

450. *Structure and Basicity. Part I. General and Experimental Considerations; the Basicity of some Common Bases in Nitrobenzene Solution.*

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A reproducible technique for the measurement of the relative basicities of compounds in solution in nitrobenzene by potentiometric titration has been evolved. The liquid junction potential of the conventional design of calomel half-cell had a pronounced temporal variation, which was eliminated by the use of a slowly flowing junction: its possible pH-dependence could not be eliminated. The glass electrodes were trouble-free.

Bases were found covering the whole of the pH range studied in the titration of which the Henderson equation, and therefore the Nernst equation, was obeyed to within a few per cent. The pronounced deviations shown by some bases have been rationalised in terms of a 1 : 1 association of the base with its conjugate acid. The relative basicities, in nitrobenzene, of a number of common mono- and di-acidic bases are recorded.

THIS Paper begins a series in which the basicities of a number of inorganic and organic compounds will be reported and discussed with particular reference to the relationship between basicity and structure. The measurements have been made by potentiometric titration with a glass electrode. In nearly all cases solutions in nitrobenzene were examined and, wherever possible, aqueous solutions as well. By using nitrobenzene, it has been possible to study compounds covering a wide range of basic strength and to include those

which are too weakly basic, or insufficiently soluble, to be titrated in aqueous solution. It was shown in preliminary work that compounds could be titrated of lower basicity in nitrobenzene than in nitromethane, chlorobenzene, or anhydrous mixtures of acetic and formic acids, and also that the levelling effect was least in this solvent.

Only a few studies of basicity have previously been undertaken by using the glass electrode in nitrobenzene,¹ for certain practical difficulties often attend the use of this electrode in solvents which are anhydrous or nearly so.²⁻⁴ It was therefore necessary to evolve a technique suitable to provide reproducible measurements.

Solutions of bases in pure nitrobenzene were titrated with a solution of perchloric acid in nitrobenzene. This also contained traces of acetic anhydride and acetic acid, arising from the use of acetic anhydride to dehydrate the acid and forming 0.1% by weight of the solvent in the half-neutralised solution: their proportions were sensibly constant in all the measurements. The concentration of base, usually 0.001M, was the lowest compatible with obtaining a sharp end-point and steady e.m.f. readings during the titration.

Consider the equilibrium between a base, B, and its conjugate acid BH⁺



Let K_a be the dissociation constant of BH⁺. If the pH and a_{H^+} , a_B , and a_{BH^+} , the activities of the various species, are referred to standard states in the solvent used, then

$$K_a = (a_{H^+} \cdot a_B) / a_{BH^+} \quad (2)$$

and

$$pK_a = pH + \log (a_{BH^+} / a_B) \quad (3)$$

As a_{BH^+} and a_B may normally be easily determined, the determination of K_a devolves upon the measurement of a_{H^+} . With the usual reservations about the measurement or calculation of single ion activities, this presents no problem in aqueous solution, wherein the pH-meter may be calibrated with aqueous solutions whose pH values are known with respect to the correct standard state. As no standard solution in nitrobenzene is available, an arbitrary scale is necessary. A 0.001M-solution of 2,2,4,4,6,6-hexa-*p*-toluidinocyclo-triphosphazatriene, N₃P₃(NH·C₆H₄·Me-*p*)₆, in nitrobenzene, half neutralised with the standard titrant, was used as a standard buffer solution and arbitrarily allotted a pH' value of 3.00, where pH' is defined by equation (4):

$$pH' = pH - b \quad (4)$$

The pH in equation (4) is again that defined with respect to a standard state in nitrobenzene; b is a constant.

In the present work, the pH' scale is such that the values of it are approximately the readings obtained if the electrode system is first calibrated with aqueous buffer solutions, *i.e.*, they are measured with respect to a standard state in water.

The index of basicity in nitrobenzene solutions thus becomes pK_a' , such that

$$pK_a' = pK_a - b \quad (5)$$

and

$$pK_a' = pH' + \log (a_{BH^+} / a_B); \quad (6)$$

b is later shown to have a value of about 10. The lowest value of pH' normally obtainable was -7, and this depended on the condition of the solvent, being raised, for example, by the presence of moisture. At the other end of the scale, readings of pH' up to about +14 were recorded.

