74. *The Acid–Base Function in Non-aqueous Solution. Part II.*[1] *The Equilibria of Mono-, Di-, and Tri-n-butylamine with 2,4-Dinitrophenol in Several Aprotic Solvents.*

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In the solvents fluorobenzene, chlorobenzene, bromobenzene, benzene, toluene, anisole, and di-n-butyl ether, the three amines mono-, di-, and tri-n-butylamine (B) react with 2,4-dinitrophenol (HA) to give equilibria of the type, $B + HA \rightleftharpoons BHA$. The equilibrium constants have been determined spectrophotometrically in the temperature range 20—60° and are expressed as changes in standard Gibbs free energies, enthalpies, and entropies.

The results demonstrate that the order of basic strength ($-\Delta G^\circ$) found in chlorobenzene[1] (mono- < di- < tri-n-butylamine) is preserved only in the halogenated benzenes. For limited groups of systems the relation between entropy and enthalpy of reaction is linear. The factors which determine deviations from this relation are discussed, and some consideration is given to the effect of the solvent on the absolute values of the thermodynamic functions measured.

IN Part I[1] of this series, the following conclusions were reached: (*a*) In chlorobenzene solution the reaction occurring between an amine, B (mono-, di-, or tri-n-butylamine), and 2,4-dinitrophenol, AH, is of the form

$$B + HA \rightleftharpoons BHA \qquad (1)$$

(*b*) The ultraviolet absorption spectra of these solutions indicate that the nitrophenol is ionized in much the same way as in water, though because of (*a*) it is always associated through a hydrogen bond with the amine cation. (*c*) The electron-inductive effect of alkyl groups is sufficient to explain the acid–base strength of the amines relatively to the nitrophenol, and steric effects are not important.

The investigation reported in this Part greatly extends our range of solvents, and we find confirmation of the principles (*a*) and (*b*) above. We find now, however, that the order of basic strength in the solvents treated in this Part is not simply related to the electron-inductive effect, and we cannot draw definite conclusions yet about the magnitude of the separate influences of this effect in comparison with solvent and steric factors. Some general conclusions are however possible, and it is becoming clear, not only from our own work, but also from that of other investigators,[2] that the salient differences between the behaviour of proton-transfer equilibria in water and in aprotic solvents are due to the different contributions made by enthalpies and entropies of solvation. In their study of the equilibria between amines and 2,4-dinitrophenol Pearson and Vogelsong[3] measured equilibrium constants at one temperature only, so that it is not possible to assess the varying contributions of enthalpy and entropy terms to the overall free energy of reaction. We have studied both these factors for the reactions of the three n-butylamines with 2,4-dinitrophenol in a set of solvents; where direct comparison with their results is possible agreement is satisfactory, but it also becomes apparent that a detailed explanation of these reactions can only be undertaken when both ΔH° and ΔS° are available for study.

EXPERIMENTAL

Reagents.—2,4-Dinitrophenol was treated as described in Part I. Mono-, di-, and tri-n-butylamine were products of Imperial Chemical Industries Limited and were dried over sodium wire; otherwise they were treated as described in Part I. Benzene (Hopkin and Williams,

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[1] Part I, Bayles and Chetwyn, *J.*, 1958, 2328.

[2] (*a*) Laidler, *Trans. Faraday Soc.*, 1959, **55**, 1725; (*b*) Mortimer and Laidler, *ibid.*, p. 1731; (*c*) Papée, Canady, Zawidzki, and Laidler, *ibid.*, p. 1734; (*d*) Zawidzki, Papée, Canady, and Laidler, *ibid.*, p. 1738; (*e*) Zawidzki, Papée, and Laidler, *ibid.*. p. 1743.

[3] Pearson and Vogelsong, *J. Amer. Chem. Soc.*, 1958, **80**, 1038.

