

Titration in Non-aqueous Media

Part II.* Basicity Order of Aliphatic Amines in Nitrobenzene Solvent

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The relative basicity order of methyl-, ethyl-, propyl- and butylamines has been determined potentiometrically with perchloric acid in nitrobenzene solvent and found to be $R_3N > R_2NH > RNH_2 > NH_3$, where $R = Et, n\text{-Pr}$ or $n\text{-Bu}$. However, for the methylamines, the order is $Me_2NH \geq Me_3N > MeNH_2 > NH_3$. The orders in primary, secondary and tertiary amines are $EtNH_2 > MeNH_2 > n\text{-PrNH}_2 > n\text{-BuNH}_2 > NH_3$; $Et_2NH > Me_2NH > n\text{-Pr}_2NH > n\text{-Bu}_2NH > NH_3$; and $Et_3N > n\text{-Pr}_3N \geq n\text{-Bu}_3N > Me_3N > NH_3$. These results show that, in general, an increase in the number of alkyl groups increases the basicity of the amine, and that an increase in the size of the alkyl group decreases the basicity. *n*-Butylamine is a stronger base than branched-chain primary butylamines.

Keywords: *Non-aqueous titration; potentiometric titration; amines; nitrobenzene solvent; basicity order*

The basicity orders of amines have been a source of considerable confusion for many years,¹⁻¹² as there are many factors which influence basicity. The factors influencing the basicities of aliphatic amines are relatively limited, although the most significant factors, such as molecular properties and solvent effects, are still operative.

In the work reported in this paper, the basicities of aliphatic amines have been determined in nitrobenzene solvent by potentiometric titration with perchloric acid, one of the strongest non-aqueous media acids available. Four different series of aliphatic amines have been titrated with perchloric acid, namely methyl-, ethyl-, *n*-propyl- and *n*-butylamine. In addition to these, isopropylamines and some branched-chain butylamines have also been titrated. All the amines showed good S-shaped potential vs. mequiv. acid or mequiv. base (milliequivalent of acid or milliequivalent of base) titration graphs. An example of the titration graphs for *n*-butylamines is given in Fig. 1.

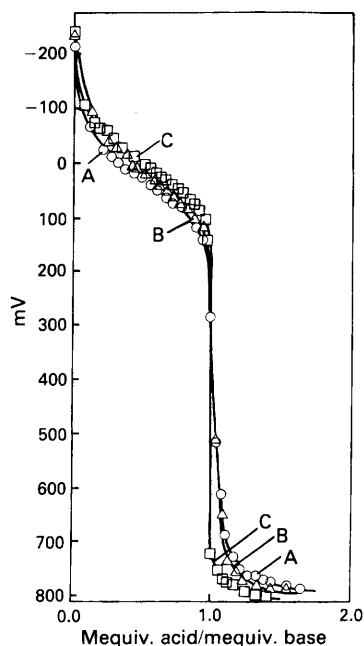


Fig. 1. Potentiometric titration graphs of *n*-butylamines with perchloric acid in nitrobenzene. A, *n*-BuNH₂; B, *n*-Bu₂NH; and C, *n*-Bu₃NH

As is evident from the shapes of the titration graphs, no homo-conjugation reactions took place during the titrations.^{1,2} This indicates that nitrobenzene is a good solvent for ionic organic compounds. Half-neutralisation potentials have been determined from the titration curves.

As the half-neutralisation potentials of the amines are slightly concentration dependent (we have carried out a number of experiments in this area), the titrations were carried out with dilute solutions (0.001 M). Also, in order to minimise the errors that would originate from the dilution of solutions during titrations, 0.034 M perchloric acid was used. The end-points were reached after the addition of about 0.5 ml of acid solution. This amount of acid solution allowed at least fifteen readings to be taken before the end-point of the titration was reached.

