469. *The Acid–Base Function in Non-aqueous Solution. Part I. The Equilibria between Mono-, Di-, or Tri-*n*-butylamine and 2 : 4-Dinitrophenol in Chlorobenzene.*

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The equilibria between mono-, di-, or tri-*n*-butylamine and 2 : 4-dinitrophenol in chlorobenzene have been shown to be of the form, $B + HA \rightleftharpoons BHA$, where B represents a butylamine and HA represents the nitrophenol. The equilibrium constants have been determined spectrophotometrically in the temperature range 20—60°, and expressed as changes in standard Gibbs free energies, enthalpies, and entropies.

With 2 : 4-dinitrophenol as the reference acid and chlorobenzene as solvent, the basic strengths of these amines fall in the order, mono- < di- < tri-*n*-butylamine, when $-\Delta G^\circ$ for the above reaction is taken as a measure of the basic strength. This order is different from that found in aqueous solution. The values of $-\Delta H^\circ$ for the reactions in chlorobenzene behave in the same way. The results indicate that solvation is a factor in determining the relative strengths of the butylamines in water, and that the steric requirements of the proton or of 2 : 4-dinitrophenol are not of major importance.

THOUGH accurate measurements on the thermodynamics of the acid–base function of amines in water and aqueous solvents have been made,[1, 2] the information on this property in solvents other than water is still very inadequate, though there is some qualitative information about the chemical entities present in these solutions. Maryott [3] has shown that the complexes formed in benzene and dioxan by various alkylammonium picrates have large dipole moments (11—12 D), and that the distance of closest approach between the positive and the negative centres is about 4·5 Å, consistently with salt formation. Infrared studies [4] have demonstrated that if the concentrations of amine and carboxylic acid in carbon tetrachloride or chloroform are decreased below approximately 10^{-3}M, the equilibrium type changes from a complex one between associated species to the simple form:

$$B + HA \rightleftharpoons BHA \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The structure of the compound BHA may be written as $^{+}BH \ldots A^{-}$ or $B \ldots HA$ according to whether the proton is or is not transferred. Barrow [5] has suggested that only with proton transfer is the reaction of true acid–base type. In carbon tetrachloride solutions containing a phenol or naphthol as proton-donor, and dioxan, acetone, methyl acetate, nitromethane, or acetanilide as acceptor, the infrared spectra [6] indicate however that the proton oscillates between two positions of minimum potential energy. Therefore it does

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[1] Everett and Wynne-Jones, *Proc. Roy. Soc.*, 1941, *A*, **177**, 499.

[2] A. G. Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 34.

[3] Maryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 1.

[4] Barrow and Yerger, *J. Amer. Chem. Soc.*, 1954, **76**, 5211; 1955, **77**, 4474, 6206.

[5] Barrow, *J. Amer. Chem. Soc.*, 1956, **78**, 5802.

[6] Nagakura and Sato, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **7**, 1007.

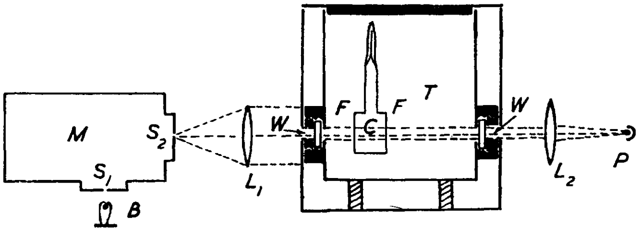
not seem possible to draw a sharp distinction between the above possibilities. Maryott's value [7] for the dipole moment of tribenzylammonium picrate in benzene is of the order to be expected for a molecule with charge separation, so in this system at least, there is strong evidence for proton transfer.

Bell and Bayles [8] have measured the equilibrium constants for the reactions between bromophenol-blue and various aromatic amines in chlorobenzene and anisole solution, and preliminary results were given for the system butylamine–2 : 6-dinitrophenol. The order of basic strength for the butylamines was found to be mono- < di- < tri-*n*-butylamine in chlorobenzene solution, and this order has also been found for the ethylamines [9] in ethanol–water or dioxan–water mixtures which are rich in the organic component. In the present work, the three amines, mono-, di-, and tri-*n*-butylamine, are studied in chlorobenzene solution, and for the first time both enthalpy and entropy changes are reported. In addition, some justification is attempted for the assumptions made in obtaining these thermodynamic quantities from the experimental measurements.

