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# CNDO/2 CALCULATIONS ON THE ACIDITIES OF ALKANES AND SATURATED ALCOHOLS AND THE BASICITIES OF METHYLAMINES

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**Abstract**—The CNDO/2 method is applied to calculation of the energetics of (1) proton loss from alkanes and saturated alcohols forming the derived carbanions and alkoxide anions and (2) protonation of ammonia and methylated amines forming the derived ammonium salts. Alkane acidities are calculated to be opposite to the inductive order observed in solution. The orders of gas phase acidities of alcohols and basicities of methylamines are reproduced by the calculations in good agreement with experiment. It is proposed that the gas phase order of alkane acidities may be in agreement with the calculations, with the order in solution inverted by solvent effects as seems to be the case for the alcohol series.

The calculations indicate the ability of alkyl groups to stabilize negative charge. The stabilities of alkyl carbanions and alkoxide anions directly correlate with the calculated delocalization of charge from the electronegative carbanion carbon or from the alkoxide oxygen. The larger or more complex the alkyl group, the greater the negative charge stabilization. Stabilization proceeds through the increase in alkyl group polarizability with increasing size or complexity. This is in contrast to alkyl group stabilization of positive charge in carbonium ions which seems to proceed through a conjugative interaction.

## INTRODUCTION

MUCH significant information has been derived concerning the electronic structure of pi electron systems using pi electron MO methods. In the area of carbanion chemistry, Streitwieser[1] has been able to correlate p*Ka*'s for a number of planar unsaturated hydrocarbons with differences in pi-delocalization energy between carbanions and parent hydrocarbons calculated by the Hückel method. With the current availability of approximate methods which consider all valence electrons, it seems worthwhile to attempt such an approach on saturated systems. The acidities of simple saturated hydrocarbons are not as easily accessible, but several approaches have been developed.[2] Agreement of the calculations with experimental data would tend to confirm each whereas disagreement would cast doubt on one or the other. The method of choice for the calculations is the CNDO/2 (Complete Neglect of Differential Overlap/2)[3,4] method developed by Pople *et al.* This method is superior to an extended Hückel approach because electron interactions are considered explicitly. For calculations on electron rich species, this is probably a valuable attribute. The CNDO/2 method has been described extensively in the literature[4] and has been successfully applied to a variety of chemical systems. Whereas, extended Hückel[5] and CNDO/2 calculations[6,7] have been reported for carbonium ion and free radical systems, almost nothing has been reported for carbanion species. Calculation of basicities for some heterocyclic compounds has been attempted[8] but calculation of acidities has been neglected. We shall be concerned in this work with the acidities of saturated hydrocarbons and saturated alcohols and the basicities of some saturated amines. Particular attention will be directed at the anion species involved, and necessarily, the ability of alkyl groups to stabilize negative charge must be considered.

## CALCULATIONS

Calculations were carried out using a modified version of the CNDO/2 program written by Gerald Segal and made available through the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana. Except for one set of calculations on the methide anion using the Wiberg parameterization,[6] all calculations utilized the original parameterization of Pople and Segal.[4] Following the suggestion of Pople and Gordon,[9] standard molecular geometries were employed. Except where indicated, all bond angles were taken as tetrahedral. The following bond lengths in angstroms were utilized for all species: C—C, 1·54; C—H, 1·11; C—N, 1·47; C—O, 1·43; O—H, 0·96; N—H, 1·03. Staggered conformations with dihedral angles of 0, 60, and 180° were used in accordance with convention. The geometries of anionic species were approximated as those of the parent compounds minus a hydrogen. Cartesian coordinates for input to the CNDO/2 program were derived through use of a coordinate program written to calculate Cartesian coordinates from bond lengths and bond angles.

## STEREOCHEMISTRY OF CARBANIONS

An immediate question of interest with regard to CNDO/2 calculations on carbanionic systems relates to predicted equilibrium geometries. It has been reported that CNDO/2 calculations on saturated carbonium and free radical species indicate preferred planar conformations,[6] and our calculations confirm this. Calculations on saturated carbanions, however, indicate preferred pyramidal conformations. This may be seen in Table 1, where the calculated equilibrium conformations with respect to variation in valence angle of the Me cation, radical and methide anion are shown together with identical calculations on ammonia and the ethide anion. The only semi-empirical calculations in the literature on the methide anion is that of Gordon and Fischer[10] using the INDO method (Intermediate Neglect of Differential Overlap) and

