413. The Kinetics of Complex-formation of 1,3,5-Trinitrobenzene with Diethylamine and Other Amines in Solution at Low Temperatures.

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The kinetics of the reaction between diethylamine and 1,3,5-trinitrobenzene, which is thought to produce a charge-transfer complex, have been studied at low temperatures by the stopped-flow method. They indicate that the reaction is reversible, of first order in trinitrobenzene, and of second order in diethylamine. The rates, equilibrium constants, ΔH, ΔS^0, and the Arrhenius parameters have been determined. The results are interpreted in terms of solvation changes and a preliminary equilibrium. The reactions of trinitrobenzene and trinitrotoluene with various aromatic amines, on the other hand, are too fast for measurement by the present technique.

In recent work on low-temperature kinetics in this laboratory, the rates have been measured of several reactions which appear to be complex-formations between the ethoxide ion and various nitro-compounds.[1,2] It is of interest to extend the investigations to complex formation between neutral molecules. A good deal is known about the thermodynamics of these complexes, and the theory of charge-transfer complexes has been developed by Mulliken and others.[3] The complexes of 1,3,5-trinitrobenzene (T.N.B) with aromatic amines and hydrocarbons have been studied by several authors;[4,5,6] they are highly coloured products, formed instantaneously at room temperature, and are probably charge-transfer complexes. The complexes of trinitrobenzene with aliphatic amines, which are also highly coloured, have been studied by Miller and Wynne-Jones[6] and by Foster.[7] Both investigations led to the suggestion that the initial product is a charge-transfer complex. We have studied the rates of formation of these coloured products, with the help of a low-temperature photometric stopped-flow apparatus recently described.[8] The reactions with aromatic amines are too fast for measurement by this technique, but the reaction with diethylamine is measurable. It appears to be a third-order reversible reaction, and we have measured rates and equilibria in selected solvents over ranges of temperature, in order to determine ΔH, ΔS^0, and the Arrhenius parameters E and A.

EXPERIMENTAL

The Low-temperature Stopped-flow Apparatus.—The mode of operation was described in our previous paper,[8] except for the following. Improvements to the non-return valves resulted in much more uniform relative rates of delivery of the two reactant solutions from their reservoirs, so that it was possible to simplify the determination of the relative rates as follows. Before each set of 5 or 6 identical kinetic runs, 6 blank runs were carried out at the same temperature with the pure solvent in one reservoir and in the other a solution of acetic acid in the same solvent; the mixed product from these blank runs (after the effluent of the first of them had been rejected) was analysed by titration, and the mean relative rates of delivery thus obtained. After the set of kinetic runs, this procedure was repeated. The two values for the relative rates nearly always agreed within about 1%, and could safely be assumed to apply to the kinetic runs. The rate constants derived from a set of 5 or 6 identical kinetic runs usually gave a standard deviation from the mean of 1—2% (cf. Tables 2a and 2b below).

Choice of Solvent.—*Aromatic amines*. The reactions with aromatic amines had to be studied at the lowest temperature possible; the limit was set by the increase of viscosity and decrease of solubility with decrease of temperature. Solubilities for α-naphthylamine and trinitrobenzene in solvents of suitably low viscosity and freezing point were systematically investigated, by stirring an excess of the solute with the solvent, drawing off samples of the saturated solution through a sintered-glass filter into the cell of a Unicam spectrophotometer, and determining the concentration of the solution by measurement of the optical density at three wavelengths. The best solvent was found to be acetone–diethyl ether, in a molar ratio 1 : 3; this solidifies below −135°. The solubility at −123° of trinitrobenzene in this solvent is 0·024 and that of α-naphthylamine is 1·2 mole l.$^{-1}$; the complex is the least soluble component of the mixture, but an adequate optical density can be obtained without precipitation at −135°. Other solvent systems investigated were toluene–acetone and toluene–ether, in various proportions, but the solubilities of trinitrobenzene were too low. As regards viscosity, which must not be too high if proper mixing is to be obtained, theory indicates that ether is satisfactory at least down to −127° and acetone at least down to −110°, and experiments have suggested that these calculated limits are too high.[8]

Trinitrobenzene and diethylamine. For this reaction the rate is such that the temperature need not be lower than −100°, and the important factors are the solubility of the amine and the

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[1] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **226**, 263.

[2] Ainscough and Caldin, *J.*, 1956, 2528, 2540, 2546.

[3] Mulliken, (*a*) *J. Amer. Chem. Soc.*, 1952, **74**, 811; (*b*) *J. Phys. Chem.*, 1952, **56**, 801; (*c*) Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3869; (*d*) Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845; (*e*) Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839; (*f*) Plyler and Mulliken, *ibid.*, 1959, **81**, 823.

[4] Bier, *Rec. Trav. chim.*, 1956, **75**, 866.

[5] Foster and Hammick, *J.*, 1954, 2685.