EXPERIMENTAL

Chemicals.—Chlorobenzene (B.D.H.) was first distilled. It was then fractionated, and the middle fraction was dried over fresh phosphoric oxide for 2—9 days. It was then refractionated, and the fraction distilling at 132° ± 0·5° was collected. An aqueous extract of a sample taken from every batch of chlorobenzene was tested with B.D.H. Universal indicator. If the pH of the extract differed from 7, the batch was discarded.

FIG. 1. *The spectrophotometer.*



2 : 4-Dinitrophenol was twice crystallized from alcohol, dried *in vacuo* (NaOH) for several days, and stored in a desiccator (P_2O_5): it had m. p. 112° (lit., 111·6°).

Mono-*n*-butylamine (B.D.H.) was dried (K_2CO_3) for 1 day, then fractionated, and the middle fraction, b. p. 77·0°, was collected. Di-*n*-butylamine (B.D.H.) was dried (NaOH) and then fractionated. The fraction of b. p. 158—159° was collected. Tri-*n*-butylamine (Imperial Chemical Industries Limited) was dried (KOH) for 15 days, and then fractionated. The fraction of b. p. 210—212° was collected. The purity of the three amines was checked by titration against standard acid.

Apparatus.—The glassware and optical cells were baked for at least 2 hr. at 150—170° before use, and left in a vacuum-desiccator over potassium hydroxide.

The Spectrophotometer.—The essential features of the spectrophotometer can be seen from Fig. 1. Light from a 30 w tungsten filament bulb, *B*, is passed through a Bellingham and Stanley direct-reading spectrometer, *M*, whose eyepiece has been replaced by a bilateral exit slit, S_2. The lens, L_1, collimates the monochromatic beam, which passes through one of four 2-litre thermostats, *T*, contained in a long rectangular trough running perpendicularly to the plane of the paper. The light is then focused on a photomultiplier tube, *P*, by the lens L_2. The thermostats are arranged to operate at approximately 30°, 37°, 47°, and 57° ± 0·05°. The sealed mercury–toluene regulators, stirrers, and glass-enclosed fish-tank heaters are not shown in the Figure. The tank windows, *W*, are of Perspex.

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[7] Maryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 7.
[8] Bell and Bayles, *J.*, 1952, 1518.
[9] Rumpf, Girault-Vexlearschi, and Schaal, *Bull. Soc. chim. France*, 1955, 554.

The bulb, monochromator, collimating and focusing lenses, and photomultiplier tube were mounted on a high-tensile light-alloy casting which itself was mounted on two parallel steel bars, not shown, along which it could slide freely. The light beam could therefore be passed through any one of the four thermostats.

The 1 cm. Pyrex cell, *C*, has a cylindrical body, optically flat fused-on end-faces, *F*, and a side-arm. These cells are completely immersed in the thermostat, and two equally good methods were used for closing them. One method is to attach a B7 cone to the side-arm and close it with a B7 cap, silicone grease being used. In the other the side-arm is drawn to a capillary, 3 cm. long by 1 mm. internal diameter, and then sealed in a flame after filling of the cell. Filling was achieved with an all-glass hypodermic syringe whose metal needle was replaced by a fused-on fine-glass capillary which could be inserted into the capillary side-arm of the cell. The comparison cell filled with solvent was prepared in the same way.

The method of measuring the optical density of a solution was similar to that used on commercial instruments. The instrumental uncertainty of measurements was ±0·002 for optical density in the region of 50% transmission or 0·3 optical density. The way in which this uncertainty changes with measured optical density runs parallel to the behaviour of the well-known commercial instruments. The resolution of the instrument for sodium D light (width of line in mμ at half its maximum intensity) is 8·1 mμ for the slit-width used in this work.

Solutions.—Approximately 0·06 g. of 2 : 4-dinitrophenol was weighed out in a 50 ml. graduated flask, and chlorobenzene was added, its weight being found by difference. This solution was then diluted by weight to give a solution with a mole fraction of 2 : 4-dinitrophenol approximately ten times that required in the final solution. A solution of amine in chlorobenzene was made in a similar way.