G.P.R. grade), anisole and bromobenzene (B.D.H. Laboratory Reagent), and toluene (B.D.H. sulphur-free) were distilled, dried (P_2O_5; 2—5 days), and then fractionated. Di-n-butyl ether (B.D.H. Laboratory Reagent) was dried (KOH), distilled in a stream of dry nitrogen, refluxed in nitrogen over sodium wire (5 hr.), then fractionated from the sodium in a stream of dry nitrogen. Solvents were tested for neutrality with Bromophenol Blue, and their aqueous extracts with Bromothymol Blue in a manner similar to that described in Part I for chlorobenzene. Di-n-butyl ether will pass these tests only if distilled in an atmosphere of nitrogen.

Apparatus and Solutions.—The glassware and optical cells were baked for at least 2 hr. at 150°, cooled in a stream of dry air, and used immediately.

The spectrophotometer and light-absorption cells, all thermostatically controlled, have been described in Part I. The side-arm of the cells was drawn to a wide-bore capillary before filling; the cells were filled from a capillary pipette provided with a rubber teat, and the side-arm was then sealed off in a small flame. Spectra at room temperature were measured on a Unicam S.P. 500 spectrophotometer, and at higher temperatures on the temperature-controlled spectrophotometer.

Solutions were made up by weight as described in Part I, and the same routine of measurement was used. Errors arising from the preparation of the initial solutions were detected since always at least two independent sets of primary solutions were made.

Strengths of Solutions for Measurement.—The spectrophotometric method is most accurate when the optical densities being measured are in the region 1·0—0·1. To make use of this, solutions were prepared at room temperature according to the following plan:

First a solution was found whose molal ratio of amine to nitrophenol was approximately 1 : 1, and whose optical density was about 0·5.

Then two other solutions were prepared with this ratio approximately 2 : 1 and 1 : 2 respectively, both having an optical density of about 0·5.

Finally two solutions with the molal ratio 1 : 1 were prepared, with optical densities of 0·2—0·3 and 0·8—1·0 severally. The optical density of all these solutions over the temperature range 20—60° then falls within the practicable range of measurement, and, in the present systems, equilibria for which the extent of reaction was either too large or too small were avoided.

RESULTS

Units.—As indicated in the preceding section, solutions were made up by weight. Concentrations are expressed in molalities, m, since this interposes a minimum of arithmetic between the experimental quantities and the figures quoted.

Extinction Coefficients.—Extinction coefficients for the complexes BHA in the various solvents were found by determining the limit reached by the quotient D_{410}/m_{AH} for given m_{AH} (where AH = nitrophenol) as the concentration of added base is increased. An experimental graph of this quotient against m_B (B = amine) is given in Part I where the solvent is chlorobenzene, and B is either mono-, di-, or tri-n-butylamine. Of the solvents under discussion here, dibutyl ether causes the greatest difference in behaviour of the amine–nitrophenol systems from that in chlorobenzene, and we show therefore in Fig. 1 the experimental graph for the system in dibutyl ether as solvent, and tabulate in Table 1 the values of ε_{410} in all the solvents. The limiting value is written $\varepsilon_{mT\lambda}$ for an experiment conducted at room temperature, T, and wavelength λ (mμ).

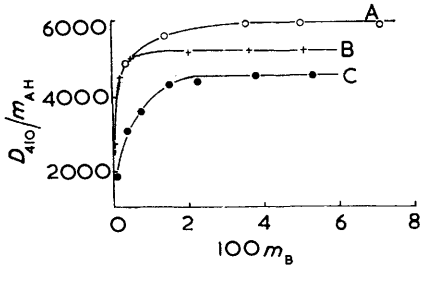


FIG. 1. *The apparent molal extinction coefficient of* 2,4-*dinitrophenol* (AH) *in di-n-butyl ether solutions containing various molalities,* m_B, *of amines. The added amine is* (A) *mono-n-butylamine,* (B) *di-n-butylamine, and* (C) *tri-n-butylamine.*

Un-ionized 2,4-dinitrophenol has a small but significant extinction coefficient at 410 mμ. This is obtained by measuring the optical density, D_{410}, at known molality and temperature,

$\boldsymbol{t}$, in the presence of 10^{-2}M-chloroacetic acid to repress any ionization of the nitrophenol by the solvent. Chloroacetic acid does not absorb light at this wavelength. This extinction coefficient is written $\varepsilon'_{m\boldsymbol{t}\lambda}$, and, in its molar form, ε'_{λ}, is also given in Table 1, column 5.