[6] Miller and Wynne-Jones, *J.*, 1959, 2375.

[7] Foster, *J.*, 1959, 3508.

[8] Allen, Brook, and Caldin, *Trans. Faraday Soc.*, 1960, **56**, 788.

equilibrium constant, which limit the optical density obtainable. In all solvents the optical density increases with decrease of temperature, presumably because the equilibrium constant increases. Acetone, and acetone–ether (1 : 3), were found to be satisfactory solvents. It is difficult to prepare acetone free from water, and 0·1% of water corresponds to a molar concentration of about 0·05, which is comparable with the lower concentrations of diethylamine used. Some runs were therefore carried out in which a volume of water equal to that of the diethylamine was added to acetone solutions; the molar ratio of water to diethylamine was 5·8. We refer to the solvent in these runs as acetone–water. It was not possible to add water in this way to acetone–ether, since its solubility at low temperatures is inadequate.

Spectrophotometry.—For the complexes with aromatic amines, the extinction coefficients and equilibrium constants in chloroform solution have been determined by Bier.[4] Similar values in the acetone–ether (1 : 3) at 25° were obtained for the α-naphthylamine–trinitrobenzene complex, by measuring optical densities and using the treatment recommended by Benesi and Hildebrand;[9] the results were $\varepsilon = 1040$ l. mole^{-1} cm.$^{-1}$, $K = 3{\cdot}8$ l. mole^{-1} = 41 (mole fraction)$^{-1}$, $\lambda_{\text{max.}} = 464$ mμ. A combination of Chance OY 8 and OB 10 glass filters was used in investigating the rate of formation of this complex; for the other aromatic-amine complexes, a Chance OB 10 or an Ilford 806 filter was used. For the diethylamine–trinitrobenzene complex, no data were available since previous measurements[6,7] have been made at room temperature and are therefore not concerned with the reaction here being studied. The complex is orange-coloured and in the kinetic runs a Chance OB 10 glass filter was used; the half-length of the absorption band of the filter runs from 365 to 475 mμ.

Materials.—1,3,5-Trinitrobenzene was recrystallised 3 times from ethanol and had m. p. 121—122°. Aromatic amines were distilled, and stored, under reduced pressure. Diethylamine was distilled from sodium hydroxide, and the fraction boiling between 55·5° and 55·6° collected (lit., 55·5°). Diethyl ether was refluxed over sodium and distilled; it had b. p. 34·6° (lit., 34·6°). Acetone was dried with potassium carbonate and distilled, then having b. p. 55·5—56·0° (lit., 56·1°).

RESULTS

Rates of Reaction of Trinitro-benzene and -toluene with Aromatic Amines.—These reactions were studied with the minimum concentrations required to give a sufficient optical density, at the lowest practicable temperature. The solvent was acetone–ether (1 : 3 molar). The amines were chosen for the relatively high values of the equilibrium constants of their complexes, and the convenient positions of their charge-transfer bands.[4,5] The reactions were all complete within a millisecond, so the first-order rate constants were all >700 sec.$^{-1}$. If the reactions are assumed to be second-order, the corresponding minimum values of the second-order rate constant k lie between 10^3 and 10^4 l. mole^{-1} sec.$^{-1}$ (Table 1). If A is assumed to be 10^{11} l. mole^{-1} sec.$^{-1}$, the corresponding maximum values of the Arrhenius energy of activation E are in the region of 5·5 kcal. mole^{-1}.

TABLE 1. *Rates of reaction of trinitro-benzene* (T.N.B.) *and -toluene* (T.N.T.) *with aromatic amines in acetone–ether* (1 : 3 molar).

Donor	Donor concn. (mole/l.)	Acceptor	Acceptor concn. (10^{-3} mole/l.)	Temp.	$10^{-3}k$ (l. mole^{-1} sec.$^{-1}$)
α-Naphthylamine	0·26	T.N.B.	0·81	−134°	>3
p-Toluidine	0·31	T.N.B.	2·39	−120	>2
Diphenylamine	0·29	T.N.B.	2·39	−120	>2
N-Methylaniline	0·11	T.N.T.	0·58	−120	>6
N-Ethylaniline	0·10	T.N.T.	0·58	−120	>6
NN-Diethylaniline	0·14	T.N.T.	0·58	−120	>5

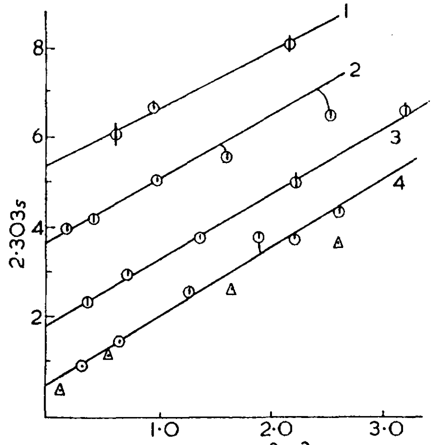
Rate of Reaction of Trinitrobenzene with Diethylamine.—Runs were carried out in acetone–ether (1 : 3 molar), in acetone, and in acetone–water containing 5·8 moles of water per mole of diethylamine. In each run, the concentration of amine (b) was at least 100 times that of trinitrobenzene (d). The half-lives range from 0·05 to 1 sec. First-order plots prepared by Guggenheim's method[10] were always linear within experimental error; this implies that the