The working solutions were obtained by weighing approximately the correct proportions of the 2 : 4-dinitrophenol and amine solutions, and finally diluting by weight with chlorobenzene to give a measurable optical density.

Measurements of the optical density of the solutions were made at room temperature on the Unicam S.P. 500 instrument, and at four higher temperatures on the spectrophotometer described above. A given solution was measured at each temperature in turn in increasing order of temperature, and then three more readings were taken at each temperature in random order to check reproducibility.

The reproducibility was of the order of magnitude to be expected from the intrumental uncertainties quoted above. Solutions which had been subjected to the procedure just described showed no visual tendency to fade, even over a period of weeks. A complete experiment on a given solution lasted for about 4 hr., and there was no tendency for the optical density to increase or decrease during this period. One solution having an optical density of 0·572 at 29·5° gave an identical reading 24 hr. later.

The above procedure was repeated for different mole fractions of amine and indicator, designed to cover the measurable range of optical densities. Fresh solutions were made up from time to time to eliminate possible errors in the various dilutions.

RESULTS

Units.—The equilibrium constant applicable to this reaction is found experimentally (see below) to have the form:

$$K = [\mathrm{BHA}]/[\mathrm{HA}][\mathrm{B}] \qquad (2)$$

It is particularly convenient in the present work to express all concentrations as mole fractions and to calculate *K* in terms of these units. This is because mole fractions are independent of temperature, and so in the preparation of solutions no corrections for the considerable coefficient of expansion of chlorobenzene need be made.

The spectrophotometric determinations of the coloured complex BHA in equation (2) lead to the concentration, *c*, of the complex in mole l.$^{-1}$ if the ordinary extinction coefficient, ε_λ, is used in conjunction with the usual equation:

$$c = D_\lambda/\varepsilon_\lambda d \qquad (3)$$

where *D* is the optical density at wavelength λ, ε_λ is the molar extinction coefficient at wavelength λ, and *d* is the optical path length through the solution.

This value for c may then be expressed as a mole fraction, x, by using the relation, true for dilute solutions:

$$x = MD_\lambda/1000\rho_T\varepsilon_\lambda d$$

or, writing,

$$\varepsilon_{x,T,\lambda} = (1000\rho_T/M)\varepsilon_\lambda$$

then,

$$x = D_\lambda/\varepsilon_{x,T,\lambda}d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The subscripts, T and λ, are retained in the new quantity, $\varepsilon_{x,T,\lambda}$ to emphasize its dependence on temperature as well as wavelength.

In using the expression (4), the value of $\varepsilon_{x,T,\lambda}$ is plotted against temperature, and interpolated for the working solution concerned. The calculation of mole fractions is then analogous to that used in finding concentrations by using ε_λ.

Strictly, the expression for K is:

$$K = (x_{\text{BHA}}/x_{\text{B}} \cdot x_{\text{HA}})(\gamma_{\text{BHA}}/\gamma_{\text{B}} \cdot \gamma_{\text{HA}})$$

and values of the activity coefficients, γ, should be estimated. In the present work we assume that the quotient of activity coefficients is unity or constant. For the free amine and nitrophenol at low concentrations this is very probably a good assumption, and though the complex, BHA, will have a relatively high dipole moment, at concentrations of the order 10^{-5} mole l.$^{-1}$ (mole fraction of the order 10^{-6}) we do not expect that dipole association will be sufficiently important to cause γ_{BHA} to depart very markedly from unity. The plots in Fig. 6 may also be taken as partial justification of the assumption.

FIG. 2.

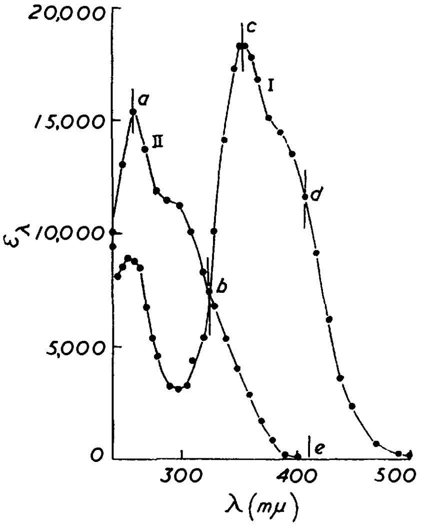


FIG. 3.