TABLE 1. *Molar extinction coefficients of* 2,4-*dinitrophenol at* 410 *m*μ.

In excess:	$Bu^n{\cdot}NH_2$	Bu^n_2NH	Bu^n_3N	$CH_2Cl{\cdot}CO_2H$
Fluorobenzene	9939	8965	8780	24
Chlorobenzene	9600	8400	8400	31·6
Bromobenzene	10,020	7840	8710	40·1
Benzene	7040	6180	8530	33·4
Toluene	8700	6210	6880	42·5
Anisole	10,100	8650	9060	137
Di-n-butyl ether	7700	6770	5900	10·2

In dilute solutions containing two light-absorbing species, AHB and AH, we have, at temperature T:

$$D_{\lambda} = m_{\text{AHB}}\varepsilon_{mT\lambda} + m_{\text{AH}}\varepsilon'_{mT\lambda}$$

i.e.,

$$m_{\text{AHB}} = \frac{D_{\lambda} - (m_{\text{AH}} + m_{\text{AHB}})\,\varepsilon'_{mT\lambda}}{\varepsilon_{mT\lambda} - \varepsilon'_{mT\lambda}}$$

where $m_{\text{AH}} + m_{\text{AHB}}$ is the stoicheiometric molality of 2,4-dinitrophenol in the solution.

Since the molality m of a dilute solution can be equated to the quotient of its molar concentration c by the density of the solvent, ρ_T, we have:

$$\frac{\varepsilon_{mT\lambda}}{\rho_T} = \frac{1}{\rho_T}\frac{D_{\lambda}}{m_{\text{AHB}}} = \frac{D_{\lambda}}{c_{\text{AHB}}} = \varepsilon_{\lambda}$$

The molar extinction coefficient ε_{λ} is independent of temperature, so,

$$\frac{\varepsilon_{mT\lambda}}{\rho_T} = \frac{\varepsilon_{m\boldsymbol{T}\lambda}}{\rho_{\boldsymbol{T}}}$$

and therefore,

$$\varepsilon_{mT\lambda} \simeq \varepsilon_{m\boldsymbol{T}\lambda}[1 + \alpha(\boldsymbol{T} - T)]$$

where α is the volume coefficient of expansion of the solvent, obtained from the temperature variation of density, and the approximation is acceptable because $\alpha(\boldsymbol{T} - T)$ is small compared with unity. Similarly,

$$\varepsilon'_{mT\lambda} \simeq \varepsilon'_{m\boldsymbol{t}\lambda}[1 + \alpha(\boldsymbol{t} - T)]$$

TABLE 2. *Experimental results for the system, amine* + 2,4-*dinitrophenol in anisole.*