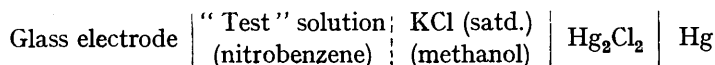
¹ Hall, *J. Phys. Chem.*, 1956, **60**, 63.

² Hills, in "Reference Electrodes," ed. Ives and Janz, Academic Press, New York and London, 1961, p. 439.

³ Bacarella, Grunwald, Marshall, and Purlee, *J. Phys. Chem.*, 1958, **62**, 856.

⁴ Schaal, *J. Chem. Phys.*, 1955, **52**, 719.

The experimental cell was



If the Nernst equation is obeyed and the liquid junction potential is independent of pH' , the e.m.f. may be written as

$$E = E^\circ + k \ln a_{\text{H}^+} \quad (7)$$

$$\text{Then} \quad E = E^\circ - k\text{pH} \quad (8)$$

$$= E^\circ - kb - k\text{pH}' \quad (9)$$

$$= E^{\circ'} - k\text{pH}', \text{ say,} \quad (10)$$

where $k = 2.3026RT/F$.

If, however, these assumptions are not correct, we must put

$$E = E^{\circ'} - k\text{pH}' + f(\text{pH}'), \quad (11)$$

where $f(\text{pH}')$ represents the pH' -dependent deviations from equation (10). Calibration with a single buffer solution, if performed sufficiently frequently, allows for any temporal variation in those parts of the cell e.m.f. which are pH' -independent, such as the asymmetry potential of the glass electrode, but if equation (10) is not obeyed then there are likely to be errors in pH' values which are much removed from that of the standard buffer. While in aqueous solution these errors can be minimised by calibration with a buffer solution close in pH to that of the unknown, this is at present impossible for nitrobenzene solutions.

The glass electrodes were mostly of type GHS23 from Electronic Instruments Ltd., and are understood to be of lithia glass. Some were of type GC23; type GM23 was used for microtitrations. These two are understood to be of uranium glass. They were all stored in water between measurements and washed in a standard manner with water and methanol (see later) before introducing them into the nitrobenzene solutions. There, they showed the temporal variation of potential characteristic of class II of the classification made by Beck, Caudle, Covington, and Wynne-Jones,⁵ namely a rapid change of pH' over a few minutes to a value steady within ± 0.05 – 0.10 pH' unit, which was taken as the equilibrium value. If, after intervals of up to 30 minutes, the electrodes were removed and the washing repeated, no significant change in the pH' value they recorded was observed on replacing them in the solution. No extensive study of the behaviour of glass electrodes was made in the present work. Mattock^{6a} has noted that lithia glasses are less affected by dehydration than MacInnes-Dole glasses, and this may explain the stability of the electrodes in nitrobenzene solutions. Reproducible results could be obtained without the prolonged equilibration of the electrodes with the organic solvent before use which was recommended by Bacarella, Grunwald, Marshall, and Purlee.³

Preliminary measurements with the calomel electrode were made by using a standard type of half-cell (Electronic Instruments Ltd. RS23). In this, the element containing calomel and mercury dipped into a saturated methanolic solution of potassium chloride, contained in a glass sheath ending in a sintered ceramic plug at which the liquid junction with the nitrobenzene solution was made. The behaviour of these half-cells was studied in a series of experiments, the results of which can be summarised as follows.

By using glass electrodes or other half-cells as reference electrodes, it was shown that a half-cell which had been aged in a nitrobenzene solution, developed an e.m.f. with respect to a fresh half-cell. The original potential could be restored by washing the ceramic plug of the half-cell with methanol, water, and then with methanol again. The liquid junction

⁵ Beck, Caudle, Covington, and Wynne-Jones, *Proc. Chem. Soc.*, 1963, 110.