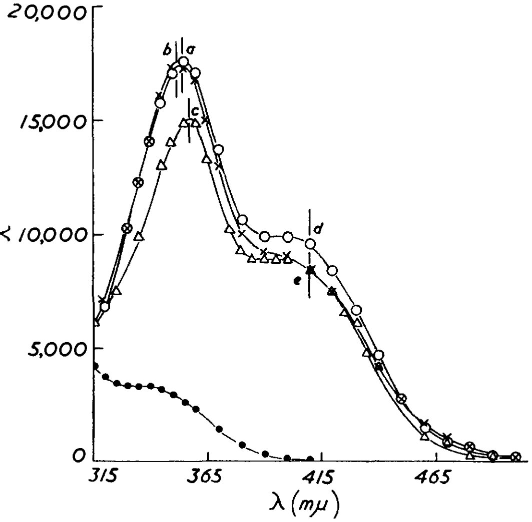


FIG. 2. *The spectra of basic* (I) *and acidic* (II) *aqueous solutions of* 2 : 4-*dinitrophenol.* λ_a = 261 mμ, ε_a = 15,300. λ_b = 323 mμ, ε_b = 7350. λ_c = 357·5 mμ, ε_c = 18,300. $\lambda_d = \lambda_e$ = 410 mμ, ε_d = 11,600; ε_e = 0. [2 : 4-$C_6H_3(NO_2)_2$·OH] = 5·758 × 10^{-5} mole l.$^{-1}$; [NaOH) in I = 0·1 mole l.$^{-1}$; [H_2SO_4] in II = 0·05 mole l.$^{-1}$.

FIG. 3. *Absorption spectra for* 2 : 4-*dinitrophenol in chlorobenzene solution in the presence of excess of chloroacetic acid,* ●; *mono*-n-*butylamine,* ○; *di*-n-*butylamine,* ×; *and tri*-n-*butylamine,* △. λ_a = 355 mμ, ε_a (for Bu^n·NH$_2$) = 17,600. λ_b = 352·5 mμ, ε_b (for Bu$^n_2$NH) = 17,400. λ_c = 357·5 mμ, ε_c (for Bu$^n_3$N) = 15,000. $\lambda_d = \lambda_e$ = 410 mμ, ε_d (for Bu^n·NH$_2$) = 9600, ε_e (for Bu$^n_2$NH and Bu$^n_3$N) = 8400.

Absorption Spectra.—2 : 4-Dinitrophenol in solution gives rise to two well-defined absorption spectra according to whether the solution contains an acidic or a basic component in addition to the 2 : 4-dinitrophenol. The spectra of acidic and basic solutions of 2 : 4-dinitrophenol in water are given in Fig. 2. These may be compared with the spectra of this substance in chlorobenzene solution to which chloroacetic acid or an amine has been added (Fig. 3).

The solutions whose spectra appear in Fig. 3 contained sufficient amine to effect complete conversion of the 2 : 4-dinitrophenol into its ionized form, and would correspond to points on the horizontal part of the curves in Fig. 4. It is seen that the wavelengths of maximum absorption, λ_a, λ_b, λ_c, in Fig. 5 agree very closely with the corresponding wavelength, λ_c, in Fig. 2. It seems justifiable therefore to suppose that in chlorobenzene solutions containing

FIG. 4. *Apparent extinction coefficient of* 2 : 4-*dinitrophenol at* 410 mμ, $D_{410}/[C_6H_3(NO_2)_2\cdot OH]$, *in chlorobenzene solutions containing various concentrations*, c_B, *of amines.* [The added amine is mono-*n*-butylamine for ○, di-*n*-butylamine for ×, and tri-*n*-butylamine for ●. The limits of the apparent extinction coefficients are 9600, 8400, and 8400 respectively.]