Mono-n-butylamine:				Di-n-butylamine:				Tri-n-butylamine:			
10^4m_{AH}	10^4m_{B}	Temp.	D_{410}	10^4m_{AH}	10^4m_{B}	Temp.	D_{410}	10^4m_{AH}	10^4m_{B}	Temp.	D_{410}
2·717	2·709	21·5°	0·360	1·372	1·375	20·0°	0·440	1·760	2·082	10·5°	0·810
2·717	2·709	36·5	0·170	1·372	1·375	19·0	0·445	1·760	2·082	35·0	0·335
2·717	2·709	49·0	0·100	1·372	1·375	31·0	0·270	1·760	2·082	48·0	0·180
2·717	2·709	57·5	0·075	1·372	1·375	49·0	0·125	1·760	2·082	57·5	0·120
				1·372	1·375	57·0	0·080				
2·920	5·124	21·0	0·650					1·290	1·187	17·0	0·350
2·920	5·124	34·5	0·335	1·820	1·129	23·0	0·430	1·290	1·187	35·0	0·165
2·920	5·124	47·5	0·185	1·820	1·129	18·0	0·510	1·290	1·187	48·0	0·090
2·920	5·124	57·5	0·125	1·820	1·129	31·5	0·305	1·290	1·187	57·0	0·060
				1·820	1·129	49·0	0·140				
3·840	3·430	22·0	0·630	1·820	1·129	57·0	0·090	1·429	2·944	18·0	0·670
3·840	3·430	35·0	0·330					1·429	2·944	35·0	0·360
3·840	3·430	47·5	0·190	0·869	1·827	23·0	0·340	1·429	2·944	48·0	0·200
3·840	3·430	57·5	0·130	0·869	1·827	20·0	0·376	1·429	2·944	57·5	0·125
				0·869	1·827	32·0	0·230				
5·985	2·854	22·0	0·750	0·869	1·827	49·0	0·100	2·821	1·405	19·5	0·605
5·985	2·854	35·0	0·420	0·869	1·827	57·0	0·065	2·821	1·405	35·5	0·360
5·985	2·854	47·5	0·250					2·821	1·405	48·0	0·205
5·985	2·854	57·5	0·175	2·850	2·561	24·0	1·080	2·821	1·405	57·0	0·140
				2·850	2·561	21·0	1·080				
5·601	4·751	23·5	1·010	2·850	2·561	32·5	0·790	2·806	2·788	20·0	1·050
5·601	4·751	35·0	0·595	2·850	2·561	49·0	0·410	2·806	2·788	35·5	0·600
5·601	4·751	47·5	0·345	2·850	2·561	57·0	0·280	2·806	2·788	48·5	0·350
5·601	4·751	57·5	0·235					2·806	2·788	57·5	0·235

Thus the expression for m_{AHB} becomes,

$$m_{\mathrm{AHB}} = \frac{D_\lambda - (m_{\mathrm{AH}} + m_{\mathrm{AHB}})\varepsilon'_{mt\lambda}[1 + \alpha(\boldsymbol{t} - T)]}{\varepsilon_{mT\lambda}[1 + \alpha(\boldsymbol{T} - T)] - \varepsilon'_{mt\lambda}[1 + \alpha(\boldsymbol{t} - T)]}$$

All the quantities on the right-hand side of this expression are experimentally obtainable, and this is the form in which the calculation was handled by the computer. The experimental procedure is to measure the molal extinction coefficients of both forms of the nitrophenol (AHB and AH) at the prevailing room temperatures, $\boldsymbol{T}$ and $\boldsymbol{t}$ respectively, and then to use the above expression to obtain m_{AHB} in working solutions at temperature T.

Equilibrium Constants and Thermodynamic Quantities.—The equilibrium constants have been quoted as mole fractional dimensionless quantities, K_x, by multiplying the molal constant K_m by $1000/M$, M being the molecular weight of the solvent. This is necessary because there is one less product molecule than there are reactant molecules. By using this system, we allow for the varying number of moles of solvent per kg. when we make comparisons between thermodynamic quantities obtained in different solvents. The thermodynamic functions are calculated from:

$$\Delta G^\circ = -\boldsymbol{R}T \ln K_x; \; \Delta H^\circ = -\boldsymbol{R}\, \partial \ln K_x/\partial T^{-1}; \; \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T.$$

TABLE 3. *Thermodynamic functions for the reaction between some amines and 2,4-dinitrophenol in various solvents.*