⁶ Mattock, "pH Measurement and Titration," Heywood and Co., London, 1961, (a) p. 109, (b) p. 343.

potential with this type of half-cell is thus time-dependent. The time-dependence could be largely eliminated by using a slowly flowing junction (see Experimental section), the potential of this type of half-cell being the same as that of a "washed" one. It was also established that the potential difference between a fresh (or washed) half-cell and an aged half-cell depended on the pH' of the solution in which the potential difference was measured, being largest for solutions of high pH'. It also depended slightly on the pH' of the solution in which the half-cell had been aged, being again largest for solutions of high pH'. The results of a typical experiment are shown in Table 1. In these measurements both

TABLE I.

The pH' of seven half-neutralised solutions was measured after calibration of the electrode-pair in the "medium" buffer (row 1). The pair was allowed to remain in the "medium" buffer for 30 min., re-standardised, and then the readings in row 2 were taken. The glass electrode and calomel half-cell were washed in water and methanol, rapidly re-standardised, and the readings in row 3 obtained.

Row 1	10.45	8.35	7.60	3.85	-1.50	-3.50
Row 2	9.70	7.85	7.10	3.70	-1.50	-3.50
Row 3	10.45	8.35	7.50	3.70	-1.60	-3.55

electrodes were washed, but separate experiments showed that the effect of washing the glass electrode was very small (0.05—0.10 pH unit), and the effect is almost entirely due to the calomel half-cell.

There is no way of knowing, at present, whether the pH-dependence of the junction potential lies in the fresh or in the aged electrodes, or in both, nor whether it is eliminated in the flowing type of junction.

To minimise the effect of the pH'-dependence, if present with this kind of junction, the following additional precautions were taken. Relative to the standard buffer solution of pH' 3.00, 0.001M-solutions of hexakisdimethylaminocyclotriphosphazatriene, $N_3P_3(NMe_2)_6$, respectively half- and one-and-a-half-times neutralised with the standard titrant had pH' values of 7.60 and -3.30, obtained as the averages of several readings. These solutions were then defined as having these particular pH' values and were used as sub-standard "high" and "low" buffer solutions. Like that of the "medium" buffer, these solutions were shown to have pH' values which were constant over long periods of time. Measurements on solutions with pH' above 5.0 were made relative to the "medium" and "high" buffers, and below 0 to the "medium" and "low" buffers. Between 0 and 5.0 pH', either pair of buffers could be used. While the use of these sub-standard buffers could not eliminate the effect of any pH'-dependence of the liquid junction potential, it gives greater confidence in the relative basicities of sets of compounds close in basicity having either "high" or "low" pK_a' values, particularly as the pH' readings are most sensitive to contamination of the solvent at the extremes of the pH' range.

The potential even of the modified liquid junction showed a small variation in time, and this and other temporal variations in the e.m.f. of the cell were reduced by using a standard, rapid measuring sequence (see Experimental section).

EXPERIMENTAL

pH' values were measured with a Cambridge bench pH meter. For the work in nitrobenzene, the reversal of the polarity of the electrodes from that found in aqueous solution necessitated the addition of a simple e.m.f. compensating circuit to the instrument.^{6b}

The titration vessel, a 30-ml. tall-form lipless beaker, rested on a layer of wax inside a second beaker around which earthed copper wire was wound. A heavy Perspex cover for the beaker had holes drilled for a nitrogen inlet tube, the tip of the microburette and the two electrodes. The glass electrode was fitted, over the middle part of its length, with an insulating sleeve of polythene, which, in turn, fitted the hole in the cover snugly. An earthed metal screen was placed round the cell.

Nitrogen, pre-saturated with solvent vapour, was led over the surface of the cell solution, which was stirred magnetically. The pH meter rested on an earthed brass sheet and was

screened from the stirrer motor. This attention to screening and insulation, and the provision of a surge-free A.C. supply to the motor, was essential for the work in nitrobenzene.