[9] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.
[10] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

reaction is of the first order with respect to trinitrobenzene, and that Beer's law is obeyed. The slopes of these plots could be estimated to about ±2%. We denote the numerical value of the slope by *s*. At each concentration of amine, five or six runs were carried out, and the mean value of *s* was calculated, with the standard deviation. These values of *s* are given in the fifth columns of Tables 2*a* and 2*b*.

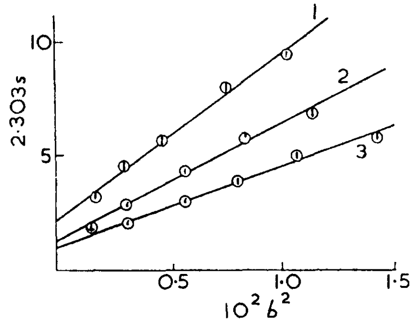
The values of *s* when plotted against b^2 give good straight lines, at least up to diethylamine concentrations (*b*) of about 0·15M; the intercept increases with temperature. The plots are shown in Figs. 1*a* and 1*b*. The linear s–b^2 relation is characteristic of a reversible reaction of the type $A + 2D \rightleftharpoons AD_2$, where A represents the acceptor trinitrobenzene and D the donor diethylamine. Such a reaction scheme predicts the following relation (see Discussion) when diethylamine is in large excess:

FIG. 1*a*. *Plot of s against b^2 for the reaction of diethylamine with trinitrobenzene in acetone–ether.*



Line 1, −58·9° (displaced 3 units downwards); 2, −66·7°; 3, −70·6°; 4, −84·8°; triangles, −85·6°. The lengths of the short lines represent standard deviations.

FIG. 1*b*. *Plot of s against b^2 for the reaction of diethylamine with trinitrobenzene in acetone–water.*



Line 1, −29·0°; 2, −39·3°; 3, −49·5°. The lengths of the short lines represent standard deviations.

$$2{\cdot}303s = b^2k + k_b, \qquad (1)$$

where k_f and k_b are the rate constants for the overall forward and reverse reactions, and are given respectively by the slope and intercept of the plot of *s* against b^2. Values of k_f and k_b derived from least-squares treatment of the plots are given, along with standard deviations, in Tables 2*a* and 2*b*.

Heats and Entropies of Activation.—The Arrhenius plots of log k_f and log k_b against $1/T$ give values of the energies of activation and *A* factors for the forward and back reactions; these are designated by E_f and E_b, A_f and A_b. The best values from a least-squares treatment, along with standard deviations, are given in Table 3. Values of the entropies and enthalpies of activation ΔS^* and ΔH^*, calculated from the relations $A = e(\boldsymbol{k}T/\boldsymbol{h}) \exp(\Delta S^*/\boldsymbol{R})$ and $\Delta H^* = E + \boldsymbol{R}T$, are also included in Table 3.

Equilibrium Data on the Trinitrobenzene–Diethylamine Reaction.—Qualitative observations on the depth of colour of solutions show (i) that in all solvents the equilibrium shifts in favour of the complex as the temperature falls, so that the forward reaction must be exothermic, and (ii) that there is considerably more complex-formation in acetone or acetone–water than in ether, ethanol, propan-2-ol, toluene, or acetone–ether. Quantitative data are obtained from the kinetic runs; the overall equilibrium constant $K = (AD_2)/(A)(D)^2 = k_f/k_b$. Values of *K* derived from those of k_f and k_b are given in Tables 2*a* and 2*b*. The corresponding values of $\Delta H = E_f - E_b$ and of $\Delta S^0 = \boldsymbol{R} \ln (A_f/A_b)$ are given in Table 3. The standard state to which

TABLE 2*a*. *Reaction of diethylamine with trinitrobenzene* (T.N.B.) *in acetone and ether* (1 : 3).

Concn. of diethylamine = *b*; concn. of T.N.B. = *d*.
Corrections for change of density with temperature have been applied.
Uncertainties are standard deviations.

