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# Gas-Phase Basicities of Amines

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**Abstract:** Relative gas-phase basicities of some aliphatic amines have been determined by ion cyclotron resonance spectroscopy. The orders are *tert*-butylamine > neopentylamine > isopropylamine > *n*-propylamine > ethylamine > methylamine > ammonia; diethylamine > dimethylamine; triethylamine > trimethylamine; trimethylamine > dimethylamine > methylamine; triethylamine > diethylamine > ethylamine; trimethylamine > *tert*-butylamine; dimethylamine ≈ isopropylamine; and trimethylamine ≈ diethylamine. It is concluded that increasing alkyl substitution increases basicity if similar substituents are compared, that increasing alkyl group size increases basicity, and that increasing degree of substitution lowers the N–H bond dissociation energy in ammonium ions. Possible origins of these effects are discussed.

In connection with our recent work on gas-phase acidities,[2,3] particularly amine acidities, we have undertaken a complementary study of relative gas-phase basicities of aliphatic amines, eq 1. The purpose of this

$$R_1R_2R_3N + H^+ \longrightarrow R_1R_2R_3NH^+ \qquad (1)$$

work was to continue our studies of simple ionic reactions in the gas phase in order to explore intrinsic effects of structure and effects of solvation on reactivity. The substantial body of evidence which has been accumulated on gas-phase negative ion reactions has given rise to hypotheses which can effectively be tested by examination of positive ion reactions. In particular, models for alkyl group effects[2d,3] can be evaluated by examining similarities and differences in positive and negative systems. Furthermore, amine basicities measured in solution have resulted in a great deal of confusion about intrinsic molecular properties, and only recently has any clarification been made.[2b,4] Thus, intrinsic basicities of amines constitute an area of considerable interest and importance.

In this paper we report on the relative gas-phase basicities of a variety of primary, secondary, and tertiary aliphatic amines. The results deal with the dependence of basicity on degree of substitution, the effect of alkyl group size on basicity, and the effect of degree of substitution on N–H bond dissociation energy in ammonium ions. The method used, as previously,[5] is to probe the preferred direction of proton transfer in reactions (eq 2) by ion cyclotron resonance (icr) and double resonance spectroscopy. The preferred direction of transfer is then related to relative basicity, in direct analogy to previous work.

$$R_1R_2R_3NH^+ + R_4R_5R_6N \rightleftharpoons R_1R_2R_3N + R_4R_5R_6NH^+ \qquad (2)$$

## Experimental Section

The instrumentation and materials were those described previously.[3] Reactions were studied at a total pressure of *ca.* $10^{-5}$ Torr and an electron energy of 15 eV. In these experiments, protonated amines were formed from proton transfer reactions of the parent molecular ions or fragment ions with the neutral amines.

## Results

Ammonium ions were generated in mixtures of amines by proton transfer from molecular ions and fragment ions. Occurrence and nonoccurrence of proton transfer reactions were determined by observation of double resonance signals.[2d,3] The results of a series of experiments are summarized in Table I. These data provide evidence for the following orders of relative proton affinities; we take these to be more or less equivalent to the intrinsic relative basicities:[6] primary amines, *tert*-butylamine > neopentylamine > isopropylamine > *n*-propylamine > ethylamine > methylamine > ammonia; secondary amines, diethylamine > dimethylamine; tertiary amines, triethylamine > trimethylamine; degree of substitution, trimethylamine > dimethylamine > methylamine > ammonia; and triethylamine > diethylamine > ethylamine; miscellaneous, trimethylamine > *tert*-butylamine; dimethylamine ≈ isopropylamine; trimethylamine ≈ diethylamine. Some of the above pairs were determined indirectly from reactions with a third amine; for example, *n*-propylamine and isopropylamine with dimethylamine.

If the ammonium ions studied in these experiments were excited, then the ordering found might be incorrect. However, the formation of these ions by secondary reactions and their internally consistent behavior give some confidence in the order. In par-

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[2] (a) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968); (b) *ibid.*, **90**, 6561 (1968); (c) *ibid.*, **91**, 2126 (1969); (d) *ibid.*, **92**, 5986 (1970).