The titrant was prepared by adding 0.70 ml. of 72% AnalaR perchloric acid (Hopkin and Williams) to 5 ml. of acetic anhydride with constant stirring. After one min. 1 ml. of the solution was added to 50 ml. of nitrobenzene. After the flask had been stoppered and shaken, it was kept overnight before use, as this appeared to give a product drier than that obtained immediately. The titrant was approximately 0.034*N*. It was standardised by potentiometric titration with a standard solution of diphenylguanidine. The titration vessel normally contained 17 ml. of a 0.001*M*-solution of the base, and 0.50 ml. of titrant were required to reach the first equivalence point. Buffer solutions were also made up in these proportions.

AnalaR nitrobenzene (Hopkin and Williams) was stored over phosphoric anhydride for 24 hr., then vacuum-distilled in an atmosphere of dry nitrogen. The distillate was redistilled to remove traces of phosphoric acid, the middle third being tested for the presence of acidic and basic impurities by determining the pH' values obtained on adding small quantities of a standard solution of diphenylguanidine and of the titrant, respectively. The arbitrary limits assigned were $\text{pH}' \geq -6.0$ for a concentration of perchloric acid of 2×10^{-5} *M*, and $\text{pH}' \leq 8.0$ for a concentration of diphenylguanidine of 2×10^{-5} *M*.

Those of the bases which were solid were purified by recrystallisation to constant m. p. The vapour of the free aliphatic amines was passed into nitrobenzene *via* a column of potassium hydroxide pellets. These solutions were titrated immediately, because a slow reaction between solute and solvent appeared to occur, which also made them unsuitable for use as standard buffers.

The calomel half-cells were modified by the addition of a side-arm to the outer glass sleeve, allowing a pressure of nitrogen to be applied to the saturated solution of potassium chloride in methanol inside. They were stored in methanol when not in use.

On beginning a measurement, or sequence of measurements, the calomel half-cell and glass electrode, or "electrode-pair," were first washed with methanol, if necessary, to remove nitrobenzene from previous measurements. The electrode-pair was then immersed in continuously stirred distilled water for 30 sec., and then a nitrogen pressure (25 cm. Hg.) was applied to the calomel half-cell until bubbles no longer appeared from the junction. With continued application of nitrogen pressure, the electrode-pair was transferred to methanol for 30 sec., removed, and dried with tissue paper. A droplet of methanol was allowed to form at the ceramic plug and the pair was dipped into nitrobenzene (to remove methanol) and the gas pressure reduced to 2 cm. Hg. The excess of nitrobenzene adhering to the pair was removed with tissue paper and the pair allowed to equilibrate in the "medium" buffer for five min. (Within any sequence of measurements the electrode-pair was merely dipped into nitrobenzene and wiped dry before being transferred to a new solution.) After adjusting the pH meter to read pH' 3.00, the electrodes were checked in the "high" buffer, then transferred to the test solution and the titration started. Additions of acid, of between 0.01 and 0.05 ml., were made at intervals of one to two min., or longer if the pH' was not then stable, and the corresponding pH' values were noted. At the end of the titration the electrodes were checked in the "low" and "medium" buffers.

Using the end-points found in the titration, a sample of the base was then half- or one-and-a-half-times neutralised with the titrant, and the pH' of the solution found by a timed sequence, as follows.

A second electrode-pair was prepared as already described, and standardised in the "medium" buffer after equilibration for five min. Thereafter a standard equilibration time of two min. was allowed for each of the readings in the following sequence.

The pair was transferred to the half-neutralised solution and the pH' read. It was then replaced in the "medium" buffer solution, and the pH' of this, which was now normally slightly different from 3.00, was noted. The pH' of the half-neutralised solution was corrected with respect to the mean of the two "medium" buffer readings. The pH' of the "high" or "low" buffer solution, as appropriate, and of the half-neutralised solution were then determined in that order. A second value of the pH' was thus obtained corrected relative to the "high" or "low" buffer. Finally the "medium" buffer was checked. The final value was the mean of the two corrected values, which normally differed only by 0.1 pH' unit or less. Although this value was preferred to that obtained directly from the titration, agreement between them showed that either pair of electrodes was free from major physical defects.

