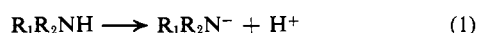


## Gas-Phase Acidities of Amines

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**Abstract:** Relative gas-phase acidities in a series of aliphatic amines have been determined by ion cyclotron resonance spectroscopy. The orders of acidity are diethylamine > neopentylamine  $\geq$  *tert*-butylamine  $\geq$  dimethylamine  $\geq$  isopropylamine > *n*-propylamine > ethylamine > methylamine > ammonia and diethylamine > water > *tert*-butylamine. Some relative stabilizing properties of alkyl groups are evaluated quantitatively.

The general problem of relating structure and reactivity in ionic reactions is substantially complicated by solvent effects. Recently, we have undertaken a study of gas-phase acidities in order to determine the intrinsic effects of structure on acid dissociation.<sup>2-4</sup> In this paper we report on the relative acidities of aliphatic amines, eq 1. The loss of a proton from an amine, pro-



ducing an amide ion, is analogous to loss of a proton from alcohol producing an alkoxide ion. As relative gas-phase acidities of alcohols have been fairly well explored,<sup>3</sup> the experiments with amines are of considerable interest. First, parallels between the behavior of amines and alcohols may be drawn, thus indicating the generality of effects. Second, quantitative evaluation of some of these effects can be made, since the structures of amines can be varied. Specifically, acidic amines can be primary or secondary, and the difference in N-H bond strengths can be related to other factors which affect the acidity.

The method used in this work involves probing the preferred direction of proton transfer in reactions (eq 2) by ion cyclotron resonance (icr) and double resonance spectroscopy.<sup>5</sup> The preferred direction of transfer can then be related to the relative acidities of the two acids involved.<sup>3</sup>



## Experimental Section

**Materials.** Neopentylamine was generated from its hydrochloride by gently warming a dry mixture with excess anhydrous barium oxide on a vacuum line. The free amine was collected at  $-190^\circ$ . All other amines were obtained commercially (gases in lecture bottles) and used as received. Ethylamine-*1,1,2,2,2-d*<sub>5</sub> (CD<sub>3</sub>CD<sub>2</sub>NH<sub>2</sub>) was prepared by reduction of acetonitrile-*d*<sub>3</sub> (CD<sub>3</sub>CN), Stohler Isotopic chemicals, with lithium aluminum deuteride, Alfa Inorganics, using a standard procedure.<sup>6</sup> The resulting ethylamine-*d*<sub>5</sub> contained greater than 99% D by mass spectral analysis.

(1) (a) Alfred P. Sloan Foundation Fellow; (b) National Science Foundation Predoctoral Fellow, 1966-1970.

(2) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968).

(3) J. I. Brauman and L. K. Blair, *ibid.*, **90**, 6561 (1968); **92**, 5986 (1970).

(4) For a preliminary account of this work, see J. I. Brauman and L. K. Blair, *ibid.*, **91**, 2126 (1969).

(5) (a) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966); (b) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967); (c) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968); (d) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968); (e) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

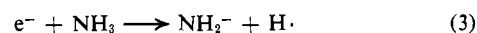
(6) L. H. Amundsen and L. S. Nelson, *J. Amer. Chem. Soc.*, **73**, 242 (1951).

**Preparation of Samples and Instrumentation.** These were carried out in a manner identical with that previously reported.<sup>3</sup> Reactions were studied at pressures of *ca.* 10<sup>-6</sup> Torr.

**Generation of Ions.** Ions were produced by secondary reactions with NH<sub>2</sub><sup>-</sup>. An electron energy of *ca.* 5.7 eV was chosen to maximize signal intensity.

## Results

Negative ions in these experiments were generated from NH<sub>2</sub><sup>-</sup>, formed from ammonia by interaction with electrons at 5.65 eV. The production of NH<sub>2</sub><sup>-</sup> has been attributed<sup>7</sup> to the dissociative resonance capture reaction (3). At this energy only small amounts of H<sup>-</sup>



are formed, in contrast to the behavior of water, which yields predominately H<sup>-</sup> and OH<sup>·</sup> at low energy. That all of the ions produced in these experiments arise from NH<sub>2</sub><sup>-</sup> was demonstrated by the coincidence of their ionization efficiency maxima (at *ca.* 5.7 eV) with that for NH<sub>2</sub><sup>-</sup>. Thus, all of the alkylamide ions are formed by secondary reactions.<sup>8</sup>

In mixtures of various amines, peaks corresponding to the corresponding negative amide ions (M - 1) were observed. Experiments carried out with C<sub>2</sub>D<sub>5</sub>-NH<sub>2</sub> showed a peak only at *m/e* 49, demonstrating that the N-H protons were removed exclusively.