Temp.	10^4d (mole/l.)	10^2b (mole/l.)	No. of runs	Mean 2·303*s* (sec.$^{-1}$)	$10^{-2}k_f$ (l.^{2} mole^{-2} sec.$^{-1}$)	k_b (sec.$^{-1}$)	$10^{-2}K$ (l.^{2} mole^{-2})
−85·60°	1·49	16·2	5	3·91 ± 0·03	1·32 ± 0·09	0·5$_8$ ± 0·15	2·3 ± 0·9
	1·49	12·9	5	2·93 ± 0·05			
	1·49	7·6	5	1·42 ± 0·01			
	1·49	3·8	6	0·62 ± 0·01			
−84·83	6·33	16·2	5	4·58 ± 0·08	1·56 ± 0·11	0·6$_8$ ± 0·20	2·3 ± 1·0
	4·06	14·9	4	4·00 ± 0·03			
	6·33	13·8	5	4·00 ± 0·08			
	6·33	11·3	5	2·82 ± 0·08			
	6·33	8·2	5	1·64 ± 0·01			
	6·33	5·7	5	1·08 ± 0·01			
−70·56	3·33	17·9	5	6·87 ± 0·11	1·49 ± 0·04	1·97 ± 0·08	0·76 ± 0·07
	3·33	14·9	5	5·18 ± 0·16			
	3·33	11·7	5	3·96 ± 0·04			
	3·33	8·6	5	3·16 ± 0·03			
	3·33	6·1	5	2·53 ± 0·07			
−66·72	1·45	15·9	5	6·67 ± 0·08	1·46 ± 0·05 *	3·8$_3$ ± 0·1	0·38 ± 0·03
	1·45	12·7	5	5·82 ± 0·06			
	1·45	9·9	5	5·29 ± 0·04			
	1·45	6·5	5	4·38 ± 0·07			
	1·45	4·4	5	4·17 ± 0·05			
−58·92	1·17	14·7	5	11·31 ± 0·20	1·28 ± 0·04	8·6 ± 0·1	0·15 ± 0·01
	1·17	9·8	5	9·94 ± 0·09			
	1·17	7·8	5	9·26 ± 0·25			

* Calculated from results at three lowest concentrations only.

TABLE 2*b*. *Reaction of diethylamine with trinitrobenzene in acetone–water*

(Notes are in Table 2*a*.)

Temp.	10^4d (mole/l.)	10^2b (mole/l.)	No. of runs	Mean 2·303*s* (sec.$^{-1}$)	$10^{-2}k_f$ (l.^{2} mole^{-2} sec.$^{-1}$)	k_b (sec.$^{-1}$)	$10^{-2}K$ (l.^{2} mole^{-2})
−49·49°	1·08	12·0	5	5·88 ± 0·10	3·52 ± 0·13	0·99 ± 0·14	3·5 ± 1
	1·08	10·4	5	5·06 ± 0·08			
	1·08	9·1	5	3·92 ± 0·08			
	1·08	7·7	5	3·06 ± 0·04			
	1·08	5·7	5	2·06 ± 0·06			
−39·27	1·19	10·7	5	6·90 ± 0·14	5·13 ± 0·11	1·26 ± 0·09	4·1 ± 0·6
	1·19	9·2	5	5·91 ± 0·11			
	1·19	7·6	5	4·37 ± 0·09			
	1·19	5·7	5	2·93 ± 0·05			
	1·19	4·2	5	1·94 ± 0·06			
−28·98	1·38	10·2	5	9·53 ± 0·08	7·28 ± 0·36	2·21 ± 0·17	3·3 ± 0·7
	1·38	8·7	5	8·08 ± 0·27			
	1·38	7·0	5	5·70 ± 0·12			
	1·38	5·6	5	4·64 ± 0·13			
	1·38	4·2	5	3·27 ± 0·09			

TABLE 3. ΔH, ΔS^0, E, A, ΔH^*, *and* ΔS^* *for reaction of diethylamine with trinitrobenzene.*

All value are " best " values by least squares, with standard deviations. Standard entropies are at 1 mole l.$^{-1}$.

	Acetone–ether	Acetone–water
ΔH (kcal. mole^{-1})	−7·7 ± 0·8	−0·2 ± 1·5
$\Delta S°$ (cal. deg.$^{-1}$ mole^{-1} at 25°)	−30 ± 4	+10 ± 6
E_f (kcal. mole^{-1})	0 ± 0·2	3·8 ± 0·3
E_b (kcal. mole^{-1})	7·7 ± 0·6	4 ± 1
$\log_{10} A_f$ (A_f in l.^{2} mole^{-2} sec.$^{-1}$)	2·2 ± 0·2	6·3 ± 0·3
$\log_{10} A_b$ (A_b in sec.$^{-1}$)	8·8 ± 0·7	4 ± 1
ΔH^*_f (kcal. mole^{-1} at 25°)	0·6 ± 0·6	4·4 ± 0·3
ΔH^*_b (kcal. mole^{-1} at 25°)	8·3 ± 0·6	5·6 ± 1
ΔS_f^* (cal. deg.$^{-1}$ mole^{-1} at 25°)	−50 ± 1	−31·$_5$ ± 1·5
ΔS_b^* (cal. deg.$^{-1}$ mole^{-1} at 25°)	−20 ± 3	−42 ± 4·5

ΔS^* refers is an ideal solution of concentration 1 mole l.$^{-1}$. Some rough estimates of the optical density at equilibrium give values for the extinction coefficient of the order of 10^3.