[3] J. I. Brauman and L. K. Blair, *ibid.*, **93**, 3911 (1971).

[4] M. S. B. Munson, *ibid.*, **87**, 2332 (1965).

[5] References to the details of the method are given in ref 2d and 3. In particular, details of the technique are outlined in ref 2d.

[6] See ref 2d and 3 for justification and discussion.

**Table I.** Double Resonance Results for Forward (F) and Reverse (R) Proton Transfer Reactions[a]

| No. | Reaction | (F) | (R) |
|---|---|---|---|
| 1 | $NH_4^+ + CH_3NH_2 = NH_3 + CH_3NH_3^+$ | (−) | (+) |
| 2 | $CH_3NH_3^+ + C_2H_6NH_2 = CH_3NH_2 + C_2H_5NH_3^+$ | (−) | (0) |
| 3 | $C_2H_5NH_3^+ + n\text{-}C_3H_7NH_2 = C_2H_5NH_2 + n\text{-}C_3H_7NH_3^+$ | (−) | (+) |
| 4 | $C_2H_5NH_3^+ + i\text{-}C_3H_7NH_2 = C_2H_5NH_2 + i\text{-}C_3H_7NH_3^+$ | (−) | (0) |
| 5 | $n\text{-}C_3H_7NH_3^+ + tert\text{-}C_4H_9NH_2 = n\text{-}C_3H_7NH_2 + tert\text{-}C_4H_9NH_3^+$ | (−) | (+) |
| 6 | $i\text{-}C_3H_7NH_3^+ + tert\text{-}C_4H_9NH_2 = i\text{-}C_3H_7NH_2 + tert\text{-}C_4H_9NH_3^+$ | (−) | (+) |
| 7 | $(CH_3)_3CCH_2NH_3^+ + tert\text{-}C_4H_9NH_2 = (CH_3)_3CCH_2NH_2 + tert\text{-}C_4H_9NH_3^+$ | (−) | (+) |
| 8 | $i\text{-}C_3H_7NH_3^+ + (CH_3)_3CCH_2NH_2 = i\text{-}C_3H_7NH_2 + (CH_3)_3CCH_2NH_3^+$ | (−) | (+) |
| 9 | $CH_3NH_3^+ + (CH_3)_2NH = CH_3NH_2 + (CH_3)_2NH_2^+$ | (−) | (+) |
| 10 | $C_2H_5NH_3^+ + (C_2H_5)_2NH = C_2H_5NH_2 + (C_2H_5)_2NH_2^+$ | (−) | (+) |
| 11 | $(CH_3)_2NH_2^+ + (CH_3)_3N = (CH_3)_2NH + (CH_3)_3NH^+$ | (−) | (+) |
| 12 | $(C_2H_5)_2NH_2^+ + (C_2H_5)_3N = (C_2H_5)_2NH + (C_2H_5)_3NH^+$ | (−) | (+) |
| 13 | $n\text{-}C_3H_7NH_3^+ + (CH_3)_2NH = n\text{-}C_3H_7NH_2 + (CH_3)_2NH_2^+$ | (−) | (+) |
| 14 | $(CH_3)_2NH_2^+ + i\text{-}C_3H_7NH_2 = (CH_3)_2NH + i\text{-}C_3H_7NH_3^+$ | (−) | (−) |
| 15 | $tert\text{-}C_4H_9NH_3^+ + (CH_3)_3N = tert\text{-}C_4H_9NH_2 + (CH_3)_3NH^+$ | (−) | (+) |
| 16 | $(CH_3)_3NH^+ + (C_2H_5)_2NH = (CH_3)_3N + (C_2H_5)_2NH_2^+$ | (−) | (−) |

[a] The sign of the double resonance signal is given. A negative sign (−) means that the product ion concentration diminished when the reactant was irradiated. A negative sign (−) is generally associated with an exothermic or thermoneutral reaction. A positive sign (+) is generally associated with endothermic reactions. A zero (0) indicates that the reaction was investigated but no signal change was observed. In conjunction with a forward (−) this suggests that the reverse reaction was not proceeding measurably.

ticular, pairwise comparisons do not give rise to inconsistencies (*e.g.*, A > B > C < A), and almost all of the reactions studied gave definitive results.