The double resonance method has been discussed previously in considerable detail.<sup>3,5</sup> Basically, the technique consists of increasing the kinetic energies of reactant ions while simultaneously monitoring the abundances of product ions. The observation of a decrease in product ion abundance on heating the reactant is evidence for occurrence of the reaction in the absence of heating, consistent with an exothermic or thermoneutral reaction. The observation of an increase in product ion abundance on heating the reactant is consistent with an endothermic reaction being "driven" under these conditions. The observation of no change in product ion abundance when a probable reactant is heated, evidence that the reaction rate is essentially unchanged, is usually taken to mean that the reaction is too slow to be significant in the presence or absence of heating. This result is consistent with an endothermic reaction. However, as activation energies may play an important role in inhibiting some reactions, it is essential that reactions be studied in both forward and reverse directions. In particular, given the consideration of microscopic reversibility, observation of a

(7) T. E. Sharp and J. T. Dowell, *J. Chem. Phys.*, **50**, 3024 (1968).

(8) For some other ion-molecule reactions of NH<sub>2</sub><sup>-</sup>, see C. E. Melton, *J. Chem. Phys.*, **45**, 4414 (1966); J. G. Dillard and J. L. Franklin, *ibid.*, **48**, 2353 (1968).

Table I. Double Resonance Results for Forward (F) and Reverse (R) Proton Transfer Reactions<sup>a</sup>