Solvent	n-Butylamine	$-\Delta G^\circ_{298}$ (kcal. mole^{-1})	$-\Delta H^\circ_{298}$ (kcal. mole^{-1})	$-\Delta S^\circ_{298}$ (cal. deg.$^{-1}$ mole^{-1})
Chlorobenzene	Mono-	4·38 ±0·01	11·80 ±0·27	24·9 ±0·9
	Di-	5·87 ±0·01	11·89 ±0·14	20·2 ±0·5
	Tri-	6·39 ±0·01	14·16 ±0·23	26·1 ±0·8
Fluorobenzene	Mono-	4·19 ±0·01	13·23 ±0·1	30·3 ±0·4
	Di-	5·96 ±0·01	12·72 ±0·1	22·6 ±0·5
	Tri-	6·33 ±0·01	13·81 ±0·1	25·1 ±0·4
Bromobenzene	Mono-	4·06 ±0·01	13·23 ±0·2	30·8 ±0·7
	Di-	6·08 ±0·01	12·91 ±0·2	22·9 ±0·7
	Tri-	6·33 ±0·01	13·49 ±0·2	24·0 ±0·7
Benzene	Mono-	4·04 ±0·01	11·86 ±0·1	26·2 ±0·5
	Di-	5·59 ±0·01	13·13 ±0·1	25·3 ±0·4
	Tri-	5·28 ±0·1	11·97 ±0·06	22·4 ±0·2
Toluene	Mono-	3·81 ±0·01	11·81 ±0·2	26·8 ±0·5
	Di-	5·35 ±0·01	13·04 ±0·1	25·8 ±0·4
	Tri-	5·00 ±0·01	11·71 ±0·1	22·5 ±0·3
Anisole	Mono-	4·97 ±0·01	12·11 ±0·1	24·0 ±0·4
	Di-	6·31 ±0·01	13·75 ±0·1	24·9 ±0·5
	Tri-	6·03 ±0·01	12·57 ±0·1	21·9 ±0·2
Dibutyl ether	Mono-	5·46 ±0·01	15·39 ±0·18	33·3 ±0·6
	Di-	5·74 ±0·01	15·22 ±0·09	31·8 ±0·3
	Tri-	4·57 ±0·01	11·24 ±0·1	22·4 ±0·4

An example of the experimental results is given in Table 2, and the derived thermodynamic quantities for all systems studied are given in Table 3. The errors given are probable errors, arrived at by the standard statistical manipulation of deviations, and the thermodynamic quantities are the result of a least-squares procedure on the variables ln K and T^{-1}. The calculations have been programmed for the Zebra electronic digital computer using actual weighings, optical densities, temperatures, molecular weights, and coefficients of expansion as input variables.

We have checked that in each system studied the relation between m_Bm_{AH} and m_{BHA} at 25° is linear. The graphs showing this are all similar to Fig. 6 of Part I, and an example may readily be constructed from Table 2.

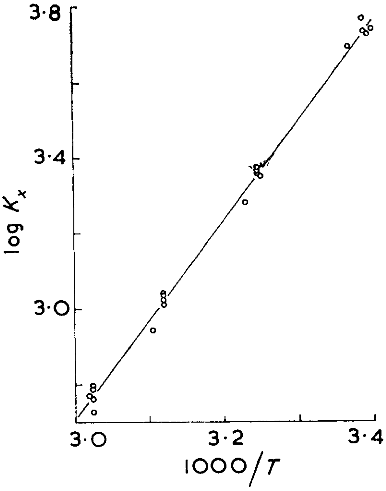


FIG. 2. *The relation between* $\log_{10} K_x$ *and* T^{-1}, *where* K_x *is the equilibrium constant (mole fraction scale) for the equilibrium,* $B + HA \rightleftharpoons BHA$, *in which* HA *is* 2,4-*dinitrophenol, and* B *is mono-n-butylamine in anisole solution.*

The magnitude of the experimental scatter in terms of the quoted probable erros can also be seen by comparing Fig. 2 with the tabulated results. In this respect the system mono-n-butylamine + 2,4-dinitrophenol in anisole is typical.

DISCUSSION

In this discussion, the results for the systems mono-, di-, and tri-n-butylamine in equilibrium with 2,4-dinitrophenol in chlorobenzene are based on the experimental results of Part I, but they have been recalculated by the method given above to allow for the small extinction coefficient of AH in chlorobenzene at 410 mμ. This is given in Table 1.

General Principles.—The thermodynamic quantities associated with the type of reaction, $B + HA \rightleftharpoons BHA$, depend on a rather complex group of influences and, though we shall not make use of all of them in the discussion that follows, it may be helpful to attempt a specification at this stage.