Half-neutralisation potentials of the amines *versus* the number of alkyl groups on the amines have been plotted in Fig. 2. It can be seen that there is a fairly good correlation between the basicity of amines and the number of alkyl groups in the amine series, with the exception of the methyl series. Ethylamines are the most basic compounds of the amines.

Isopropylamine and branched-chain butylamines are not included in Fig. 2.

Another set of experiments was performed in a nitrobenzene - light petroleum (1 + 3) system. All the experiments were repeated under identical conditions and almost the same series order was found. The anomaly observed in the methylamine series remained unchanged.

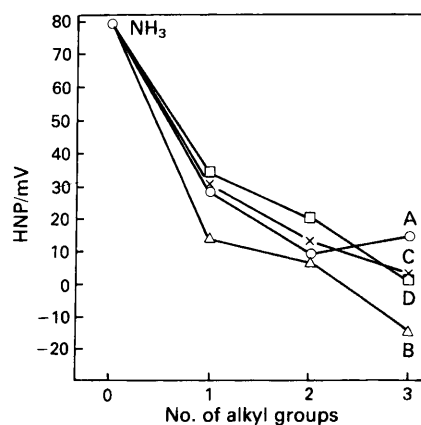


Fig. 2. Half-neutralisation potentials of the aliphatic amines in nitrobenzene *versus* number of alkyl groups. A, Methyl; B, ethyl; C, *n*-propyl; and D, *n*-butyl

* For Part I of this series, see *Analyst*, 1986, **111**, 949.

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Experimental

Apparatus and Chemicals

Potentiometer and accessory. An Orion Model 801 A digital pH meter equipped with glass and calomel electrodes was used throughout this work. The saturated KCl solution of the calomel electrode was removed and the electrode washed several times with anhydrous methanol. After drying, the electrode was then filled with saturated KCl solution in non-aqueous methanol. A pressure of 20 mmHg was applied to the solution in the calomel electrode in order to prevent the diffusion of the solution into the electrode. After each titration the electrode was washed twice with anhydrous methanol to remove nitrobenzene solution from the surface of the electrodes. Pure anhydrous methanol dries easily without leaving any stains. Before using again, electrodes were dipped into pure nitrobenzene solvent to remove any traces of methanol.

A magnetic stirrer was used in the titrations and titrations were carried out in a 50-ml beaker wound with copper wire. The copper wire and all other electrical equipment were earthed.

A semi-microburette, which could be read to 0.01 ml, was used for the titrations.

Nitrobenzene. Nitrobenzene (Merck) was used after purification in the following way: 10 g of P_2O_5 were introduced into 1 l of nitrobenzene. After shaking, the mixture was left overnight and then distilled twice at reduced pressure by the aid of a suction pump equipped with a liquid air-cooled trapper. The solvent prepared in this way was straw-yellow and its refractive index was 1.5513.

Purified nitrobenzene is a fairly good solvent for molecular and some ionic compounds. It has a large titration interval extending from -700 mV (basic side) up to $+800$ mV (acidic side).

Perchloric acid solution. Anhydrous 0.034 M perchloric acid solution was used in all the titrations. This was prepared by taking 0.072 ml of 70% perchloric acid (Merck) with a micro-pipette and adding this dropwise to 5 ml of ice-cooled pure acetic anhydride. At higher temperatures, a vigorous reaction takes place and a dark brown solution is obtained instead of a light yellow solution. The resulting light yellow solution was left for 5–6 h at room temperature, and then 1.00 ml of solution was taken from it and introduced into a 50.0-ml calibrated flask before being diluted to 50.0 ml by the addition of nitrobenzene. The concentration of the final solution was determined against a primary standard, diphenylguanidine, and was found to be 0.034 M. This solution was stable for 3–4 months, if kept under refrigeration in a dark flask.

Amines. The amines used were all of analytical-reagent grade. Diethylamine was obtained from Riedel de Hën and the others from BDH Chemicals. Methylamines were prepared from their hydrochlorides. Each hydrochloride was treated with aqueous sodium hydroxide and the gas evolved was passed over dry NaOH and then introduced directly to the solvent.