| No. | Reaction  | (F) | (R) |
|-----|---|-----|-----|
| 1   | $\text{NH}_2^- + \text{CH}_3\text{NH}_2 = \text{NH}_3 + \text{CH}_3\text{NH}^-$   | (-) | (0) |
| 2   | $\text{NH}_2^- + \text{C}_2\text{H}_5\text{NH}_2 = \text{NH}_3 + \text{C}_2\text{H}_5\text{NH}^-$   | (-) | (*) |
| 3   | $\text{NH}_2^- + \text{C}_2\text{D}_5\text{NH}_2 = \text{NH}_3 + \text{C}_2\text{D}_5\text{NH}^-$   | (-) | (*) |
| 4   | $\text{NH}_2^- + n\text{-C}_3\text{H}_7\text{NH}_2 = \text{NH}_3 + n\text{-C}_3\text{H}_7\text{NH}^-$   | (-) | (*) |
| 5   | $\text{NH}_2^- + i\text{-C}_3\text{H}_7\text{NH}_2 = \text{NH}_3 + i\text{-C}_3\text{H}_7\text{NH}^-$   | (-) | (*) |
| 6   | $\text{NH}_2^- + \text{tert-C}_4\text{H}_9\text{NH}_2 = \text{NH}_3 + \text{tert-C}_4\text{H}_9\text{NH}^-$   | (-) | (*) |
| 7   | $\text{NH}_2^- + (\text{CH}_3)_2\text{NH} = \text{NH}_3 + (\text{CH}_3)_2\text{N}^-$  | (-) | (*) |
| 8   | $\text{NH}_2^- + (\text{C}_2\text{H}_5)_2\text{NH} = \text{NH}_3 + (\text{C}_2\text{H}_5)_2\text{N}^-$  | (-) | (*) |
| 9   | $\text{CH}_3\text{NH}^- + \text{C}_2\text{H}_5\text{NH}_2 = \text{CH}_3\text{NH}_2 + \text{C}_2\text{H}_5\text{NH}^-$   | (-) | (0) |
| 10  | $\text{C}_2\text{H}_5\text{NH}^- + n\text{-C}_3\text{H}_7\text{NH}_2 = \text{C}_2\text{H}_5\text{NH}_2 + n\text{-C}_3\text{H}_7\text{NH}^-$                     | (-) | (0) |
| 11  | $\text{C}_2\text{H}_5\text{NH}^- + i\text{-C}_3\text{H}_7\text{NH}_2 = \text{C}_2\text{H}_5\text{NH}_2 + i\text{-C}_3\text{H}_7\text{NH}^-$                     | (-) | (0) |
| 12  | $i\text{-C}_3\text{H}_7\text{NH}^- + \text{tert-C}_4\text{H}_9\text{NH}_2 = i\text{-C}_3\text{H}_7\text{NH}_2 + \text{tert-C}_4\text{H}_9\text{NH}^-$           | (-) | (0) |
| 13  | $\text{tert-C}_4\text{H}_9\text{NH}^- + (\text{CH}_3)_3\text{CCH}_2\text{NH}_2 = \text{tert-C}_4\text{H}_9\text{NH}_2 + (\text{CH}_3)_3\text{CCH}_2\text{NH}^-$ | (-) | (-) |
| 14  | $\text{CH}_3\text{NH}^- + (\text{CH}_3)_2\text{NH} = \text{CH}_3\text{NH}_2 + (\text{CH}_3)_2\text{N}^-$  | (-) | (0) |
| 15  | $n\text{-C}_3\text{H}_7\text{NH}^- + (\text{CH}_3)_2\text{NH} = n\text{-C}_3\text{H}_7\text{NH}_2 + (\text{CH}_3)_2\text{N}^-$                                  | (-) | (0) |
| 16  | $i\text{-C}_3\text{H}_7\text{NH}^- + (\text{CH}_3)_2\text{NH} = i\text{-C}_3\text{H}_7\text{NH}_2 + (\text{CH}_3)_2\text{N}^-$                                  | (-) | (-) |
| 17  | $\text{tert-C}_4\text{H}_9\text{NH}^- + (\text{CH}_3)_2\text{NH} = \text{tert-C}_4\text{H}_9\text{NH}_2 + (\text{CH}_3)_2\text{N}^-$                            | (-) | (-) |
| 18  | $(\text{CH}_3)_2\text{N}^- + (\text{CH}_3)_3\text{CCH}_2\text{NH}_2 = (\text{CH}_3)_2\text{NH} + (\text{CH}_3)_3\text{CCH}_2\text{NH}^-$                        | (-) | (0) |
| 19  | $(\text{CH}_3)_3\text{CCH}_2\text{NH}^- + (\text{C}_2\text{H}_5)_2\text{NH} = (\text{CH}_3)_3\text{CCH}_2\text{NH}_2 + (\text{C}_2\text{H}_5)_2\text{N}^-$      | (-) | (0) |
| 20  | $(\text{CH}_3)_2\text{N}^- + (\text{C}_2\text{H}_5)_2\text{NH} = (\text{CH}_3)_2\text{NH} + (\text{C}_2\text{H}_5)_2\text{N}^-$                                 | (-) | (0) |
| 21  | $\text{NH}_2^- + \text{H}_2\text{O} = \text{NH}_3 + \text{OH}^-$  | (-) | (0) |
| 22  | $\text{C}_2\text{H}_5\text{NH}^- + \text{H}_2\text{O} = \text{C}_2\text{H}_5\text{NH}_2 + \text{OH}^-$  | (-) | (+) |
| 23  | $(\text{CH}_3)_2\text{N}^- + \text{H}_2\text{O} = (\text{CH}_3)_2\text{NH} + \text{OH}^-$   | (-) | (+) |
| 24  | $\text{tert-C}_4\text{H}_9\text{NH}^- + \text{H}_2\text{O} = \text{tert-C}_4\text{H}_9\text{NH}_2 + \text{OH}^-$  | (*) | (+) |
| 25  | $\text{OH}^- + (\text{C}_2\text{H}_5)_2\text{NH} = \text{H}_2\text{O} + (\text{C}_2\text{H}_5)_2\text{N}^-$   | (-) | (*) |

<sup>a</sup> 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. An asterisk (\*) indicates that the reaction was not investigated.