(*a*) Valency force. This will not depend on the solvent, and will increase as the total electron-inductive effect of alkyl groups on nitrogen increases. It will by itself cause tertiary amines to have more negative values of $\Delta G°$ (*i.e.*, be stronger bases) than secondary, and secondary to be stronger than primary, so long as the alkyl groups concerned all have an electron-donating effect. This contribution to the measured thermodynamic quantities may be represented for convenience by making use of an operator symbol Δ_q. We may expect that Δ_q will always make a negative contribution to $\Delta H°$ and $\Delta S°$ and we also expect that the contribution to $\Delta S°$ will be proportional to the effect on $\Delta H°$ [*i.e.*, $\Delta_q(\Delta S°) = a\Delta_q(\Delta H°)$] because the stronger the bond between AH and B, the less free to rotate will the participants be when combined.

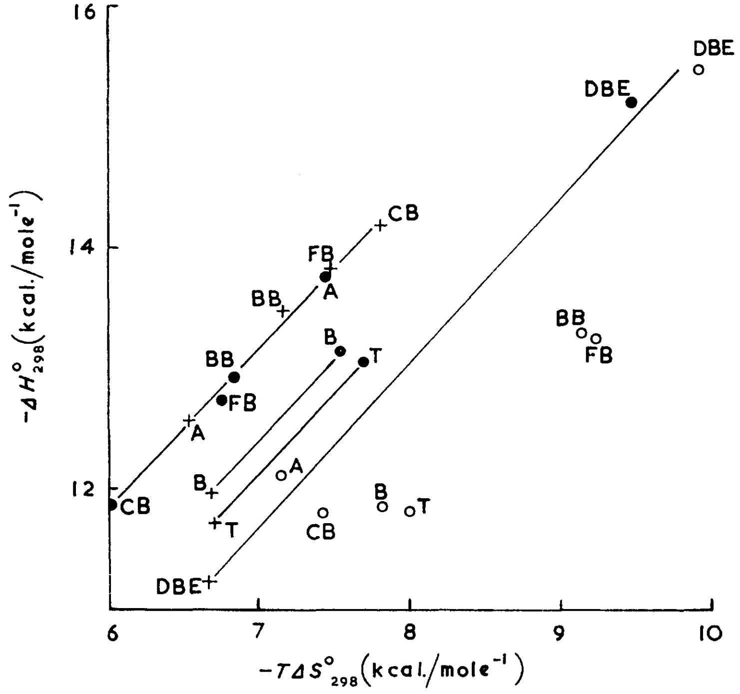
(*b*) Other solvent-independent factors. Among these may be mentioned:

(i) The dipole analogue of the Born charging in ionic systems. This will depend on the dimensions of AH and B, and on the length of the AHB bond. We do not at present consider that this effect will show sufficient variation between the systems we study to be capable of analysis.

(ii) The large negative contribution to ΔS° which may be thought of as arising from the simple fact that two independently rotating molecules join to form one, with the consequent limitation on the translation–rotation factors in the partition coefficient of the product molecule as compared with those of the two reactant molecules.

(iii) The statistical effect. In comparing entropies of reactions involving amines with more than one functional amino-group per molecule, we should consider $\Delta S^\circ + \boldsymbol{R} \ln n$ where n is the number of functional groups per molecule. This is unity in all systems in the present work.

FIG. 3. *The relation between standard enthalpy and entropy of the reaction* $\mathrm{B} + \mathrm{HA} \rightleftharpoons \mathrm{BHA}$ *at* 25° *in various solvents.* HA *is* 2,4-*dinitrophenol.* B *is mono-n-butylamine for* ○, *di-n-butylamine for* ●, *and tri-n-butylamine for* +. *Point labels for solvent are*: A *anisole*, B *benzene*, BB *bromobenzene*, CB *chlorobenzene*, FB *fluorobenzene*, DBE *di-n-butyl ether*, T *toluene.*



(*c*) Solvent interactions. It has been suggested that the peculiar order of basic strength exhibited in water by amines arises because the aminium ions are solvated to an extent dependent on the number of hydrogen atoms attached to the nitrogen atom, and that this effect is opposite to the Δ_q effect above. We may conveniently represent the overall solvent effect by Δ_s.