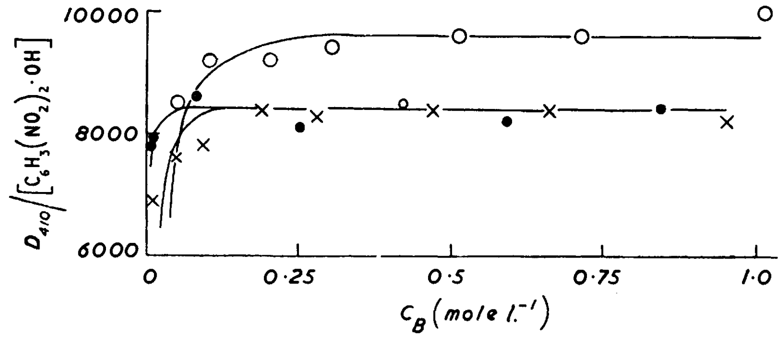


FIG. 5.

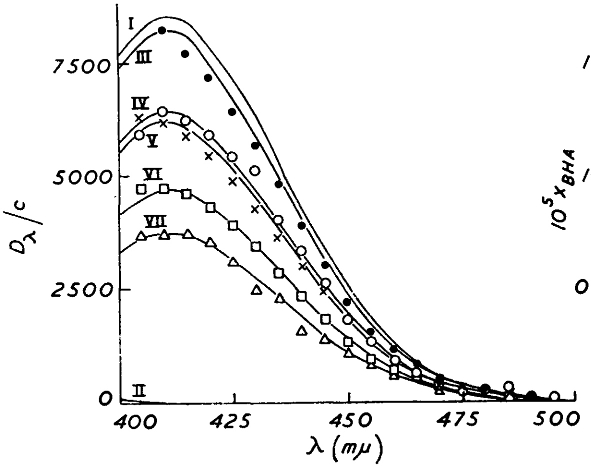


FIG. 6.

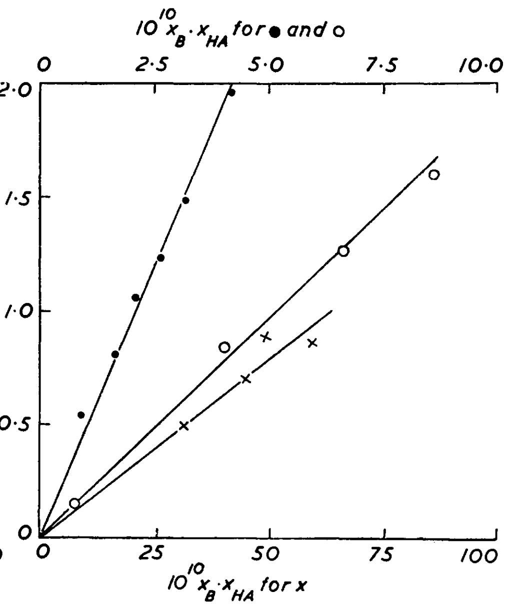


FIG. 5. *A solution of di-*n*-butylamine and* 2 : 4-*dinitrophenol at different temperatures*: *comparison of observed spectra* (*plotted points*) *with those calculated* (*full curves*) *from the spectra of the acid and basic forms of* 2 : 4-*dinitrophenol.*

I: *Spectrum of* 2 : 4-*dinitrophenol*, 100% *basic form*, *from Fig.* 3, *curve* ×. II: *Spectrum of* 2 : 4-*dinitrophenol*, 100% *acidic form*, *from Fig.* 3, *curve* ●. III: *Calc. for* 97·3% *basic form.* ●: *Experimental points at* 17·5°. IV: *Calc. for* 75·5% *basic form.* ○: *Experimental points at* 30·5°. V: *Calc. for* 73·2% *basic form.* ×: *Experimental points at* 35·5°. VI: *Calc. for* 55·7% *basic form.* □: *Experimental points at* 47·5°. VII: *Calc. for* 44·1% *basic form.* △: *Experimental points at* 57·5°.

FIG. 6. *Test of the equilibrium in chlorobenzene solution*, $\mathrm{B} + \mathrm{HA} \rightleftharpoons \mathrm{BHA}$, *in which* HA *is* 2 : 4-*dinitrophenol and* B *is mono-*n*-butylamine* (×), *di-*n*-butylamine* (○), *or tri-*n*-butylamine* (●). x_B, x_{HA}, *and* x_{BHA} *are mole fractions at equilibrium.*

2 : 4-dinitrophenol and amine in excess, the former is present in the ionized state. At 410 mμ the difference between the extinction coefficients of the acidic and the basic form is greatest, and this wavelength is therefore used in determinations of the relative amounts of each in equilibrium mixtures in the solvent. It is convenient that the acidic form of 2 : 4-dinitrophenol does not absorb at this wavelength.