negative change in the forward direction coupled with a positive or zero change in the reverse direction is strong evidence that the forward direction is exothermic. Conclusions of this type can be vitiated if the reactant ions are not in their ground states. Consequently, it is also imperative that pairwise combinations be studied to demonstrate consistency. Thus, the observation of  $\text{AH} + \text{B}^- \rightleftharpoons \text{A}^- + \text{BH}$ , and  $\text{BH} + \text{C}^- \rightleftharpoons \text{B}^- + \text{CH}$ , implies  $\text{AH} > \text{CH}$  irrespective of the energetics of  $\text{B}^-$ , provided that  $\text{B}^-$  has the same energy in both reactions. This can be achieved either by examining a mixture of  $\text{AH}$ ,  $\text{BH}$ , and  $\text{CH}$  or by allowing  $\text{B}^-$  to be formed by the same process in both reactions. In our experiments, both techniques were utilized; the formation of all negative ions from  $\text{NH}_2^-$  suggests that each is formed with a reproducible amount of energy.

The results of a number of experiments are given in Table I; the sign of the double resonance signal is indicated. Experiments 1-8 involve reactions with ammonia; experiments 9-13 involve reactions of primary amines with primary amines; experiments 14-20 involve reactions of secondary amines with primary and secondary amines; and experiments 21-25 involve reactions of various amines with water. Taken together, the data suggest an order of ability to transfer a proton of diethylamine  $>$  neopentylamine  $>$  *tert*-butylamine  $>$  dimethylamine  $>$  isopropylamine  $>$  *n*-propylamine  $>$  ethylamine  $>$  methylamine  $>$  ammonia; and diethylamine  $>$  water  $>$  *tert*-butylamine  $>$  ammonia. The symbol  $>$  indicates that while essentially thermoneutral behavior was observed (both forward and back reaction products decreased on heating reactants), an order could be inferred from other experiments. For example, reaction 16 suggests isopropylamine  $\approx$  dimethylamine; from 17, *tert*-butylamine  $\approx$  dimethylamine; but from 12, *tert*-butylamine  $>$  isopropyl-

amine. Thus, we arrive at the order *tert*-butylamine  $>$  dimethylamine  $>$  isopropylamine.

Some of the reactions were not studied in both directions since the other results clearly indicate (through pairwise comparisons) the expected outcome of these experiments. The reactions of some of the amide ions with water (no. 24-25) could not be probed directly because of signal-to-noise problems. However, the reverse reactions appear relatively unambiguous and the order appears to be well defined.

## Discussion

In previous work we have related the preferred direction of proton transfer to relative thermodynamic acidity.<sup>3</sup> The observation of a reaction, eq 2, in a preferred direction suggests that the reaction is energetically feasible in this direction and thus  $\Delta E^\circ$  and  $\Delta H^\circ$  (since there is no volume change) are negative or zero. Assuming  $\Delta S^\circ \approx 0$  for the reaction, which is almost surely true for any pair in a related series,<sup>9a</sup> leads to an ordering of thermodynamic acidities which is the same as the relative order of preferred proton transfer.

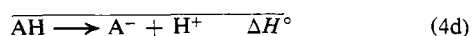
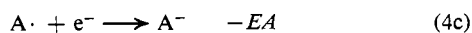
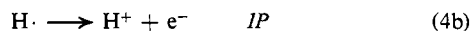
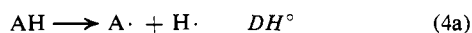
The assumption of  $\Delta S^\circ \approx 0$  is actually true only for intrinsic contributions to the entropy. An additional contribution arises when reactants and products have different symmetry numbers or when there are different reaction path degeneracies for the forward and back reactions. Thus, in comparing acidities of a primary and a secondary amine for which  $\Delta H^\circ$  in eq 2 = 0, the primary amine would be more acidic by a factor of 2 since it has two acidic protons. The determinations carried out in this work depend upon energetics and thus formally relate to acidity per N-H bond. How-

(9) (a) K. S. Pitzer, *J. Amer. Chem. Soc.*, **59**, 2365 (1937); (b) for an example of statistical corrections to intrinsic thermochemical properties, see S. W. Benson, *et al.*, *Chem. Rev.*, **69**, 279 (1969).

ever, the acidity per N-H bond is itself more useful in structure-reactivity relationships, and in any event, the statistical correction<sup>9b</sup> can be applied subsequently if a pair of acids of different symmetry properties are found to have the same energetics. In terms of energies these statistical corrections are likely to be fairly small, for example  $R \ln 2$  is equivalent to 0.4 kcal/mol at 25°.