TABLE 1. CNDO/2 CALCULATIONS ON SOME $AB_3$ MOLECULES

| Molecule | Equilibrium geometry | Equilibrium valence angle (deg) | Inversion barrier (kcal/mole) | $E_{\text{tetrahedral}} - E_{\text{planar}}$[a] (kcal/mole) |
|---|---|---|---|---|
| $CH_3^+$ | Planar | 120 | 0 | 33·57 |
| $CH_3^{\cdot}$ | Planar | 120 | 0 | 11·48 |
| $CH_3^-$ | Pyramidal | 106 | 17·82 | — |
| $CH_3^-$[b] | Pyramidal | 104·1 | 15·4 | — |
| $CH_3^-$[c] | Planar | 120 | 0 | 3·51 |
| $NH_3$ | Pyramidal | 106 | 13·49 | — |
| $C_2H_5^-$[d] | Pyramidal | 107 | 13·43 | — |

[a] Difference in energy between tetrahedral and planar conformation. Listed in order to indicate steepness of potential function for compounds with planar equilibrium conformations.

[b] INDO calculation of Gordon and Fisher.[10]

[c] Using parameterization proposed by Wiberg.[6]

[d] Me—C—H and H—C—H valence angles constrained to same values.

is listed in the Table. In addition, a calculation using the set of CNDO/2 parameters proposed by Wiberg[6] is shown for the methide anion. It is evident that the calculated equilibrium conformations for the methide and ethide carbanions using the Pople parameters are pyramidal and in fact near tetrahedral. A pyramidal structure for alkyl carbanions is in accord with current thinking in the literature on this question.[11, 12] The only direct determination has been an X-ray diffraction study on the tricyanocarbanion $(CN)_3C^-$,[13] a species where conjugative effects would be expected to favor a planar conformation. Nevertheless, this species was found to be slightly non-planar. Ab initio calculative procedures have predicted both pyramidal[15] and planar conformations[14] for $CH_3^-$, but the latest and best of these calculations predicts a pyramidal near tetrahedral conformation.[15] In so far as our CNDO/2 calculations with the Pople–Segal parameters also indicate near tetrahedral equilibrium conformations for alkyl carbanions, we have approximated the geometries of these species by those of the corresponding hydrocarbons with one hydrogen removed. It may also be seen that the Wiberg parameterization, which had produced reasonable agreement with experimental heats of formation for a number of hydrocarbons and had predicted reasonable equilibrium geometries for hydrocarbons and some derived cations, radicals, and cation radicals,[6] yields a shallow planar minimum for the methide anion. This may detract somewhat from the attractiveness of this parameterization, but firm conclusions in this connection must await more definitive experimental evidence on equilibrium conformations of carbanions.

## ACIDITY OF ALKANES

MO methods which consider all valence electrons allow direct calculation of the energetics of the following transformation.

$$RH \rightarrow R^- + H^+$$

The energy of a proton at infinite separation is zero so the energy of the transformation reduces merely to the difference in energy between anion and hydrocarbon as indicated below.

$$\Delta E = E_{R^-} - E_{RH}$$

$\Delta E$'s calculated for a number of simple alkane species are indicated in Table 2. It is clear that the order of acidities predicted by these calculations is diametrically opposite to that commonly accepted by organic chemists. A number of studies, primarily by Applequist and Dessy[2] have led to the following order of alkane acidities as summarized by Cram:[16] $CH_4 > C_2H_6 >$ methylene hydrogen > methine hydrogen. This ordering has been taken as a reflection of stabilities of the derived carbanions. Successive substitution of alkyl groups for hydrogen is believed to produce destabilization of the carbanions through the presumed electron-donating properties of alkyl groups. It should be noted that the CNDO/2 method has reproduced quite well the relative energetics along a series of alkanes of the carbonium ion-forming reaction shown below,[7]

$$R-H \rightarrow R^+ + H^{\cdot} + e^-$$

and it would probably be somewhat surprising and disillusioning that it should fail so badly for alkane acidities.

