Mechanism of Alkyl Group Stabilization of Negative Charge. Analysis of CNDO/2 Calculations of the Acidities of Some Alcohols

Robert B. Hermann

Contribution from Eli Lilly and Company, Indianapolis, Indiana 46206.
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Abstract: A good correlation is obtained between the acidities of a number of alcohols as theoretically calculated and the results of recent experimental gas-phase determination of these acidities by ion cyclotron resonance and pulsed-double-resonance spectroscopy. From an analysis of the theoretical results for alcohols, alkyl groups stabilize the conjugate base by providing a region of peripheral hydrogen atoms for some of the electronic charge to expand onto. Usually, the larger this region, the more charge can be accommodated and the more stable the anion should be.

Ion cyclotron resonance and pulsed-double-resonance studies have shown that the acidities of aliphatic alcohols are reversed in order from that usually found in solution.[1] Results using this technique are in agreement with some earlier work by Munsen[2] for alkyl ammonium ions. From the gas-phase experiments, alkyl groups actually appear to stabilize the negative ion. This is consistent with a model where the polarizability of the alkyl group stabilizes the charge on the heteroatom with an induced dipole. The usual assumption is that the negative charge resides almost entirely on the heteroatom.

CNDO/2 molecular orbital theory has been successful in accounting for the long-range field effects of groups on acidities[3] and in providing an understanding of the effect of the methyl group on the charge distribution in chemical systems, especially conjugated systems.[4] In such molecules, the methyl group—owing to its dipolar character—drives electrons off the adjacent carbon onto others. In this paper an additional effect of alkyl groups in general is examined.

Results

The total CNDO/2 energy differences, ΔE, between the acids and the conjugate bases are presented in column 1[5] of Table I. In some cases a number of conformations of the same molecule were calculated. The results of Table I may be compared to the following experimental order found for the alcohols: neopentyl > *t*-butyl > isopropyl > ethyl > methyl > water and *t*-butyl $\simeq$ *n*-pentyl $\simeq$ *n*-butyl > *n*-propyl > ethyl.

The experimental orders of *t*-butyl > neopentyl and *t*-butyl $\simeq$ *n*-pentyl are the only real sources of disagreement.[6] For comparison with experiment the most stable conformation was used. It would not be justifiable, without varying bond lengths and angles to minimize the energy of each conformation, to weigh the several conformations in approximating the internal energy.

From Table I several rules may be given to predict results of CNDO/2 ΔE calculations: (1) a methyl group on the α carbon contributes 0.002 au toward the stability of the negative ion, (2) a methyl group on the β carbon and *trans* to the CO bond contributes 0.002 au, (3) a methyl group on the β carbon and *gauche* to the CO bond contributes 0.004 au, (4) a methyl group on the γ and/or δ carbon contributes 0.001 au. In the case of the ring compounds, the same carbon may be counted twice since it may be α to the OH group by one route and δ by another.

By taking the parameter $(I + A)/2$ for hydrogen to be -5.03 instead of -7.176,[7] there is no change in the order among the compounds for which experimental data exist. The last column of Table I gives ΔE. Conformational orders are affected among some entries, *e.g.*, the order of *trans* and *gauche* *n*-propyl alcohol is reversed, and neopentyl alcohol is now only 0.0009 au lower than *t*-butyl alcohol. Then, as a general rule, an α-methyl group stabilizes the anion by 0.004 au, a *trans* β-methyl group by 0.002 au, a *gauche* β-methyl group by 0.0025 au, and a γ or δ methyl group by 0.0005 au. Using the value -5.03 eV for the $(I + A)/2$ parameter for hydrogen, the acidity is

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(1) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

(2) M. S. B. Munson, *ibid.*, **87**, 2332 (1965).

(3) R. B. Hermann, *ibid.*, **91**, 3152 (1969).

(4) J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967).

(5) Lewis has recently used the CNDO/2 method to calculate the acidities of a similar series of compounds: T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969).