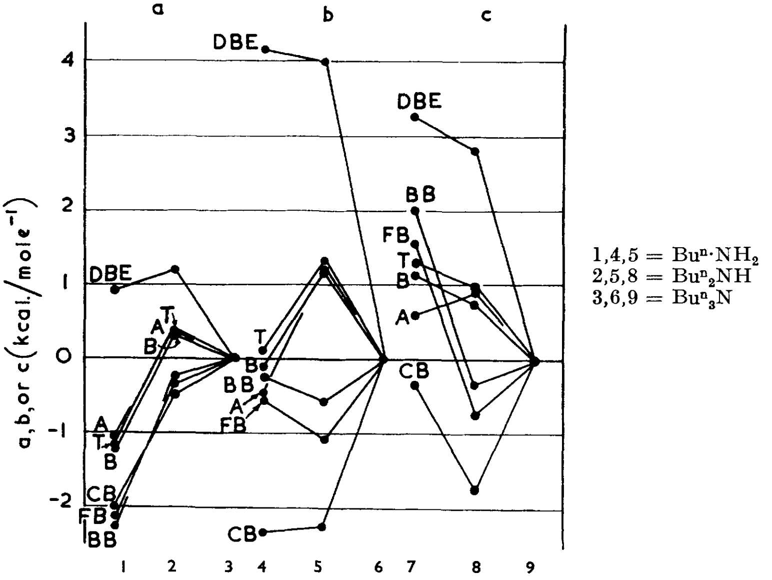
The Relation between Enthalpy and Entropy of Reaction.—We have looked for the proportionality between ΔH° and ΔS° suggested in (*a*) above, and in Fig. 3 it is seen that a relation of this kind holds for the secondary and tertiary amines in the halogenated benzenes and in anisole. Deviations from the line are all on the side of high entropy-loss, or low enthalpy-loss. We prefer to explain them in terms of high entropy-loss because in this type of solvent it seems rather unlikely that the enthalpy of solvation, $\Delta_s(\Delta H)$, will be very significant.

We have also drawn tentative lines through the points for the secondary–tertiary pair of amines in benzene and toluene showing that these amines in these solvents can be solvated to an extent dependent on the solvent but not on the amine type. One may also suggest that all three amines are affected by solvation to the same extent in dibutyl ether.

The points for mono-n-butylamine show that equilibria involving this amine are very sensitive to solvent, and we believe this to be caused by the protons attached to nitrogen but not involved in the hydrogen bond to the phenolic oxygen atom. If this view is correct, then another conclusion to be drawn from Fig. 3 is that it is necessary for there to be two such hydrogen atoms for solvent-specific abnormalities of this kind to appear.

Treatment of Properties relatively to Those of Tri-n-butylamine.—The evidence of the last paragraph points to a way of considering the behaviour of the thermodynamic quantities in reactions of the type (1). We have calculated the difference in the $-\Delta G^\circ$, $-\Delta H^\circ$,

FIG. 4. (a) $-\Delta G^\circ_{298}$, (b) $-\Delta H^\circ_{298}$, (c) $-T\Delta S^\circ_{298}$ *for the reaction* $B + HA \rightleftharpoons BHA$ *in various solvents, relatively to the corresponding values for* B = *tri-n-butylamine. Point-labels to indicate solvent are as in Fig.* 3.



$-T\Delta S^\circ$ values for mono- and di-n-butylamine as compared with the value for tri-n-butylamine, and plotted these relative values as ordinates against the amines spaced uniformly on a horizontal scale.

It is at once apparent from Fig. 4a that $-\Delta G^\circ$ increases in all solvents when di-n-butylamine replaces mono-n-butylamine in reaction (1). The increase in $-\Delta G^\circ$ on replacing di-n-butylamine by tri-n-butylamine is never as great as this, and in some cases (dibutyl ether, toluene, benzene, anisole) becomes negative. In view of the behaviour of $-\Delta H^\circ$ and $-\Delta S^\circ$ which will next be discussed, we think that there is no simple explanation of this. Laidler [2a] has recently come to the same conclusion in connection with related equilibria in water for which, however, the detailed explanations are not applicable to these systems.