DISCUSSION

The Nature of the Complex between 1,3,5-Trinitrobenzene and Diethylamine.—Recent work [6,7] has shown that trinitrobenzene and diethylamine can undergo a series of reactions. Foster [7] followed the development of optical density with time in chloroform solutions at room temperature; he observed an initial instantaneous reaction, followed by changes lasting several minutes. The composition of both the initial and the final product was 3 molecules of diethylamine to 1 of trinitrobenzene. It was suggested that the initial instantaneous product was a charge-transfer complex, and the final product a covalent compound. At the temperatures and concentrations used in the present work, the rates of the later reactions are negligible, and our results refer to the initial reaction. The molar ratio in our solvents appears to be 2 : 1, as the next section shows.

The Mechanism of the Reaction between Trinitrobenzene and Diethylamine.—Interpretation of the rate–concentration relation. The observed linear relation between the first-order constants of the individual runs and the squares of the diethylamine concentrations,

$$2{\cdot}303s = b^2k_f + k_b. \qquad (1)$$

may be explained on the assumption that the rate-determining process is a reversible reaction producing a complex of formula AD_2:

$$A + 2D \underset{k_b}{\overset{k_f}{\rightleftharpoons}} AD_2. \qquad (2)$$

It is, however, important to enquire whether the experimental results are compatible with alternative schemes. A possible scheme, leading to a complex AD, is:

$$A + D \underset{k_b}{\overset{k_f}{\rightleftharpoons}} AD. \qquad (3)$$

This would lead to the relation:

$$2{\cdot}303s = bk_f + k_b. \qquad (4)$$

Our results are not compatible with this relation, since plots of s against b are curved; the points at higher concentrations might be represented quite well by straight lines, but these lines would give negative intercepts which would be difficult to interpret. These results cannot be attributed to the unavoidable traces of water present in acetone, in quantities comparable to the lower concentrations of diethylamine, since they are observed also when water equivalent to the diethylamine is added. An alternative scheme, in which AD_2 is first formed as in equation 2 and then dissociates in a rapid equilibrium to AD + D, also leads to equation 4 and may therefore be rejected. A scheme leading to a complex of formula AD_3:

$$A + 3D \underset{k_b}{\overset{k_f}{\rightleftharpoons}} AD_3, \qquad (5)$$

is likewise excluded, since it leads to the relation

$$2{\cdot}303s = b^3k_f + k_b, \qquad (6)$$

whereas the plots of s against b^3 are found to be markedly curved. The same applies to the variant in which AD_2 is formed as in equation 2 and then undergoes further reaction with D in a rapid equilibrium $AD_2 + D \rightleftharpoons AD_3$. If the correct equation involves an integral power of b, it is certainly equation 1, corresponding to the scheme given in equation 2. Our results do not, however, rule out some fractional power of b such as 1·5, which would correspond to concurrent reactions giving AD and AD_2. Since such a scheme would lead to much greater complexity, we have not pursued it further.

In what follows we have adopted the scheme given in equation 2 for the overall reaction. It is not, however, necessary to suppose that AD_2 is formed by termolecular collisions. The kinetic equation 1 is equally consistent with a preliminary rapid equilibrium and a bimolecular rate-determining step, as in the following alternative schemes:

$$2D \overset{\text{Fast}}{\rightleftharpoons} D_2; \quad D_2 + A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AD_2, \tag{7}$$

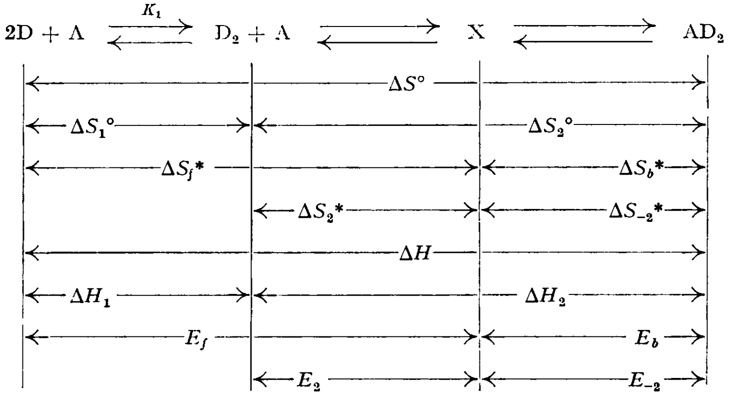
$$A + D \overset{\text{Fast}}{\rightleftharpoons} AD; \quad AD + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AD_2, \tag{8}$$

Analysis shows that the forward rate constant k_f determined from the experimental results by means of equation 1 would then be equal to K_1k_2, where K_1 is the equilibrium constant $(D_2)/(D)^2$ or $(AD)/(A)(D)$; and the reverse rate constant k_b would be equal to k_{-2}. Intermediates of this kind are very commonly invoked to account for third-order kinetics.