(6) A possible source of the disagreement may be in the fact that ΔS for the gas-phase reaction is not, in general, zero. Assuming once again only the most stable conformations, *t*-butyl alcohol has three equally stable conformations (the O–H bond is staggered with respect to the three methyl groups in three equal positions) while neopentyl alcohol has only one low-energy conformation for the O–H bond. Because of this difference in degeneracy, the change in entropy associated with the proton ionization of *t*-butyl alcohol will be smaller by the quantity R ln 3 than the change in proton ionization of neopentyl alcohol. There is, therefore, a free energy contribution $\Delta F' = -T(-R \ln 3)$ to the proton ionization in the case of *t*-butyl alcohol, making the calculated energy of the *t*-butyl anion less stable by 0.65 kcal or 0.001 au at room temperature than predicted on the basis of the CNDO/2 results only. The same argument may be applied to the comparison of *t*-butyl alcohol and *n*-pentyl alcohol, making the *n*-pentyl anion relatively more stable. The improvement is in the right direction and is the right order of magnitude, but it is not sufficient to reverse the order of acidities of neopentyl alcohol and *t*-butyl alcohol.

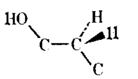
(7) Parameters were originally chosen for CNDO/1 so that the calculated charge densities agreed with results of calculations (limited basis set) on small molecules. In making the comparison to limited basis set calculations, the CNDO ZDO wave function must be transformed to a nonorthogonal basis with a Löwdin transformation. When this is done for CNDO/2 calculations on ethane, however, there is obtained 0.029 for the charge population on hydrogen and -0.086 for carbon, while an LMO calculation [W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966)] gives 0.124 for hydrogen and -0.372 for carbon. Adopting the parameter -5.03 instead of -7.176 for hydrogen, there are obtained for ethane the charge densities above using the optimized bond lengths for CNDO/2: G. A. Segal, *J. Chem. Phys.*, **47**, 1876 (1967).

Table I. CNDO/2 Results for Alcohols

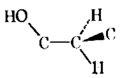
Acid[c]	1 ΔE, au[a] ($E_{\text{acid}} - E_{\text{anion}}$ for α-H = −7.176)	2 Oxygen atom charge density in anion, $q_0(\text{B})$	3 Oxygen atom charge density in acid, $q_0(\text{A})$	4 $q_0(\text{B}) - q_0(\text{A})$ Δq_0	5 V_{B}	6 V_{A}	7 Average charge density on alkyl hydrogens in acid, $q_{\text{H}}(\text{A})$	8 Average charge density on alkyl hydrogens in base, $q_{\text{H}}(\text{B})$	9 Δq_{H}	10 ΔE (α-H = −5.03)
Water[b]	−0.96587	−0.82898	−0.29028	−0.5387	−0.15664	−0.80844	−0.8549	−1.1710	−0.3161	−0.92543
Methanol[b]	−0.90175	−0.68109	−0.24649	−0.4346	−0.08557	−0.80789	−1.0082	−1.1511	−0.1429	−0.86976
Ethanol[b]	−0.89753	−0.67176	−0.25484	−0.4169	−0.07331	−0.81706	−1.0017	−1.0891	−0.0874	−0.86560
n-Propyl alcohol[b] (*trans*)[d]	−0.89542	−0.67055	−0.25850	−0.4120	−0.06856	−0.81961	−1.0037	−1.0802	−0.0765	−0.86320
n-Propyl alcohol (*gauche*)[e]	−0.89345	−0.66785	−0.25551	−0.4123	−0.06847	−0.81639	−1.0053	−1.0697	−0.0644	−0.86265
Isopropyl alcohol[b]	−0.89127	−0.66509	−0.26545	−0.3996	−0.06381	−0.82006	−0.9965	−1.0628	−0.0663	−0.86143
Isopropyl alcohol (*trans*)[f]	−0.89166	−0.66679	−0.25872	−0.4081	−0.06439	−0.81864	−1.0050	−1.0556	−0.0506	−0.86041
Isobutyl alcohol (*gauche*)[g]	−0.88977	−0.66483	−0.25640	−0,4084	−0.06429	−0.81557	−1.0060	−1.0582	−0.0522	−0.86106
n-Butyl alcohol[b]	−0.89459	−0.66904	−0.25897	−0.4100	−0.06650	−0.82073	−1.0042	−1.0522	−0.0480	−0.86216
t-Butyl alcohol[b]	−0.88592	−0.66022	−0.27430	−0.3859	−0.06076	−0.82235	−0.9932	−1.0481	−0.0549	−0.85840
n-Pentyl alcohol[b]	−0.89425	−0.66854	−0.25911	−0.4094	−0.06552	−0.82137	−1.0044	−1.0436	−0.0392	−0.86167
Neopentyl alcohol[b]	−0.88826	−0.66388	−0.25924	−0.4046	−0.05570	−0.81762	−1.0053	−1.0485	−0.0432	−0.85938
Cyclopentanol	−0.88616	−0.65948	−0.26611	−0.3933	−0.05555	−0.82067	−1.0042	−1.0542	−0.0500	−0.85516
Cyclohexanol (ax)	−0.88207	−0.65855	−0.26642	−0.3921	−0.05211	−0.81764	−1.0086	−1.0530	−0.0445	−0.85425
Cyclohexanol (eq)	−0.88597	−0.66191	−0.27101	−0.3909	−0.05313	−0.82325	−1.0071	−1.0485	−0.0415	−0.85539