The relative acidities of the amines bear a striking parallelism to those of the alcohols. Thus, the acidity order of primary amines, *tert*-butylamine > isopropylamine > ethylamine > methylamine is the same as that observed for alcohols,<sup>10</sup> the primary amine with the larger alkyl group being more acidic. The same trend is also observed in the secondary amines, diethylamine > dimethylamine. These orderings are those which would be expected, given the model of a localized anion (charge largely restricted to nitrogen) and essentially identical bond dissociation energies within the series.<sup>11</sup> Thus, the charge is stabilized by the alkyl group acting as a polarizable medium.<sup>3,4,13</sup> Although we have as yet been unable to generate simple alkyl anions, it is to be expected that alkanes will exhibit similar behavior.

We have previously<sup>3,14</sup> analyzed acidities in terms of the thermochemical cycle (4). Examination of this



cycle indicates why the various primary and secondary amines might be expected to overlap in their relative acidities. Although little thermochemical data are available, it is to be expected that the N-H bond dissociation energies in primary amines are higher than those in secondary amines.<sup>15</sup> Consequently, a secondary amine will experience enhanced acidity through lowering of (4a). On the other hand, large alkyl groups tend to increase the electron affinity, thus lowering (4c). In combination, one large alkyl group in (4c) may compensate for the effect of two small groups in (4a). This is precisely what is observed, *tert*-butylamine being approximately equal in acidity to dimethylamine. More importantly, the observation of this equality allows us to obtain a quantitative estimate of the effects of these alkyl groups. If we assume that primary N-H bonds are *ca.* 8 kcal/mol stronger than secondary N-H bonds,<sup>15</sup> then the electron affinity of the *tert*-butylamino radical must be *ca.* 8 kcal/mol greater than the electron affinity of the dimethylamino radical. The size of this effect is consistent with polarizability stabi-

lization by the alkyl groups, as suggested previously. It is not possible at the present time to provide any quantitative confirmation, since the proper polarizabilities are not known.

Other work demonstrates that the increase in acidity with increasing alkyl group size is not due to an inductive or dipole stabilization type effect. Munson<sup>17</sup> has shown that the relative basicities of ethers and alcohols fall in the order  $\text{Et}_2\text{O} > \text{Me}_2\text{O}$  and  $\text{EtOH} > \text{MeOH}$ . And we have now determined the relative basicities of a series of primary amines,<sup>18</sup> and they, too, fall in a similar order. Thus, large alkyl groups can stabilize both positive and negative charges in ions where the charge is localized—an observation which makes polarizability stabilization a particularly attractive explanation.

The relative acidities of ammonia and water are of considerable interest, but the available thermochemical data are not sufficiently reliable to calculate the relative acidities directly. (In fact, it is even possible to conclude that ammonia is a stronger acid than water.)<sup>19</sup> Consequently, the direct determination is of importance. Although both  $\text{NH}_2^-$  and  $\text{OH}^-$  have been observed previously,<sup>7,20</sup> the proton transfer reaction,  $\text{NH}_2^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{OH}^-$ , had not been investigated. Bohme and Fehsenfeld attempted, but were unable, to observe the reverse reaction, suggesting that water was the stronger acid.<sup>21</sup> The results obtained in this work provide strong evidence that  $\text{H}_2\text{O} > \text{NH}_3$ . This is concluded from a study of the reaction itself; the indirect evidence of water with amines, and these amines with ammonia; and finally, the observed dependence of the  $\text{OH}^-$  ion intensity on electron energy, maximizing at the maximum for  $\text{NH}_2^-$ .