Of the two possible intermediates, the complex D_2 seems not unlikely. There is evidence for some degree of association of diethylamine by hydrogen-bonding in the liquid phase; the frequency of the N–H stretching frequency is lower in liquid diethylamine than in the vapour,[11] and is shifted in solution in carbon tetrachloride and ethanol.[12] For the gas phase, the abnormally high values of the second virial coefficient have been interpreted in terms of dimerisation;[13] calculations on this basis gave, for $2D \rightleftharpoons D_2$, $\Delta H = -3{\cdot}3$ kcal. mole^{-1}, $\Delta S^0 = -20{\cdot}3$ cal. deg.$^{-1}$ mole^{-1}. The last figure is derived from values of K_p expressed in atm.; to convert the units into mole l.$^{-1}$, it is necessary to subtract 6·4, and we obtain $\Delta S^0 = -27$ cal. deg.$^{-1}$ mole^{-1}.

We therefore adopt the reaction scheme expressed in equation 7. Our general conclusions would, however, be unaffected if the scheme given in equation 8 were correct. The various quantities concerned in the equilibria and kinetics are shown in Fig. 2. Of these, the following have been experimentally determined (Table 3); ΔH, ΔS^0, E_f, ΔS_f^*, $E_b = E_2$, and $\Delta S_b^* = \Delta S_2^*$.

FIG. 2. *Reaction scheme.*



Interpretation of the Equilibrium Data.—The values of the overall standard entropy change ΔS^0 shown in Table 3 can be interpreted as follows in terms of the reaction scheme given in equation 7. The association of three molecules into one ($2D + A \longrightarrow AD_2$) would by itself lead to a considerable decrease of entropy (cf. the value -27 cal. deg.$^{-1}$ mole^{-1} derived above for $2D \longrightarrow D_2$ in the gas phase). The experimental value for acetone–water solutions, however, is $+10$ cal. deg.$^{-1}$ mole^{-1}, indicating that considerable

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[11] Barr and Hazeldine, *J.*, 1955, 4169.

[12] Chulanovski, *Izvest. Akad. Nauk, U.S.S.R., Ser. Fiz.*, 1953, **17**, 624; *Chem. Abs.*, 1954, **48**, 5651.

[13] Lambert and Strong, *Proc. Roy. Soc.*, 1950, *A*, **200**, 566.

desolvation accompanies the complex-formation. The value in acetone–ether, —30 cal. deg.$^{-1}$ mole^{-1}, indicates that there is less desolvation of the reactants in this solvent.

The fact that there is considerably more complex-formation in acetone than in ethanol or propan-2-ol, although all these solvents have comparable dielectric constants, implies that some specific interaction is concerned. This presumably is the association of diethylamine with the solvents by hydrogen bonding; for acetone, there is independent evidence of this from infrared observations on the N–H stretching frequency.[14,15] (Related instances of equilibria not controlled by the dielectric constant are the associations of trinitrobenzene with naphthalene[16] and with dimethylaniline.[5]) Again, in acetone–water the complex-formation is considerably greater than in acetone–ether, in the temperature range used; here again the diethylamine is presumably preferentially solvated.

The overall enthalpy change ΔH will likewise include contributions due to desolvation, and the difference of $7{\cdot}5 \pm 2$ kcal. mole^{-1} between the values for acetone–ether and acetone–water represents the additional desolvation energy in the latter solvent. This is a reasonable value, corresponding roughly with the breaking of two $\text{N–H}\cdots\text{O}$ hydrogen bonds.[17]

Interpretation of the Kinetic Data.—The observed entropies of activation. The observed values of $\Delta S_b{}^*$ (Table 3) refer to the process $AD_2 \longrightarrow X$, where X is the transition complex in the reverse reaction $AD_2 \longrightarrow D_2 + A$ (see Fig. 2). It is striking that the values of $\Delta S_b{}^*$ in both solvents are large and negative (—20 and —42 cal. deg.$^{-1}$ mole^{-1}), although incipient dissociation of one molecule into two would be itself lead to a positive value. It must be inferred that the transition complex X is more solvated than AD_2; and there will be still more solvation as X goes over to the products $D_2 + A$. The difference between the two solvents is also interesting. For acetone–water, the value of $\Delta S_b{}^*$ is double that for acetone–ether, in accordance with the greater solvating power of acetone–water, which will lead to a greater difference of solvation between AD_2 and X.