Where the equivalence point in the titration of a very weak base lay so low that the titration curve could not be completed, the half-neutralised solution was prepared, rather less accurately, by calculation from the weight of base taken to prepare the solution. pK_a' values of very weak bases were calculated from the pH' values of their solutions when neutralised to extents varying between 1/100 and 1/10, assuming the validity of equation (16).

The general accuracy of the pK_a' results is ± 0.25 pH' unit in the range -3.3 to 7.6 pH' , outside this it is ± 0.4 pH' unit. These figures were arrived at after performing experiments to determine the effects of contamination by water and methanol; after assessing the accuracy with which the half-neutralisation point could be found, after determining the reproducibility of different electrode-pairs (0.05 — 0.10 pH' unit), and after allowing for a temperature variation from 18 to 23° (thermostatic control was inconvenient: all measurements are recorded as being made at 20°). Another experiment established that the acetic acid present in the titrant was insufficiently ionised to affect the titration curves. The *relative* accuracy of pH' readings within a particular titration is much greater, probably ± 0.02 pH' unit, enabling sensitive tests of the Henderson equation to be made.

Measurements in aqueous solution were usually made at a solute concentration of $0.002M$, in an atmosphere of nitrogen, using standard techniques.⁷ Corrections for non-ideality were made by using the limiting law of Debye and Hückel. The accuracy of the results is ± 0.05 pH unit.

DISCUSSION

Let xc moles of a fully dissociated acid be added to a solution containing c moles of base. Let α be the fraction of base converted into the protonated form. Then equation (2),

$$K_a = (a_{H^+} \cdot a_B) / a_{BH^+} \quad (2)$$

can be written

$$K_a = \frac{(x - \alpha)(1 - \alpha)c f_{H^+} \cdot f_B}{\alpha f_{BH^+}} \quad (12)$$

It is easily shown that if K_a is small, and $x < 1$,

$$\alpha \approx x \quad (13)$$

in which case equation (14), derived from (6),

$$pK_a' = pH' + \log \left(\frac{\alpha}{1 - \alpha} \right) \frac{f_{BH^+}}{f_B} \quad (14)$$

assumes the form

$$pK_a' = pH' + \log \left(\frac{x}{1 - x} \right) \frac{f_{BH^+}}{f_B} \quad (15)$$

Ignoring deviations from ideality

$$pK_a' = pH' + \log \left(\frac{x}{1 - x} \right) \quad (16)$$

the Henderson equation. If $x = 1/2$,

$$pK_a' = pH_{1/2}' \quad (17)$$

Equation (17) has been used to determine the pK_a' values in most cases.

In discussing the application of these equations to the present results it is first convenient to have some idea of the absolute values of K_a , *i.e.*, of the constant b (equation 5).

$$\text{We may put} \quad pH \approx -\log c_{H^+} \quad (18)$$

In checking the purity of the nitrobenzene, the pH' values of solutions $10^{-4}M$ in perchloric acid were determined, and comparison of these with the pH values calculated from equation (18) gives $b \sim 11$. A rough estimate is also possible by comparison of the pH'

⁷ Albert and Serjeant, "Ionisation Constants of Acids and Bases," Methuen and Co., London, 1962.

readings obtained in titrations, after the equivalence point, with calculated pH values from equation (18). These tend to give lower and more variable values of b (~ 9.5), probably because of progressive contamination of the solvent with water and methanol during the titration. If we take $b = 10$, then the absolute values of K_a observed in this work range from about 10^{-4} to 10^{-19} ($pK_a' - 6$ to 9).

According to Wright, Murray-Rust, and Hartley,⁸ perchloric acid is 55% dissociated in nitrobenzene at a concentration of 0.001M, corresponding to a dissociation constant $\sim 10^{-2}$ — 10^{-3} , *i.e.*, 10—100 times larger than of any base studied. Treating the acid as completely dissociated will nowhere introduce an error into a pK_a' value calculated from equation (17) larger than the experimental error, and for bases of $pK_a' > -4$ the effect will be negligible. Some departures from equation (16) for bases of very low pK_a' (Table 2) may be due to incomplete dissociation of perchloric acid.

TABLE 2.