There are, however, a number of indications in the literature that alkyl groups can stabilize negative charge as well as positive charge.[17, 18] Schubert and coworkers[17] have determined the effect of *p*-alkyl substituents on the energy of electronic transitions of phenol, anisole, aniline, and N,N-dimethylaniline. These transitions, which have been shown to involve migration of negative charge from the functional group to the aromatic ring,[24] seem to be reduced in energy by *p*- alkyl substitution. This may be interpreted in terms of stabilization of the electron-rich rings in the excited states by the alkyl groups and, therefore, stabilization of negative charge by alkyl groups acting as electron acceptors. These workers have also demonstrated that alkyl groups reduce the energy of transitions in which there is migration of charge from the ring to the substituent and, therefore, as expected alkyl groups also stabilize positive charge acting as electron donors. For both types of transitions, more highly branched alkyl groups seem to produce larger reductions in transition energies. These data were derived in the gas phase and, of course, it should be emphasized that gas phase data are what one wants for correlations with MO calculations. In solution Schubert has observed that the ordering of alkyl group stabilizations may be altered, and he has interpreted this in terms of steric hindrance to solvation. Schubert has concluded that alkyl groups can function either as electron donors or electron acceptors relative to hydrogen depending on the nature of the electron demand on the alkyl group. He believes alkyl groups have a greater "substituent polarizability" than hydrogen and can, therefore, be more responsive to either positive or negative electron demands.

TABLE 2. ENERGIES OF CARBANION FORMATION

| Reaction | $\Delta E$ (a.u.)[a] |
|---|---|
| $CH_4 \rightarrow CH_3^- + H^+$ | 1·0382 |
| $C_2H_6 \rightarrow CH_3CH_2^- + H^+$ | 1·0022 |
| $C_3H_8 \rightarrow CH_3CH_2CH_2^- + H^+$ | 0·9937[b] |
|  | 0·9990[c] |
| $C_3H_8 \rightarrow (CH_3)_2CH^- + H^+$ | 0·9735 |
| $(CH_3)_3CH \rightarrow (CH_3)_3C^- + H^+$ | 0·9496 |
| $(CH_3)_3CH \rightarrow (CH_3)_2CHCH_2^- + H^+$ | 0·9866[b] |
|  | 0·9915[c] |

[a] Wiberg[6, 7] has noted that the values for the CNDO/2 energies of hydrocarbons and their derived cations, radicals, and cation radicals are invariably too large by a factor of about three. It is likely that the same is true for anions and, therefore, for the listed energy differences. Note: 1 a.u. = 627·46 kcal/mole.

[b] Hydrogen lost is *gauche* to the carbon plane.

[c] Hydrogen lost is in the carbon plane.

## ACIDITY OF ALCOHOLS

Quite recently some additional evidence has been reported demonstrating that alkyl groups can stabilize anionic species. This is derived from a study of Brauman and

**Blair[18] on the gas phase acidities of alcohols by ion cyclotron resonance. They have observed the following order of acidities: neopentyl alcohol > t-butyl > isopropyl >** ethyl > methyl > water; and t-butyl ≈ n-pentyl ≈ n-butyl > n-propyl > ethyl. These results are again opposite to the normal inductive ordering derived from solution measurements and indicate the inherent ability of alkyl groups to stabilize negative charge in gas phase species. Encouraged by these results, we applied the CNDO/2 method to calculation of the energetics of the transformation indicated below.

$$ROH \rightarrow RO^- + H^+$$

Energies for this process are shown for water and for a number of alcohols in Table 3. The orderings observed by Brauman and Blair are reproduced except for the position of neopentyl alcohol. Neopentyl alcohol is still considerably more acidic than any of the other primary alcohols listed so that the calculations have definitely captured the experimental trends.

TABLE 3. ENERGIES OF ALKOXIDE ION FORMATION

| Reaction | $\Delta E$ (a.u.)[a] |
|---|---|
| $H_2O \rightarrow OH^- + H^+$ | 0·9085 |
| $CH_3OH \rightarrow CH_3O^- + H^+$ | 0·8994 |
| $C_2H_5OH \rightarrow CH_3CH_2O^- + H^+$ | 0·8956 |
| n-$C_3H_7OH \rightarrow CH_3CH_2CH_2O^- + H^+$ | 0·8936 |
| $CH_3CH_2CH_2CH_2$—$OH \rightarrow CH_3CH_2CH_2CH_2O^- + H^+$ | 0·8930 |
| $CH_3CH_2CH_2CH_2CH_2$—$OH \rightarrow CH_3CH_2CH_2CH_2CH_2O^- + H^+$ | 0·8930 |
| $(CH_3)_2CHOH \rightarrow (CH_3)_2CHO^- + H^+$ | 0·8861 |
| $(CH_3)_3COH \rightarrow (CH_3)_3O^- + H^+$ | 0·8847 |
| $(CH_3)_3CCH_2OH \rightarrow (CH_3)_3CCH_2O^- + H^+$ | 0·8865 |

[a] Same as in Table 2.