## Discussion

Amine basicity orders have long been a source of considerable confusion.[7,8] No simple explanation was able to accommodate the solution basicity order of trimethylamine < dimethylamine > methylamine. Both molecular properties and solvent effects have been invoked to explain the observation that the sequence of base strengths often does not fall in the usual inductive order. Calculations suggested that "B-strain" [8c] was likely to be too small to account for the effect.[8d] Steric hindrance to solvation has been invoked as an explanation,[8e,f] as has the influence of the number of N–H bonds available for hydrogen bonding.[8g] The problem of primary *vs.* secondary *vs.* tertiary amines was settled by Munson,[4] who showed that the relative order of gas-phase basicities was $Me_3N > Me_2NH > MeNH_2 > NH_3$.

We had previously[2b] confirmed this result, and in this paper report also the order $Et_3N > Et_2NH > EtNH_2$. The result is important in that it confirms the generality of the intrinsic order tertiary > secondary > primary where amines with the same substituent groups are compared. Interestingly, the aqueous solution ordering of the ethylamines is also anomalous,[9] suggesting that the reversal between gas and solution is itself consistent. As the anomaly appears to be associated with a solution effect, steric hindrance to solvation or number of available hydrogen bonds appear to be the most economical explanations. We believe that these orderings should put to rest any doubts regarding relative intrinsic basicities. The basicities toward acids other than $H^+$ may, of course, appear in different order due to other effects such as "F-strain."[7,8c] Also, when a Lewis acid is used, the resulting salt is formally neutral, and the effects of substitution in charge stabilization may be less pronounced.

The data clearly indicate that as the size of the alkyl group increases, amines become more basic. This is true for the primary series *tert*-butylamine > isopropylamine > ethylamine >methylamine; the secondary series diethylamine > dimethylamine; and the tertiary series triethylamine > trimethylamine. This trend has also been observed in the basicities of the methyl and ethyl alcohols and ethers.[4]

There are a number of possible sources for the stabilizing effects of the alkyl groups. Probably the most obvious of these is the inductive (or dipole type) effect. For many years this explanation has found considerable favor. However, our observation that alkyl groups enhance acidity[2b–d,3] as well as basicity preclude this effect as the major source of stabilization. (This is not to say that there may not be dipole type stabilization, but it cannot be too large.)

Another source of alkyl group stabilization involves rehybridization energy. For example, alkyl groups stabilize olefins relative to alkanes, and can stabilize both positively and negatively charged systems if bonded to a center which is $sp^3$ in the neutral and becomes $sp^2$ in the ion.[10] As amines are pyramidal and ammonium ions are more or less tetrahedral, it is doubtful if effects such as this are important in amine basicities.

Finally, a major source of charge stabilization is the charge-induced dipole, or polarizability, effect. This explanation accounts for essentially all of the observations. Because the stabilization is independent of the sign of the charge, one expects stabilization in both positively and negatively charged ions, eq 3, where $U(r)$ is the stabilization energy of a charge-induced dipole, $\alpha$ is the polarizability, $q$ is the charge, $\epsilon$ is the dielectric constant, and $r$ is the distance.[11] Further, one expects

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(7) See L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, pp 284–292, for an extensive discussion. Also, J. Clark and D. D. Perrin, *Quart. Rev., Chem. Soc.*, **18**, 295 (1964).

(8) (a) H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956); (b) D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 2387 (1964); (c) H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Amer. Chem. Soc.*, **66**, 435 (1944); (d) R. Spitzer and K. S. Pitzer, *ibid.*, **70**, 1261 (1948); (e) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); (f) A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, 47, 34 (1951); (g) E. J. King, "Acid-Base Equilibria," Pergamon Press, New York, N. Y., 1965, p 151, and references cited therein.

(9) H. C. Brown, *J. Amer. Chem. Soc.*, **67**, 1452 (1945).