Extinction Coefficients in Chlorobenzene Solution.—It was found that the apparent extinction coefficient of 2 : 4-dinitrophenol in the presence of mono-, di-, and tri-*n*-butylamine reached a limit as the concentration of amine in the solution was increased. This is shown in Fig. 4 where the values of the extinction coefficients at 410 mμ, ε_{410}, for the three amines at this limit are indicated.

The actual nitrophenol concentrations were varied in making up the solutions for Fig. 4. The same limit of extinction coefficient is reached whatever the nitrophenol concentration, and so Beer's law must be obeyed.

Variation of Absorption Spectrum with Temperature.—The calculation of ΔH for the reaction between 2 : 4-dinitrophenol and the butylamines depends on the assumption that, as the temperature changes in solutions containing these components, the resultant changes in absorption spectrum are due solely to an alteration in the relative concentrations of the species BHA and HA. The free amine does not absorb light in the spectral region concerned, so it remains necessary to show that no species are produced other than those accounted for by the chemical equation.

TABLE 1. *Experimental results for the equilibria in chlorobenzene:*

$$2:4\text{-}(NO_2)_2C_6H_3\cdot OH + B \rightleftharpoons 2:4\text{-}(NO_2)_2C_6H_3\cdot O\cdot H\cdot B,$$

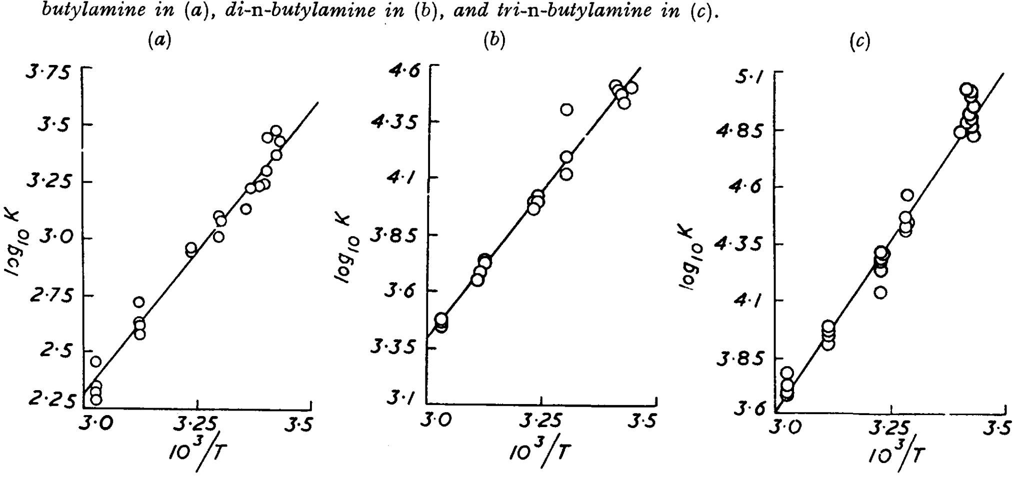
where X_B and X_I are the stoicheiometric mole fractions of B *and* 2 : 4-*dinitrophenol present in the equilibrium solutions. The values for D_{410} are mean values.*