## BASICITY OF AMINES

In order to develop more confidence in the calculations, we have also examined the basicities of aliphatic amines by calculating the energetics of the transformation shown below for the series $NH_3$, $MeNH_2$, $Me_2NH$, and $Me_3N$.

$$R_3N + H^+ \rightarrow R_3NH^+$$

The basicities of this series have also been examined in the gas phase by Brauman and Blair[18] by ion cyclotron resonance and by Munson[19] by mass spectrometry, and they are reported to be in the normal inductive order $Me_3N > Me_2NH > MeNH_2 > NH_3$ and, therefore uncomplicated by the steric and solvation effects observed for solution measurements.[23] Our calculations are indicated in Table 4, and quite obviously the order of basicities has been reproduced perfectly.

The successes of the calculations in the alcohol and amine series have led us to speculate that the gas phase acidities of alkanes may, indeed, be in the order predicted by the calculations. If one is to use arguments involving steric hindrance to solvation to explain solvent effects on carbonium ion reactions,[25] one must certainly consider their possible applicability in situations where something like an alkyl carbanion is involved. A possible model for solvation of an alkyl carbanion may be approach of an electrophilic moiety toward the isoelectronic amine. Steric effects for carbanions might be expected to be larger than for the corresponding amines since the carbanion lone pair is certainly more electronegative than the amine lone pair, and a solvation shell would certainly be tighter for it. Brown and coworkers[20] have observed the reaction of trimethylboron with amines. They note that increase in size of the alkyl groups bound to the nitrogen can greatly decrease the stability of the derived amine–trimethylboron complexes. A similar phenomenon for alkyl carbanions can result in destabilization of the anion solvation shell with increasing alkyl group size and complexity. Solvation considerations would then, of course, favor less substituted carbanions and account for the observed order of alkane acidities.

TABLE 4. ENERGIES OF PROTONATION OF SOME ALIPHATIC AMINES

| Reaction | $\Delta E$ (a.u.)[a] |
|---|---|
| $NH_3 + H^+ \rightarrow NH_4^+$ | −0·4701 |
| $CH_3NH_2 + \rightarrow CH_3NH_3^+$ | −0·4883 |
| $(CH_3)_2NH + H^+ \rightarrow (CH_3)_2NH_2^+$ | −0·5022 |
| $(CH_3)_3N + H^+ \rightarrow (CH_3)_3NH^+$ | −0·5134 |

[a] Same as in Table 2.

## DISCUSSION OF CALCULATIONS

We shall now proceed to examine the calculations in more detail to determine electronic features which may have given rise to the orders of stabilizations. It should be noted that Hoffmann[5] in an extended Hückel study of carbonium ion stabilities has observed that greater stabilization of the ion is obtained when the missing H atom is in the plane of the C atom chain, Hoffmann has termed this phenomenon the "trans effect" since the missing hydrogen hole is *trans* to the alkyl chain, and it is observed that this conformation allows for facile delocalization of positive charge from the positive hole to the *trans* alkyl group. This *trans* effect may also be observed using the CNDO/2 method, and it is indicated in Fig. 1 for the n-propyl cation which is illustrated in a tetrahedral rather than a planar conformation. It can be seen that for the *trans* form there is considerable delocalization of positive charge and stabilization relative to the *gauche* form. Also indicated in this Fig. are Wiberg's bond indices $p^2$ between the Me carbon and the electron deficient carbon (the bond index between two atoms is defined as the sum of the squares of the bond orders between the atoms).[7] This bond index is much larger for the *trans* conformation than for the gauche conformation and indicates a substantial "bonding" interaction between the Me carbon and the electron deficient carbon for the *trans* conformation. Moreover, of the total value of 0·14126 for the *trans* 1,3 bond index, 0·11941 derives from the 2p–2p contribution. Effectively, therefore, the Me group is contributing negative charge into the vacant positive hole through what one may truly call a pi conjugative (or hyperconjugative) interaction. On the other hand, for the n-propyl anion no such *trans* effect may occur. This is also indicated in Fig. 1, and the conformation with the hydrogen lost *gauche* to the Me group is now calculated to be more stable than the *trans* conformation. This was also seen in Table 1 where the energetics of formation of the *gauche* n-propyl and isobutyl anions are indicated to be lower than for the corresponding *trans* anions. The difference between *gauche* and *trans* conformations for the anions is less than one-third the difference between *trans* and *gauche* conformations for the cations. There is a slightly larger 1,3 bond index for the *trans* anion but this is probably necessitated more by geometry than be any stabilizing force.