Titration of 2,2-dichloro-4,4,6,6-tetrakis-*p*-chlorophenylcyclotriphosphazatriene,
 $N_3P_3(C_6H_4Cl-p)_4Cl_2$.

1	2	3	4	5	6	7
Fraction neutralised	pH'	pK_a' (calc.)	pK_a' (calc.) - $pH_{1/2}'$			
1/4	-5.50	-5.98	-0.13	-0.06	-0.01	-0.02
1/2	-5.85	-5.85	0	0	0	0
3/4	-6.14	-5.66	+0.19	+0.05	+0.04	+0.03

Witschonke and Kraus⁹ showed that while quaternary ammonium salts are strongly dissociated in nitrobenzene, as would be expected from its high dielectric constant, the salts of primary, secondary, or tertiary amines are less so, suggesting a specific binding of anion with cation through a hydrogen atom on the latter. The only salt studied which was at all comparable with those formed here was *n*-butylammonium perchlorate, $BuNH_3^+ClO_4^-$, having a dissociation constant of 2.53×10^{-3} . If dissociation constants of this order of magnitude are assumed for the salts present at the half-neutralisation point the error in pK_a' values calculated from equation (17) (~ 0.05 unit) will be well within the experimental error and about the same for all bases studied. A very small deviation from equation (16) should occur, but is probably barely detectable.

For the neutralisation of a di-acidic base, equation (15) becomes, after the first end-point,

$$pK_a' = pH' + \log \left(\frac{x}{1-x} \right) \frac{f_{BH_2^{2+}}}{f_{BH^+}}, \quad (19)$$

where x is now the number of moles of acid added after the first equivalence point.

The dissociation of salts which could be models for the perchlorates of di-protonated bases does not appear to have been studied yet. Here, too, the more important interaction between cation and anion is probably specific and the presence of a second proton on another part of the cation may increase the association constant only slightly. The presence of a strong association would be revealed in large deviations from equation (16), and these are not found.

As low concentrations only are involved, f_B is taken as unity. The contribution of ion-association to f_{BH^+} and $f_{BH_2^{2+}}$ is seen to be small, and the effect of long-range interionic interactions is negligible. In addition, for a series of mono-acidic bases of not dissimilar chemical type, the deviations from ideality from all sources are probably so similar, that

$$\log \frac{f_{BH^+}}{f_B} = \text{constant},$$

and they may in any case be ignored if only relative basic strengths are required.

⁸ Wright, Murray-Rust, and Hartley, *J.*, 1931, 199.

⁹ Witschonke and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 2474.

It is also unlikely that any serious error arises if we put

$$\log \frac{f_{\text{BH}_2^{2+}}}{f_{\text{BH}^+}} = \log \frac{f_{\text{BH}^+}}{f_{\text{B}}}$$

for a given compound, and ignore the effects of non-ideality in the comparison of $\text{p}K'_{\text{a},1}$ and $\text{p}K'_{\text{a},2}$ values.

Thus the effects of non-ideal behaviour have been ignored and the $\text{p}K'_\text{a}$ values recorded are the pH' values at half-neutralisation (equation 17).

Equation (16) has been tested for all the bases studied by comparing the values of $\text{p}K'_\text{a}$ calculated for various stages of the neutralisation from $x = 1/4$ to $x = 3/4$. Where the calculated value of $\text{p}K'_\text{a}$ is constant with variation in x , the Nernst equation (7) must also hold. A large number of bases have been found in the present work in the titration of which equation (16) is obeyed to within about $\pm 5\%$. These cover a range from -4.0 to 8.0 pH' , and it is suggested that the Nernst equation is obeyed to this accuracy over this range.