(10) Many examples in carbonium ion chemistry are known. For an example of a stabilized carbanion, see J. I. Brauman, preprints of the Division of Petroleum Chemistry, Symposium on Properties of Anions, C-5, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

that stabilization should increase as the polarizability of

$$U(r) = -\frac{1}{2}\frac{\alpha q^2}{\epsilon r^4} \tag{3}$$

the substituent increases, and as the polarizability depends on the number of atoms, bonds, etc., it increases as alkyl size increases. The order isopropylamine > *n*-propylamine is consistent with this picture, since isopropyl would lower the energy more owing to the greater proximity of atoms to the charge. The relative order of *tert*-butylamine and neopentylamine indicate, as expected, that at about this size all alkyl groups have approximately the same effect. Overall orders such as this have been observed in our acidity studies also.[2b-d,3] Thus, it is clear that polarizability stabilization by alkyl groups is of substantial importance in simple, aliphatic, saturated, ionic systems. These effects are likely to be fairly small, and given the extremely high heats of solution of ions, may well be swamped out in solution ionic equilibria. Thus, attempts to interpret solution acidities or basicities of saturated aliphatic systems in terms of intrinsic isolated molecule properties are likely to be unsuccessful.

Examination of the data suggests that another factor may be important in determining amine basicities. The relations $Me_2NH \approx i\text{-}PrNH_2$ and $Me_3N \approx Et_2NH$ show that it is possible for a large alkyl group to compensate for increasing degree of substitution. Thus, the order tertiary > secondary > primary holds only if the alkyl size is constant. The order can be reversed if the groups are changed (*e.g.*, *tert*-butylamine > dimethylamine). Because of the equalities found, it is possible to evaluate a quantity which has not previously been accessible—the differences in bond dissociation energies in substituted ammonium ions. Consider the thermochemical cycle (4). If a pair of amines are of equal

$$\begin{array}{lll}
A \longrightarrow A\cdot^{+} + e^{-} & IP(A) & (4a) \\
H^{+} + e^{-} \longrightarrow H\cdot & -IP(H\cdot) & (4b) \\
\underline{A\cdot^{+} + H\cdot \longrightarrow AH^{+}} & \underline{-DH°(AH^{+})} & (4c) \\
A + H^{+} \longrightarrow AH^{+} & \Delta H° & (4d)
\end{array}$$

basicity (equal $\Delta H°$), the difference in bond dissociation energies in the ammonium ions should be equal to the difference in ionization potentials of the parent amines. Making use of the ionization potentials[12,13] (in electron volts) $Me_2NH = 8.24$, $i\text{-}PrNH_2 = 8.72$; and $Me_3N = 7.82$, $Et_2NH = 8.01$; we can deduce for the differences in N–H bond dissociation energies $DH°(i\text{-}PrNH_3^+) - DH°(Me_2NH_2^+) \approx 11$ kcal/mol, and $DH°(Et_2NH_2^+) - DH°(Me_3NH^+) \approx 4$ kcal/mol.

The difference between secondary and tertiary amines of *ca.* 4 kcal/mol seems quite reasonable in view of differences found in amines[14] (∼8 kcal/mol per alkyl group) and hydrocarbons[15] (∼3.5 kcal/mol per alkyl group). However, the difference of *ca.* 11 kcal/mol between primary and secondary systems seems somewhat large. Although the ionization potentials quoted are the "best available,"[13] they may still be somewhat in error because of low cross sections at the threshold.[12] In any case, the ordering is such that it is clear that the bond dissociation energies in ammonium ions do decrease with increasing alkyl substitution, behavior similar to that found in neutral systems. Thus, this effect tends to make less highly substituted amines more basic in contrast to the polarizability effect, although it is not sufficiently large to overcome it. If we assume that the bond dissociation energy in the alkylammonium ions is independent of substituent size and depends only upon the degree of alkyl substitution, then the stabilizing effect of alkyl groups on ammonium ions can be evaluated from the ionization potentials of the neutral amines.[12,13] Examination indicates that the size of the effect in stabilizing positive charge is roughly the same as that inferred[3] for stabilizing negative charge. Finally, if it is true that the bond dissociation energies are constant within the primary series, then the relative basicity differences between methyl-, ethyl-, isopropyl-, and *tert*-butylamines are 2.5, 1.4, and 1.8 kcal/mol.

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(11) For example, see M. Davies, "Some Electrical and Optical Aspects of Molecular Behavior," Pergamon Press, New York, N. Y., 1965, p 160.

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