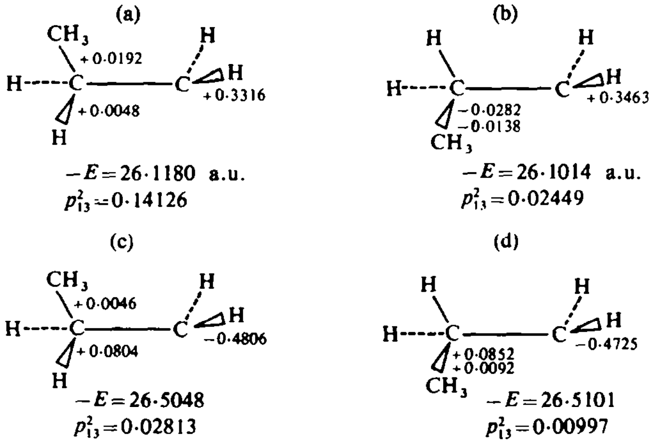

FIG. 1 The propyl cation and anion: (a) cation with hydrogen lost *trans* to methyl group; (b) cation with hydrogen lost *gauche* to methyl group; (c) anion with hydrogen lost *trans* to Me group; (d) anion with hydrogen lost *gauche* to Me group. The numbers next to the structural formulas are total charge densities on carbon; $E$ is the calculated total energy; $p_{13}^2$ is the 1,3 bond index.

Some secondary features of Fig. 1 may seem puzzling and deserve comment. It may be seen that the C-2 positions of anions c and d are actually more positively charged than the C-2 positions of cations a and b. This phenomenon seems to arise through polarization of electron density by the anion carbon acting as a $+I^+$ substituent described by Pople and Gordon.[9] The negative anion carbon seems to repel negative charge onto hydrogen positions, particularly those bound to the C-2 carbon. This is an example of the charge alternation noted by Pople and Gordon, and obviously much more charge (these hydrogens have total charge densities of −0·10 to −0·13) is delocalized onto these hydrogens than onto the C-3 carbon. Indeed, in the anions, all hydrogen positions seem to accommodate a good deal of negative charge. For the propyl cations, particularly in the case of cation b where no conjugative effects are observed, the cation carbon seems to function as a $-I^-$ substituent. Considerable positive charge (about +0·1) is accommodated by the C-2 hydrogen positions and to a smaller extent by the other hydrogen positions. Molecular orbital methods usually predict these charge polarizations, and it is perhaps not too surprising that we encounter them in this work. Hoffmann[5] has calculated by the extended Hückel method formal negative charges on carbons alpha to the cation carbon in alkyl carbonium ions, and Wiberg[7] has calculated by the CNDO/2 method an increase in negative charge density on the ring position next to the cation carbon on formation of the planar cyclopropylcarbinyl cation from methylcyclopropane. The validity of the calculated charge polarizations is also supported by the excellent agreement between experimental and calculated dipole moments achieved by Pople and Gordon using the CNDO/2 method.

It has been noted by Hoffmann[21] and by other workers using both semiempirical[7] and more sophisticated methods[22] that the more substituted a saturated hydrocarbon position, the larger the positive charge density on that position. This trend is also produced by the CNDO/2 method and led us to speculate that our observed order of alkyl carbanion stabilities may arise simply from the ability of the particular carbon position to accommodate negative charge. In Table 5 we have listed the total CNDO/2 charge densities on the anion carbon in both the parent hydrocarbon and in the anion itself. Also listed is the change in charge density on this position in going from the hydrocarbon to the anion. A number of trends are immediately apparent from this Table. First of all, not only do parent hydrocarbon positions become less negatively charged with increasing alkyl substitution, but the derived anion positions also become less negatively charged. Moreover, the increase in negative charge density on anion formation ($\Delta q$) seems to decrease the less negatively charged the original hydrocarbon position. The implication seems to be that the less negative the original position, the greater its ability to accommodate increased negative charge. The accommodation seems to proceed through delocalization of negative charge mainly onto hydrogen positions. The stabilization of negative charge by alkyl groups therefore, contrasts sharply with the stabilization of positive charge. In the latter case there is a direct pi conjugative stabilization, while in the former case, charge stabilization proceeds more through the polarizability of the alkyl group. It is evident that both the $\Delta q$'s and $q$ (anion) in Table 5 correlate well with the $\Delta E$'s in Table 2 and quite evidently the trend in the $\Delta E$'s is determined by the facility of negative charge delocalization in the alkyl carbanion.

