients for the molecular complex are relatively constant in the various solvent mixtures; at 450 $m\mu$ the maximum variation is less than 10%. This suggests that there are no large changes in the degree of solvation of the 1,3,5-trinitrobenzene-naphthalene complex as the chloroform-ethanol proportions are varied. For this series of measurements, the general trend is for the equilibrium constant for complex formation to decrease as the dielectric constant increases. Two factors are operative in bringing about this result. For the 1,3,5-trinitrobenzene-naphthalene complex, the polar, charge-transfer structure makes only a small contribution of the total structure. The constancy of the spectrum of the complex as the dielectric constant is varied from 5 to almost 25 points to an absence of the sort of increasing solvation with increasing dielectric constant which would be expected if the polar structure were making a large contribution. If solvation of the complex is relatively constant with solvent changes, then the decreasing equilibrium constant, as the dielectric constant increases, must be due to increasing solvation of either naphthalene or 1,3,5-trinitrobenzene. It is not unreasonable to expect hydrogen bonding between 1,3,5-trinitrobenzene and ethanol and increasing solvation of the former with increasing ethanol concentration. The low value of the equilibrium constant in the chloroform-ethanol azeotrope is also reasonable on the same basis, since this is a solvent composition region where $-TS_x^E$ is a minimum²³; *i.e.*, in this region a change in composition in either direction results in more association of the solvent components.

The results with the 1,3,5-trinitrobenzene-aniline complex (Table III) in the same solvent mixtures are strikingly different. For this complex there are large changes in the extent of solvation as the solvent is varied, and at any single wave length, the maximum change in the extinction coefficient is greater than 45%. These changes could be indicative of either changes in the intensity of absorption or of shifts of the absorption maximum.²⁴

The spectral changes show that solute-solvent interactions involving the molecular complex are present in this case. The general trend is for the equilibrium constant to increase as the ethanol mole fraction increases. This is in accord with expectations, if, with increasing ethanol concentration, the molecular complex is being solvated more than

(24) Our data do not permit us to choose between these alternatives and, in actual fact, both a shift in the maximum and a change in intensity may be occurring simultaneously. In general, the maximum of an R-band is shifted to lower wave lengths and the intensity of absorption is increased slightly by an increase in the dielectric constant of the solvent, whereas the reverse is true for a K-band (see ref. 15, chap. 8). However, this sort of generalization is of questionable value. As E. A. Braude (*J. Chem. Soc.*, 490 (1945)) has pointed out, "It is clear that there is no simple relationship between band position, extinction coefficient, and fine-structure resolution on the one hand, and dielectric constant, dipole moment, or other physical property of the solvent on the other." For some carefully considered attempts to find such relationships see S. E. Sheppard, P. T. Newsome and H. R. Brigham, *THIS JOURNAL*, **64**, 2923 (1942); S. E. Sheppard and P. T. Newsome, *ibid.*, **64**, 2937 (1942).

either the donor or the acceptor. This suggests that for this complex the dative, charge-transfer structure makes a more appreciable contribution to the total structure. In the solvent composition region between 50–75 weight per cent. ethanol, the equilibrium constants change strikingly and go through a sharp maximum. In this solvent composition region both the excess entropy and heat content of mixing go through a minimum. Beyond this minimum, as the solvent becomes richer in chloroform, large solvent clusters, in which aggregates of alcohol molecules are loosely bound together by chloroform molecules, are breaking up and forming smaller aggregates containing one chloroform molecule and one or several ethanol molecules. To explain the observed results we would invoke a specific solvation effect in which one or more of these newly-formed, smaller aggregates has just the correct spatial and charge configuration to be particularly effective in solvating the 1,3,5-trinitrobenzene–aniline complex.

That these results are not attributable to or directly related to changes in the dielectric constant of the solvent is clearly demonstrated by the values found for formation of the 1,3,5-trinitrobenzene–aniline complex in dioxane–water mixtures (Table V). In these studies we have covered with dioxane–water mixtures the identical range of dielectric constants covered with the chloroform–ethanol mixtures. Although the equilibrium constants again increase with increasing dielectric constant, they are all very much lower than the values found at equivalent dielectric constants with the chloroform–ethanol mixtures. Moreover, a smooth curve can be drawn through all of the experimental points, and there is no evidence of the sharp maximum in the equilibrium constant observed between dielectric constants of 17 and 22 with the chloroform–ethanol solvents.

The very different responses to solvent changes shown by the 1,3,5-trinitrobenzene–naphthalene and 1,3,5-trinitrobenzene–aniline complexes suggest structural differences between these two complexes. We have suggested that, in the latter case, the dative, charge-transfer structure makes a larger contribution to the total structure of the ground state. In Tables II and IV we have reported

heats, free energies and entropies of formation for the two complexes in 75% chloroform–25% ethanol. The heats of formation are in both instances low and negative, -3.3 kcal. for the naphthalene complex and -5.1 kcal. for the aniline complex. This is not a sufficient difference to demand a basically different type of bonding, but it does point to stronger bonding in the latter complex. The entropy difference of almost 9 e.u. is, however, large enough to be significant and suggests that the 1,3,5-trinitrobenzene–aniline complex has a more restricted configuration and that bonding, in this case, is more localized.

The 1,3,5-trinitrobenzene–aniline complex has potentialities for bonding which are not available to the naphthalene complex. These are attributable to the presence of the amino group in the donor moiety. The type of bonding suggested by the work of Abrahams and Robertson¹⁰ would involve a bond between an oxygen atom of a nitro group and one of the ring atoms in the aniline molecule. Such a linkage seems improbable, since it would involve a negative oxygen atom and a ring position made relatively negative by resonance interaction of the amino group with the aromatic ring.

A more probable type of interaction is suggested by the work of Lewis and Seaborg²⁵ on the acidity of aromatic nitro compounds toward amines. This work leads us to suggest that in the 1,3,5-trinitrobenzene–aniline complex, the two aromatic rings are positioned one above the other and that primary attachment between donor and acceptor comes from π -electron overlap and the resultant charge-transfer bond. The two aromatic rings are twisted slightly so that the amino group is positioned between two nitro groups. This permits three types of secondary bonding forces to become operative: hydrogen bonding between amino hydrogens and the oxygen of the nitro groups, bonding between the amino nitrogen and a carbon atom of the trinitrobenzene ring, and bonding between the amino nitrogen and the nitrogen of the nitro group.

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(25) G. N. Lewis and G. T. Seaborg, *THIS JOURNAL*, **62**, 2122 (1940).