Two classes of compounds show deviations from equation (16). Firstly, compounds with low $\text{p}K'_\text{a}$ values (< -4). An example is shown in Table 2. Here the $\text{p}K'_\text{a}$ values calculated from equation (16), column 3, are less than the value at $x = 1/2$ for $x < 1/2$, and greater than the value at $x = 1/2$ for $x > 1/2$. The deviations are listed in column 4. These have the trend expected from failure of equation (13), and from ignoring the incomplete dissociation of the perchloric acid. The expected deviations, taking $K_\text{a}(\text{BH}^+) = 10^{-4}$ and $K_\text{a}(\text{HClO}_4) = 10^{-2}$, are listed in columns 5 and 6, with respect to a deviation of 0 at $x = 1/2$. These will only be significant for very weak bases. In column 7 are listed the deviations arising from incomplete dissociation of $\text{BH}^+\text{ClO}_4^-$, $K_\text{a}(\text{BH}^+\text{ClO}_4^-)$ being taken as 2.5×10^{-3} . These would, however, be expected for bases of all strengths. It will be seen that the sum of the effects is of the correct order of magnitude: the first two will be rather sensitive to the values of the absolute dissociation constants chosen.

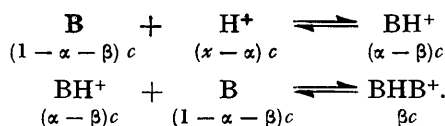
Secondly, many of the bases studied show deviations in the opposite sense. An example is shown in Table 3. These are most pronounced (i) with the aliphatic amines NH_2R ,

TABLE 3.
Titration of triethylamine.

1	2	3	4	5
Fraction neutralised	pH'	$\text{p}K'_\text{a}$ ' (calc.) from eqn. (16)	$\text{p}K'_\text{a}$ ' (calc.) - $\text{pH}_{1/2}'$	$\text{p}K'_\text{a}$ ' - $\text{pH}_{1/2}'$
1/4	8.11	7.63	+0.34	+0.82
1/2	7.29	7.29	0	0
3/4	6.48	6.96	-0.33	-0.81

NHR_2 , NR_3 ($\text{R} = \text{Me}$ and Et) and NH_2Pr^i , and (ii) in the first protonation of cyclic phosphazenes of the type $\text{N}_3\text{P}_3(\text{NHR})_6$ and $\text{N}_4\text{P}_4(\text{NHR})_8$, $\text{R} = \text{Me}$, Et , and Pr^i . Deviations in this sense may not easily be explained other than by postulating a strong association of the cation BH^+ with the base B.

Now, if this is the case we may write:



As before $\alpha \approx x$, thus

$$\text{p}K'_\text{a} = \text{pH}' + \log \left(\frac{x - \beta}{1 - x - \beta} \right) \quad (20)$$

It is easily shown that equation (20) leads to deviations from equation (16) in the observed sense. When $x = 1/2$, $\text{p}K'_\text{a} = \text{pH}'$, as before. It may also be shown that, for

pairs of points on the neutralisation curve for which $x = x'$ and $x = (1 - x')$, ($\text{pH}'_{x'} - \text{pH}'_{1/2} = -(\text{pH}'_{(1-x')} - \text{pH}'_{1/2})$). This condition is accurately obeyed in the case of the aliphatic amines (see Table 3), but there are slight deviations from it in the case of the phosphazenes, where the equilibria of the polyacidic bases involved are somewhat more complex.

If the association of the base and the cation is very strong then the form of the titration curve is completely changed and an equivalence point is found corresponding to hemiprotonation, according to the equation



This has been observed in the titration of a number of phosphine oxides, *e.g.*, trisdimethylaminophosphine oxide ($\text{NMe}_2)_3\text{PO}$. It may be noted that Bode, Bütow, and Lienau¹⁰ have reported solid hemi-hydrochlorides of two aminophosphazenes.

From equation (20) we may obtain β , the degree of association, and hence calculate values of an equilibrium constant K_{ass} , such that

$$K_{\text{ass}} = \frac{a_{\text{BHB}^+}}{a_{\text{BH}^+} a_{\text{B}}}$$

Deviations from ideality being ignored,

$$K_{\text{ass}} = \frac{\beta}{(1 - x - \beta)(x - \beta)c} \quad (21)$$

In the cases mentioned, K_{ass} varies from 10^3 to 10^4 . The lower figure corresponds to the weakest association which can be detected with certainty in these measurements.

TABLE 4.
Mono-acidic bases.