TABLE 5. TOTAL CNDO/2 CHARGE DENSITIES ON HYDROCARBON AND ANION POSITIONS

| Anion | $q$ (hydrocarbon) | $q$ (anion) | $\Delta q$ |
|---|---|---|---|
| Methyl | −0·0460 | −0·5325 | −0·4865 |
| Ethyl | −0·0043 | −0·4812 | −0·4769 |
| n-Propyl[a] | −0·0050 | −0·4725 | −0·4675 |
| n-Propyl[b] | −0·0050 | −0·4806 | −0·4756 |
| Isopropyl | +0·0256 | −0·4337 | −0·4593 |
| Isobutyl[a] | −0·0050 | −0·4656 | −0·4606 |
| Isobutyl[b] | −0·0050 | −0·4725 | −0·4675 |
| t-Butyl | +0·0465 | −0·3918 | −0·4383 |

[a] Hydrogen lost in forming anion is *gauche* to plane of carbon chain.

[b] Hydrogen lost in forming anion is in plane of carbon chain.

In proceeding to the series of alcohols, we now note that there is, of course, always only one alkyl group attached to the O atom but this group varies in size and complexity. In Table 6, the charges on oxygen in alcohol and alkoxide ion and the change in charge on alkoxide ion formation are indicated. Clearly the larger or more complex the alkyl group, the larger the negative charge on the oxygen in the alcohol. This was also seen for the hydrocarbons in Table 5 since the n-propane one position had a larger negative charge density than the ethane position. In going to the alkoxide anions, however, an opposite order of negative charge on oxygen and size and complexity of the alkyl group is observed. The smaller less complicated alkyl groups now are associated with larger negative charges on oxygen. Apparently, when there is a large excess of negative charge, the larger alkyl groups can exert greater stabilizations, and this is an interesting example of Schubert's idea[17] of the variation in the stabilizing ability of alkyl groups according to the electron demands placed on them. It is, indeed, possible that it is only in the gas phase that alkyl groups may stabilize negative charge, since in solution the charge may be solvated sufficiently that there is little stabilization demand on the alkyl groups. It is evident again in Table 6 that the $\Delta q$'s and $q$ (alkoxide)'s correlate with $\Delta E$'s in Table 3. Again the dispersal of negative charge is apparently through some alkyl group polarizability mechanism.

TABLE 6. TOTAL CNDO/2 CHARGE DENSITIES ON OXYGEN IN ALCOHOLS AND DERIVED ALKOXIDE ANIONS

| Alcohol | $q$ (alcohol) | $q$ (alkoxide) | $\Delta q$ |
|---|---|---|---|
| Methanol | −0·2473 | −0·6772 | −0·4299 |
| Ethanol | −0·2556 | −0·6681 | −0·4125 |
| n-Propanol | −0·2586 | −0·6677 | −0·4091 |
| Isopropanol | −0·2687 | −0·6625 | −0·3938 |
| n-Butanol | −0·2598 | −0·6674 | −0·4076 |
| t-Butanol | −0·2741 | −0·6589 | −0·3848 |
| n-Pentanol | −0·2592 | −0·6670 | −0·4078 |
| Neopentanol | −0·2591 | −0·6608 | −0·4017 |

## CONCLUSION

The gas phase orders of alcohol acidities and amine basicities are well reproduced by the calculations. For each of these series, the orderings in solution are modified and for the alcohols actually inverted by solvent effects. Our calculations indicate an order of alkane acidities opposite to that observed in solution. It is possible that here again solvent effects invert the trend, and the gas phase order of alkane acidities is that predicted by our calculations. This conclusion, of course, needs experimental verification.

An ability of alkyl groups to stabilize negative charge is indicated. In contrast to carbonium ion stabilization which seems to proceed through a conjugative interaction, the trend in carbanion stabilization seems to involve merely the increase in polarizability of alkyl groups with increasing size and complexity.

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*Note in Proof*—The trends in ΔE's and Δq's for alkanes and alcohols have also been reproduced using the MINDO method of Baird and Dewar. This method is parameterized so that carbon positions become more negative with increasing alkyl substitution. The calculations still indicate, however, that the more substituted positions are better able to accommodate the increased negative charge on anion formation.