As has already been mentioned, the inductive effect of alkyl groups must make a positive contribution primarily to the enthalpy loss in these reactions, and therefore if this were the only effect, all traces in Fig. 4b would coincide to give one line, both legs of which would have a positive slope. Both parts of the trace for amines in chlorobenzene do have a positive slope, and we suspect that in this solvent there is a minimum of disturbance to the simple behaviour. Chlorobenzene is a solvent whose dipole moment is not large (1·55 D) and in which the benzene ring is depleted of electrons inductively so that it will not be readily polarized. Bromobenzene and fluorobenzene are similar to chlorobenzene on both these counts, but the more abnormal behaviour of mono-n-butylamine prevents even the approximation to simple behaviour which is seen in chlorobenzene.

At the other extreme of behaviour is the solvent di-n-butyl ether. In this solvent there is a very high loss of both entropy and enthalpy for the reactions of the primary and secondary amine relatively to the tertiary (Figs. 4b and 4c). This is most probably because the exposed dipole of the ether has a greater affinity for the dipolar B^+HA^- than for either the amine or the nitrophenol molecules.

The two effects, separately dominant in chlorobenzene and dibutyl ether, operate together and contribute nearly equally to the behaviour of the amines in the other solvents. The result is that in toluene, anisole, and benzene, the Figs. 4b and 4c show intermediate behaviour between the two extremes. It may seem a little surprising that in benzene which has no dipole moment we should suggest that solvation is stronger than in bromobenzene, but it must be remembered that the molecule of benzene is readily polarized, and that the attachment through polarized π-electrons may be quite strong, with a strength, $\Delta_s(-\Delta G^\circ)$, whose value is determined more by the relatively low entropy loss than by the low enthalpy loss associated with π-electron interactions. These interactions demand little orientational specificity from the attaching molecule.

The System Tri-n-butylamine + 2,4-Dinitrophenol.—We next consider the properties of the tertiary amine in the various solvents. The order of entropy loss in these is, anisole $\simeq$ dibutyl ether = benzene $\simeq$ toluene < bromobenzene $\leqslant$ fluorobenzene $\leqslant$ chlorobenzene. The order of enthalpy loss is, di-n-butyl ether < toluene < benzene < anisole < bromobenzene < fluorobenzene < chlorobenzene. The entropy loss therefore distinguishes between the halogenated benzenes (high values) and the rest of the solvents, and there is no point in writing down orders within these two groups of three solvents. The same grouping may be read into the order of solvents by enthalpy loss, but here one may specify order within the groups because of the more uniform spread of values and smaller probable errors.

We have examined the dependence of $-\Delta G^\circ_{298}$ (all systems) on the reciprocal dielectric constant, D^{-1}, for if the molecular size parameters are constant (*i.e.*, for given AH and B) the electrical contribution to the experimental ΔG°_{298} will be proportional to D^{-1}. Only the results for tri-n-butylamine + 2,4-dinitrophenol in anisole and the halogenated benzenes can be represented by a relation of this kind, for which the equation is

$$-\Delta G^\circ_{298} = 7{\cdot}583 - 6{\cdot}74D^{-1},$$

and the deviations of the points from this line are less than the probable errors quoted in Table 3. The discussion on Fig. 3 led us to suggest that specific solvent interactions could be small for the systems involving di- and tri-n-butylamine in anisole and the halogenated benzenes, so this evidence from the dependence of $-\Delta G^\circ_{298}$ on D^{-1} confirms the interpretation for tri-n-butylamine and confirms the range of solvents. It does, however, cause us to doubt whether the evidence of Fig. 3 alone is reliably indicative of solvation since the results for di-n-butylamine do not obey a D^{-1} relation.

The solvents in which the tri-n-butylamine system does not obey a D^{-1} relation are benzene, toluene, and di-n-butyl ether. The last may be anomalous because of its exposed dipole and because it has no aromatic system. We suggest that benzene and toluene are anomalous because the polarizability of the aromatic electrons is relatively high. In the halogenated benzenes, on the other hand, the inductive effect of the halogen atoms removes this effect.

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