Amine solutions were titrated immediately after preparation.

Results and Discussion

Until now, no simple explanation of the basicity orders of aliphatic amines has been given.^{2,4–17} This is probably because of the number of factors that influence the basicity of the amines.

Potentiometric titrations of ammonia solution and aliphatic amines with perchloric acid in nitrobenzene have shown some interesting and unexpected relative basicity orders: $Et_3N > Et_2NH > EtNH_2 > NH_3$; $n-Pr_3N > n-Pr_2NH > n-PrNH_2 > NH_3$; $n-Bu_3N > n-Bu_2NH > n-BuNH_2 > NH_3$. These relative basicity orders are identical with the orders found by other

workers in the gas phase.^{5,11,12,15,18} (It is very difficult to give a theoretical explanation of these similarities, because one set of experiments were carried out in the gas phase and the other set of experiments were carried out in the condensed phase. In the gas phases intrinsic electronic factors affect the basicity without the interference of the solvent.)

There are also interesting orderings among the primary, secondary and tertiary amines, although these orderings are in conflict with the results of other workers^{5,7–12}: $EtNH_2 > n-PrNH_2 > n-BuNH_2 > NH_3$; $Et_2NH > n-Pr_2NH > n-Bu_2NH > NH_3$; $Et_3N > n-Pr_3N \geq n-Bu_3N > NH_3$.

For the methylamine series, a different order was found: $Me_2NH > Me_3N > MeNH_2 > NH_3$. This order unexpectedly parallels the order found in water by Brown.⁴ In water there are two main opposing effects influencing the basicities of the amines, namely hydration and inductive effects. The hydration effect decreases with an increase in the number of alkyl substitutions, whereas the inductive effect increases with an increase in the number of alkyl substitutions. However, in nitrobenzene solvent, this explanation is not applicable.

The order determined for the methylamines disagrees with the findings of Benoit and co-workers in dimethyl sulphoxide.^{9,10}

The relative basicity orders of primary, secondary and tertiary amines, including methylamines, are as follows: $EtNH_2 > MeNH_2 > n-PrNH_2 > n-BuNH_2 > NH_3$; $Et_2NH > Me_2NH > n-Pr_2NH > n-Bu_2NH > NH_3$; $Et_3N > n-Pr_3N > n-Bu_3N > Me_3N > NH_3$.

The extended primary and secondary amines, including isopropylamine and branched-chain butylamines, give the following orders: $EtNH_2 > MeNH_2 > iso-PrNH_2 > n-PrNH_2 > n-BuNH_2 > sec-BuNH_2 > tert-BuNH_2 > iso-BuNH_2 > NH_3$; $Et_2NH > Me_2NH > n-Pr_2NH > n-Bu_2NH > iso-Pr_2NH > NH_3$. Unfortunately, a good theoretical explanation as to why ethylamines are stronger bases than their methyl analogues has not been found.

Conclusions

From the investigations described above, the following conclusions can be drawn.

(1) *F*-strain seems to be very likely because any ethylamine is a stronger base than its propyl and butyl analogues.^{4,16,19} $EtNH_2 > PrNH_2$; $Et_2NH > Pr_2NH$; $Et_3N > Pr_3N$. Identical orderings hold true for butylamines.

(2) *B*-strain is not observed in this work because tri-n-propylamine is more basic than n-propylamine. The same sequence is true also for tri-n-butylamine and n-butylamine.

(3) Basicity decreases with increase in size of the alkyl group, with the exception of methylamines. This finding is the opposite of findings reported in the literature.^{7,9–12}

(4) n-Butylamine is more basic than the branched-chain butylamines. This is also in disagreement with data in the literature.^{7,10–12}

(5) It is concluded that the order of basicities of amines may be entirely opposite when the titrations are carried out in different media.^{7–12,19}

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