Mono-*n*-butylamine				Di-*n*-butylamine				Tri-*n*-butylamine			
10^5X_B	10^5X_I	Temp.	D_{410}	10^5X_B	10^5X_I	Temp.	D_{410}	10^5X_B	10^5X_I	Temp.	D_{410}
145·9	0·711	19·0°	0·52	1·407	0·725	20·5°	0·17	2·968	3·616	18·0°	1·51
		20·5	0·50			30·0	0·09			19·5	1·44
		30·0	0·43			35·5	0·07			31·5	0·95
		35·5	0·37			47·0	0·04			36·5	0·80
		47·0	0·25	2·802	2·872	19·5	0·83			48·0	0·51
		57·0	0·16			20·0	0·85			57·5	0·34
241·7	1·095	19·0	0·91			30·0	0·58	5·785	1·803	21·0	1·12
		20·5	0·90			35·5	0·45			31·5	0·85
		30·0	0·77			47·0	0·27			36·5	0·73
		35·5	0·70			57·0	0·16			48·0	0·46
		47·0	0·56	3·667	5·750	18·5	1·60			57·5	0·30
		57·0	0·41			19·0	1·58	5·801	3·563	18·5	2·12
155·9	1·244	15·5	0·97			30·5	1·12			31·5	1·32
		18·0	0·95			35·5	0·97			36·5	1·22
		22·0	0·85			36·5	0·95			48·0	0·84
		24·5	0·79			47·0	0·62			57·0	0·56
		47·0	0·45			48·5	0·55	4·055	1·306	18·0	0·73
		57·0	0·28			57·0	0·39			18·5	0·75
115·3	1·087	21·1	0·678	6·375	2·564	22·8	1·078			19·0	0·78
		24·0	0·668			24·5	1·05			31·5	0·50
		29·5	0·587			37·0	0·710			36·5	0·44
		30·0	0·572			48·0	0·456			47·0	0·27
		47·1	0·305			56·7	0·310			57·5	0·19
		57·0	0·180					8·056	1·348	18·5	0·98
										19·5	0·98
										31·0	0·70
										36·5	0·63
										47·0	0·45
										57·0	0·29
								7·877	6·569	18·5	0·48
										19·5	0·46
										31·0	0·36
										36·5	0·32
										47·0	0·21
										57·0	0·14

The point is partly met in Fig. 6 where the form of the equilibrium constant is demonstrated, but, in addition, we mave measured the absorption spectra of a solution containing di-*n*-butylamine and 2 : 4-dinitrophenol over a range of temperature, and the results are plotted in Fig. 5. The reaction is exothermic and, as the temperature of the equilibrium mixture is increased, the characteristic absorption due to the ionized form of the nitrophenol decreases in intensity. This is due to displacement of the equilibrium (1) towards the reactant side. It is seen that the experimental points can be reproduced quantitatively by the curves, which have been calculated for the stated degrees of conversion of 2 : 4-dinitrophenol into its ionized form. If any light-absorbing species other than BHA of equation (1) were produced reversibly as the temperature increased, such agreement would not be expected. Any irreversible reaction would be detected by the method we have adopted for measuring the optical densities over a temperature range. This has been described under *Solutions*.

Form of K at Constant Temperature.—The optical density of solutions containing 2 : 4-dinitrophenol and amine was measured over a range of temperatures to yield the results reported below for the dependence of log K on temperature. The optical density of each solution was interpolated at 25° from these results, and expressed as mole fraction of complex, x_{BHA}. This has been plotted against the product of the mole fractions of the 2 : 4-dinitrophenol and amine, $x_{\mathrm{HA}} \,.\, x_{\mathrm{B}}$, in each corresponding solution at equilibrium, and yields the set of linear graphs shown in Fig. 6. This is evidence that the equilibrium constant is of the form,

FIG. 7. *The relation between* $\log_{10} K$ *and* T^{-1}, *where* K *is the equilibrium constant (mole fraction scale) for the equilibrium,* $\mathrm{B} + \mathrm{HA} \rightleftharpoons \mathrm{BHA}$, *in which* HA *is 2 : 4-dinitrophenol, and* B *is mono-*n*-butylamine in (a), di-*n*-butylamine in (b), and tri-*n*-butylamine in (c).*



$$K = x_{\mathrm{BHA}}/x_{\mathrm{B}} \,.\, x_{\mathrm{HA}}$$

and hence that (*a*) the equilibrium studied is of the type (1) and (*b*) the activity coefficient quotient either is unity or remains constant over the range of concentration used. The concentrations are so low that we consider it likely that the quotient is unity.

Variation of Equilibrium Constant with Temperature.—In Figs. 7*a*, *b*, *c*, are shown the graphs of log K against T^{-1} where the lines drawn are obtained by the method of least squares. The ΔG° values at 25° are calculated by interpolation, and ΔH° and ΔS° from the slope. The results obtained are presented in Table 2, in which the estimated probable errors (*i.e.*, 0·67 times the standard errors) are obtained by applying standard statistical procedures to the probable errors of the slopes and intercepts of the lines drawn in the Figures.