	$\text{pK}'_{\text{a}} (\text{C}_6\text{H}_5\text{NO}_2)$		$\text{pK}_{\text{a}} (\text{H}_2\text{O})^*$
	This work	Hall	
NH_2Me	6.85 §	7.05	10.62
NHMe_2	7.45 §	7.50	10.77
NMe_3	6.95 §	7.05	9.80
NH_2Et	7.05 §	6.75	10.63
NHEt_2	7.10 §	7.25	10.93
NEt_3	7.30 §	7.10	10.87
Piperidine	6.7 ± 0.6	7.30	11.22
<i>p</i> -Toluidine	-0.20	-0.75	5.12
NEt_2Ph	2.10	-0.20	6.56
$\text{NH}_2\text{Pr}^{\dagger}$	6.50 §	6.55	10.63
Diphenylguanidine	5.85	—	10.12
<i>N</i> -Methylmorpholine	4.85	—	7.41 ‡
Pyridine	2.05	—	5.23
		(± 0.30)	

* From ref. 7, except for ‡. † Ref. 1. § Associated to $[\text{BHB}]^+$, $K_{\text{ass}} \sim 10^3 - 10^4$.

Di-acidic bases.

	$\text{C}_6\text{H}_5\text{NO}_2$ (this work)		H_2O	
	$\text{pK}'_{\text{a},1}$	$\text{pK}'_{\text{a},2}$	$\text{pK}_{\text{a},1}$	$\text{pK}_{\text{a},2}$
$\text{NH}_2 \cdot [\text{CH}_2]_2 \cdot \text{NH}_2$	5.5 ± 0.4	1.7 ± 0.4	10.09	7.00
$\text{NH}_2 \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$	6.8 ± 0.4	2.5 ± 0.4	10.62	8.64
<i>o</i> - $\text{C}_6\text{H}_4(\text{NH}_2)_2$	-0.05	*	4.47	**
<i>m</i> - $\text{C}_6\text{H}_4(\text{NH}_2)_2$	-0.20	-4.00	4.88	**
<i>p</i> - $\text{C}_6\text{H}_4(\text{NH}_2)_2$	1.70	-3.25	6.08	**
$2\text{-NH}_2 \cdot \text{C}_5\text{H}_4\text{N}$	3.70	*	6.86	**
$3\text{-NH}_2 \cdot \text{C}_5\text{H}_4\text{N}$	3.70	*	5.98	**
$4\text{-NH}_2 \cdot \text{C}_5\text{H}_4\text{N}$	6.85	*	9.17	**

* Not detectable, < -6.0 . ** Not detectable, < 2.0 .

¹⁰ Bode, Bütow, and Lienau, *Ber.*, 1948, **81**, 547.

Kolthoff, Stocesoca, and Lee¹¹ showed spectrophotometrically that pyridine associated with its conjugate acid in nitrobenzene, and gave $K_{\text{ass}} = 56$. So weak an association would not be detected by our method.

These effects are not observed in aqueous solution wherein the cation can more readily form hydrogen bonds with the solvent molecules than in nitrobenzene.

This effect is only at all marked where plausible structures for the complex can be written. Thus, in the case of the aliphatic amines we have a structure of type $[\text{R}_3\text{N}-\text{H} \cdots \text{NR}_3]^+$.

The case of the phosphazenes will be discussed in Part II.

In Table 4 are listed $\text{p}K_{\text{a}}'$ values for a number of common bases, determined in nitrobenzene. For nine of the compounds a comparison with the results of Hall is possible. As his standard buffer differed from ours, the two sets of results have been brought into correspondence by the method of least squares, rather than by arbitrarily choosing one compound as a standard in the two cases, and Hall's results have been converted into pH' units. The agreement between the two sets is within the sum of their experimental errors, except in the case of NEt_2Ph , the figures for which were therefore omitted from the least squares calculation. Literature values for $\text{p}K_{\text{a}}$ in water are included in Table 4 for comparison.

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¹¹ Kolthoff, Stocesoca, and Lee, *J. Amer. Chem. Soc.*, 1953, **75**, 1834.