The N-H bond strength in ammonia is now believed<sup>15</sup> to be  $110 \pm 2$  kcal/mol. Thus, the electron affinity of  $\text{NH}_2\cdot$  must be less than 32 kcal/mol, since that of  $\text{HO}\cdot$  is 42 kcal/mol.<sup>22</sup> Since a reasonable number of compounds have acidities between water and ammonia, the *EA* of  $\text{NH}_2\cdot$  may, in fact, be substantially less than this. However, no quantitative estimate can be made.<sup>22a</sup>

The direct determination of  $\text{H}_2\text{O}$  *vs.*  $\text{NH}_3$  now defines the acidity order  $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$ . In other experiments we have shown that ammonia is a weaker acid than  $\text{CH}_3\text{Cl}$ ; however, no proton transfer could be observed from reactions of  $\text{NH}_2^-$  with saturated alkanes. From this we may infer that  $\text{NH}_3 > \text{CH}_4$ . The periodic trend can be rationalized on the basis of a simple model.<sup>23</sup>

**Acknowledgment.** We thank Dr. J. D. Baldeschwieler for helpful discussions and J. V. Garcia for technical assistance. We gratefully acknowledge support from the National Science Foundation (GP-10621, GP-4924),

(10) See ref 3. For the larger primary amines and alcohols, the acidities appear to become roughly equal when the molecules contain four or five carbon atoms.

(11) Although this has not been established for amines, it is true for hydrocarbons<sup>12a,b</sup> and alcohols.<sup>12c</sup>

(12) (a) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); (b) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); (c) S. W. Benson and R. Shaw, *Advan. Chem. Ser.*, No. 75, 288 (1968).

(13) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962); T. L. Brown, *J. Amer. Chem. Soc.*, **81**, 3229, 3232 (1959); S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(14) (a) J. C. McCoubrey, *Trans. Faraday Soc.*, **51**, 743 (1955); (b) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965).

(15) For example, recent determination<sup>16</sup> of N-H bond dissociation energies are:  $\text{NH}_3$ ,  $110 \pm 2$ ;  $\text{CH}_3\text{NH}_2$ , 103;  $(\text{CH}_3)_2\text{NH}$ , 95 (kcal/mol).

(16) R. K. Solly, N. A. Gac, D. M. Golden, and S. W. Benson, submitted for publication. Previous determinations<sup>12a</sup> show similar differences, but lower absolute values.

(17) M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 2332 (1965).

(18) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

(19) C. D. Ritchie and H. F. King, *ibid.*, **90**, 838 (1968).

(20) See J. F. Paulson, *Advan. Chem. Ser.*, No. 58, 28 (1966).

(21) D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.*, **47**, 2715 (1969).

(22) L. M. Branscomb, *Phys. Rev.*, **48**, 11 (1966).

(22a) NOTE ADDED IN PROOF. Recent determination of the photo-detachment energy of  $\text{NH}_2^-$  suggests  $EA(\text{NH}_2^-) \cong 17$  kcal/mol: K. C. Smyth, R. T. McIver, Jr., J. I. Brauman, and R. W. Wallace, *J. Chem. Phys.*, **54**, 2758 (1971).

(23) J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. C. Comisarow, and K. C. Smyth, *J. Amer. Chem. Soc.*, in press.

the National Institutes of Health (GP-14752), the donors of the Petroleum Research Fund administered by the American Chemical Society (2917-A4), the

National Aeronautics and Space Administration (NGL-05-020-250), and the Center for Materials Research, Stanford University.

## Gas-Phase Basicities of Amines

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, and the Department of Chemistry, Universidade de São Paulo, São Paulo, Brazil. Received October 7, 1970

**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  $\approx$  isopropylamine; and trimethylamine  $\approx$  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.

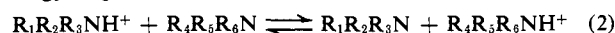
In connection with our recent work on gas-phase acidities,<sup>2,3</sup> particularly amine acidities, we have undertaken a complementary study of relative gas-phase basicities of aliphatic amines, eq 1. The purpose of this



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<sup>2d,3</sup> 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.<sup>2b,4</sup> 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,<sup>5</sup> 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.



### Experimental Section

The instrumentation and materials were those described previously.<sup>3</sup> Reactions were studied at a total pressure of *ca.*  $10^{-6}$  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.<sup>2d,3</sup> 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:<sup>6</sup> 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  $\approx$  isopropylamine; trimethylamine  $\approx$  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-

(6) See ref 2d and 3 for justification and discussion.

(1) (a) Stanford University; (b) Alfred P. Sloan Foundation Fellow; (c) Universidade de São Paulo; (d) National Science Foundation Predoctoral Fellow, 1966-1970.

(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.