The values of $\Delta S_f{}^*$, which refer to the process $2D + A \longrightarrow D_2 + A \longrightarrow X$ (see Fig. 2), are negative, as might be expected from the decrease in the number of molecules. The value for acetone–water is considerably more positive than that for acetone–ether (—32 against —50 cal. deg.$^{-1}$ mole^{-1}); this indicates that considerably more desolvation occurs in acetone–water.

The observed energies of activation. The values of E_b or E_{-2}, for the reverse reaction $AD_2 \longrightarrow X$, reflect the interpretation given to $\Delta S_b{}^*$. They will include terms for the dissociation of AD_2 and for solvation changes. The smaller value in acetone–water (4 against 7·7 kcal. mole^{-1}) reflects the greater heat of solvation in this solvent; the difference between the contributions from solvation is thus $3{\cdot}7 \pm 1{\cdot}6$ kcal. mole^{-1}. This is an appreciable fraction of E_b. Similar large contributions to E from solvation changes have been noted for other reactions.[18] The values of E_f, if our interpretation of $\Delta S_f{}^*$ is correct, will be influenced by the desolvation that accompanies the process $2D + A \longrightarrow D_2 + A \longrightarrow X$; the difference of $3{\cdot}8 \pm 0{\cdot}9$ kcal. mole^{-1} between the two solvents corresponds to the greater energy of desolvation required in acetone–water.

The individual steps of the reaction: kinetic and thermodynamic parameters. It is of interest to attempt estimates of the energy and entropy functions (see Fig. 2) for the individual reactions $2D \rightleftharpoons D_2$ (ΔH_1, $\Delta S_1{}^0$) and $D_2 + A \longrightarrow X \longrightarrow AD_2$ (ΔH_2, E_2, $\Delta S_2{}^0$, $\Delta S_2{}^*$). In the following, singly primed quantities refer to acetone–ether as solvent and doubly primed to acetone–water.

The energy parameters may be estimated as regards order of magnitude from the

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[14] Dodd and Stephenson, in "Hydrogen Bonding," ed. Hadži and Thompson, Pergamon Press, 1959, p. 177.

[15] Mizushima, Tsuboi, Shimanouchi, and Tsuda, *Spectrochim. Acta*, 1955, **7**, 106.

[16] Ross and Labes, *J. Amer. Chem. Soc.*, 1955, **77**, 4916.

[17] Pimentel and McClellan, "The Hydrogen Bond," Freeman, San Francisco and London, 1960, pp. 214, 224.

[18] Caldin, *J.*, 1959, 3345.

following considerations: (i) it is very unlikely that E_2 will be negative, since, although in the absence of solvation the formation of an outer complex may proceed with zero or small activation energy,[3b,3c] there will be a positive contribution from desolvation; and (ii) on account of desolvation, ΔH_1 will have a more positive value than that in the vapour phase ($-3{\cdot}3$ kcal. mole^{-1}), as in the case of the analogous dimerisation of carboxylic acids.[19] Assuming then that (i) $E_2 > 0$ and (ii) $\Delta H_1 > (-3{\cdot}3)$ kcal. mole^{-1}, and using the relations (see Fig. 2) $\Delta H_2 = \Delta H - \Delta H_1$ and $E_2 = E_f - \Delta H_1$, we conclude that in acetone–ether E_2' lies between 0 and 3·5, $\Delta H_2'$ between $-8{\cdot}7$ and $-3{\cdot}6$, and $\Delta H_1'$ between $-3{\cdot}3$ and $+0{\cdot}2$ kcal. mole^{-1}. The values for the two solvents are collected in Table 4.

TABLE 4. *Estimated rate and equilibrium parameters for the individual reactions.*

(Entropies in cal. deg.$^{-1}$ mole^{-1} at 25°; energies in kcal. mole^{-1}.)

Reaction	Function	Solvent	
		Acetone–ether	Acetone–water
$2D \longrightarrow D_2$	ΔH_1	$-3{\cdot}3$ to $+0{\cdot}2$	$-3{\cdot}3$ to $+4{\cdot}1$
	$\Delta S_1{}^0$	*ca.* -17	*ca.* -7
$D_2 + A \longrightarrow AD_2$	ΔH_2	$-8{\cdot}7$ to $3{\cdot}6$	$-5{\cdot}8$ to $+4{\cdot}6$
	$\Delta S_2{}^0$	*ca.* -13	*ca.* $+17$
	E_2	0 to 3·5	0 to 7·4
	$E_{-2} = E_b$	$7{\cdot}7 \pm 0{\cdot}6$	4 ± 1
	$\Delta S_2{}^*$	*ca.* -33	*ca.* -25
	$\Delta S_{-2}{}^* = \Delta S_b{}^*$	-20 ± 3	$-42 \pm 4{\cdot}5$