DISCUSSION

It is evident from Table 2 that if $-\Delta G^{\circ}$ for the reaction (1) between a set of amines, B, and 2 : 4-dinitrophenol, HA, is taken as the measure of the strength of the bases, then for mono-, di-, and tri-*n*-butylamine the strengths in chlorobenzene increase in this order. This is in marked contrast to the behaviour of aliphatic amines in water,[1,2,10] and the

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[10] N. F. Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

simplest interpretation, following Trotman-Dickenson,[11] is that in aqueous solution solvation of the aminium ions is greater for those ions carrying the most hydrogen atoms and the fewest alkyl groups. The solvation of the ions is also assumed to be greater than that of the free amines in solution. The basic strengths in chlorobenzene increase in the manner predicted by the known inductive effect of the alkyl groups, leading to an increase of the electron-density on the nitrogen atom with the number of alkyl groups attached. We notice that in both chlorobenzene and aqueous solution the enthalpy changes are high and negative, indicating proton-transfer, and that they could lie in the sequence which would result if the energy of reaction in both solvents were largely determined by the electron-density on the nitrogen atom. Hence it seems that the contribution of solvation energies to the ΔH° values in water and in chlorobenzene is small. The entropies of solvation however will depend, not directly on the strength of binding of the solvation shells, but on their influence on the freedom of movement of the interacting entities. The ΔS° values for the reaction between mono-, di-, and trimethylamine and the hydroxonium ion in water are [1] 4·7, 9·5, and 15·2 cal. deg.$^{-1}$ mole^{-1}, and, because the equilibrium is of the type, $AH + B \rightleftarrows A^- + BH^+$, these values do not depend on the concentration scale chosen. The roughly constant difference of 4 cal. deg.$^{-1}$ mole^{-1} in these equilibria has been ascribed to the effect of solvation.[2] In chlorobenzene solutions of the butylamines, values of ΔS° for the reaction (1) (mole fraction units being used) are large and negative (Table 2). The three values all lie within a range of 4·5 cal. deg.$^{-1}$ mole^{-1}, which is only just outside the limits of experimental error, and there is no consistent change from mono- to di- to tri-*n*-butylamine.

TABLE 2. *Thermodynamic functions for the equilibria at 25° in chlorobenzene:*
$2:4\text{-}(NO_2)_2C_6H_3{\cdot}OH + B \rightleftharpoons 2:4\text{-}(NO_2)_2C_6H_3{\cdot}O{\cdot}H{\cdot}B$.

Amine, B	$10^{-3}\partial\log_{10}K/\partial T^{-1}$	log K	ΔG° (kcal. mole^{-1})	ΔH° (kcal. mole^{-1})	ΔS° (cal. deg.$^{-1}$ mole^{-1})
$Bu^n{\cdot}NH_2$ ...	2·64 ± 0·06	3·23 ± 0·24	−4·39 ± 0·33	−12·1 ± 0·3	−25·8 ± 1·5
Bu^n_2NH ...	2·56 ± 0·03	4·31 ± 0·12	−5·87 ± 0·16	−11·7 ± 0·2	−19·7 ± 0·7
Bu^n_3N	3·09 ± 0·05	4·68 ± 0·19	−6·37 ± 0·26	−14·1 ± 0·2	−26·0 ± 1·2

Brown [12] has suggested that competition between inductive and steric factors accounts for the low basic strengths of 2 : 6-di-*tert.*-butylpyridine, and possibly of *o*-methyl- and *o*-*tert.*-butyl-aniline. If steric factors were of importance in determining the basic strengths of the butylamines, the effect should be greater in the present systems in chlorobenzene where there is association with 2 : 4-dinitrophenol, than in water where dissociation takes place. If steric factors predominated, tributylamine would therefore be even weaker in relation to mono- and di-butylamine in chlorobenzene as solvent than it is in water. The fact that we find the reverse indicates that steric factors are not of determining importance in the systems discussed in the present work.

The results of Hall [13] on the electromotive force of cells containing a wide variety of bases in various organic solvents led to the conclusion that solvation effects "are not important enough to cause major disturbances in the order of base strengths" in non-aqueous solvent as compared with the order in water. The present work demonstrates that, though the effect may be small in comparison with that of major structural changes in the molecule, it is more important than the simple inductive effect accompanying the exchange of a hydrogen atom for an alkyl group on a nitrogen atom.

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