Estimation of the entropy parameters is more difficult. In the gas phase, $\Delta S_1{}^0 = -27$ cal. deg.$^{-1}$ mole^{-1}, and in solution we may expect a less negative value on account of desolvation; thus we may conclude that $\Delta S_1{}^{0''} > \Delta S_1{}^{0'} > -27$ cal. deg.$^{-1}$ mole^{-1}. In the analogous dimerisation of acetic acid, which likewise involves hydrogen bonds, the standard entropy changes even in non-polar solvents exceed the gas-phase values by 10 cal. deg.$^{-1}$ mole^{-1} or more,[20] so this figure will not be too large for acetone–ether. We therefore take $\Delta S_1{}^{0'} = -17$ cal. deg.$^{-1}$ mole^{-1}. The relations (see Fig. 2) $\Delta S_2{}^0 = \Delta S^0 - \Delta S_1{}^0$ and $\Delta S_f{}^* = \Delta S_1{}^0 + \Delta S_2{}^*$ then lead to values of -13 cal. deg.$^{-1}$ mole^{-1} for $\Delta S_2{}^{0'}$ and -33 cal. deg.$^{-1}$ mole^{-1} for $\Delta S_2{}^{*'}$. This value $\Delta S_2{}^{*'}$ is of the right order for a bimolecular association, and to this extent justifies the estimate used for $\Delta S_1{}^{0'}$; a higher estimate than 10 cal. deg.$^{-1}$ mole^{-1} for the desolvation contribution to $\Delta S_1{}^{0'}$ would make $\Delta S_2{}^{*'}$ unduly high.

In view of the higher solvating power of acetone–water than of acetone–ether, it is natural to suppose that $\Delta S_1{}^{0''} > \Delta S_1{}^{0'}$; thus our estimate of the desolvation contribution to $\Delta S_1{}^{0''}$ must be at least 10 cal. deg.$^{-1}$ mole^{-1}. On the other hand, the same principle requires that $\Delta S_2{}^{*''}$ be more positive than $\Delta S_2{}^{*'}$, and this entails that the contribution to $\Delta S_1{}^{0''}$ does not exceed 28 cal. deg.$^{-1}$ mole^{-1} (if the contribution to $\Delta S_1{}^{0'}$ is 10). As a compromise we may tentatively adopt the value 20 cal. deg.$^{-1}$ mole^{-1}; we then obtain the values $\Delta S_2{}^{0''} = +17$ and $\Delta S_2{}^{*''} = -25$ cal. deg.$^{-1}$ mole^{-1}.

The values relating to the separate dimerisation and complex-formation reactions are collected in Table 4. It will be seen that they are self-consistent and reasonable values for association accompanied by some desolvation, the desolvation effects being greater in acetone–water. No great reliance, however, can be placed on the absolute values of these tentative estimates. The possibility of a positive value of E_2 for the complex-formation is interesting, since it would be attributable mainly to the energy required for desolvation, as for the complex-formation between trinitrobenzene and ethoxide ion.[18]

Comparison with the Rates of Reaction of Trinitrobenzene with Aromatic Amines.—It is noteworthy that, in contrast to the reaction with diethylamine, the rates of formation of the complexes between trinitrobenzene and various aromatic amines were too fast for measurement (Table 1). The explanation may be that only the diethylamine reaction goes *via* the dimer, whose concentration is probably low; the observed 1 : 1 stoicheiometry

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[19] Allen and Caldin, *Quart. Rev.*, 1953, **7**, pp. 272 *et seq.*

[20] Davies, Jones, Patnaik, and Moelwyn-Hughes, *J.*, 1951, 1249.

of the complexes with aromatic amines [5] suggests that their formation will follow equation 3 rather than 2. It may be, however, that the reaction with the diethylamine dimer has the higher activation energy also. If the reactions with aromatic amines are bimolecular, the kinetic observations imply that their energies of activation are less than about 5·5 kcal. mole^{-1}; it is thus possible that these energies of activation are less than that for the diethylamine reaction (E_2 in Table 4).

General Conclusions on the Reaction of Trinitrobenzene with Diethylamine.—(i) The reaction is reversible. In the forward direction it appears to follow third-order kinetics, first-order in trinitrobenzene and second-order in diethylamine. This is interpreted in terms of a rapid preliminary equilibrium, possibly the dimerisation of diethylamine. (ii) The entropy and energy parameters derived from the observed rate and equilibrium constants suggest that desolvation occurs progressively in the several stages of the forward reaction. Solvation changes are greater in acetone–water than in acetone–ether, as would be expected if solvation were due to hydrogen bonding. (iii) Of the rate and equilibrium parameters for the association reaction $D_2 + A \rightleftharpoons AD_2$ (or possibly $D + AD \rightleftharpoons AD_2$) only those derived from the rates of the reverse reaction can be directly determined (E_{-2} and ΔS_{-2}*). The rest can be given reasonable values of varying reliability. The values of E_{-2} show that considerable contributions are made by changes of solvation.

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