[a] Atomic unit = 627.71 kcal/mol. [b] These CNDO/2 energies of these structures have recently been computed by Lewis (ref 5). [c] The free energy, ΔF, for the acid–base reaction is correlated here with the total CNDO/2 electronic energy difference, ΔE. In computing E for a given acid or conjugate base, all angles between bonds on C, O, and H were 109° 28′ except in cyclopentane where the carbon skeleton was a regular pentagon. The bond distances used were $r_{\text{CH}} = 1.09$, $r_{\text{OH}} = 0.960$, $r_{\text{CC}} = 1.540$, and $R_{\text{CO}} = 1.423$ Å (see L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 18, Supplement, The Chemical Society, London, 1965, pp S1-S23).

[d]



[e]



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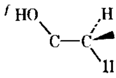

[g]

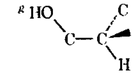

Table II. Acidities of Alcohols from Direct Calculation of Energy of the Negative Charge on the Anion, from Eq 11

	Charge density of acid H q_{H}	Hydrogen atom energy[a] $-E_1 - \Sigma_{\text{A}\neq 1} E_{\text{A}1}$	Energy of electron in field of core[b] $\Sigma_{\text{A}\neq 1}\Delta E_{\text{A}} + \Sigma_{\text{A}\neq\text{B}}\Delta E_{\text{AB}}$	Energy of electron in field of idealized core[b]
CH_3OH	−0.8574	+1.15227	−0.25051	−0.44738
C_2H_5OH	−0.8647	+1.15311	−0.25557	−0.45434
$(CH_3)_2CHOH$	−0.8661	+1.15404	−0.26277	−0.46045
t-BuOH	−0.8675	+1.15477	−0.26885	−0.46537
n-BuOH	−0.8667	+1.15364	−0.25904	−0.46087

[a] Contribution to the proton ionization potential $-\Delta E$ due to the electronic charge in the vicinity of the acid proton. [b] Contribution to the proton ionization potential $-\Delta E$ due to the electronic charge moving to the vicinity of the core.

less conformation dependent and there is more difference between the influence of alkyl substituents on the α and β atoms.

Mechanism of Action of Alkyl Groups. The above results from the original CNDO/2 parameters may be profitably analyzed to determine the mechanism of action of alkyl groups generally.

Schubert, Murphy, and Robins[8] have suggested that alkyl groups can act as apparent electron acceptors by a mechanism of "substituent polarizability." The mechanism was purposely left vague but was meant to include a possible direct polarization of bonding electrons to the substituent and possible internal dispersion force polarization.

It has been suggested that alkyl groups influence acidity by stabilizing alkoxy ions according to the following argument.[1] The process of removing the proton from the acid is first formally regarded as two steps: (1) removing the hydrogen atom, leaving an alkoxy radical and (2) removing the electron from the hydrogen atom and placing it back on the alkoxy radical to form the anion. Since the homolytic bond energies are about equal for all aliphatic alcohols,[9] stabilizing the electron by placing it on the alkoxy radical must be the source of the energy difference.

An analysis of the CNDO/2 results upholds this conclusion and further illustrates the reason for the order of anion stabilities. From the CNDO/2 charge densities of Figure 1, it can be seen how the electronic charge density originally on the acid hydrogen has distributed itself over the remaining atoms in the anion. Less than half of the charge has been deposited on the basic atom and the remainder has distributed itself over the alkyl hydrogens. The carbon skeleton, while somewhat polarized, picks up little charge. Column 4 in Table I shows that the total charge increase on the basic atom correlates with the calculated acidities. Column 9 gives the average increase of charge density per alkyl hydrogen, and indicates that usually the more hydrogen atoms present, the less the charge density increase per hydrogen.

The above observations suggest that the excess charge is stabilized by spreading out over the peripheral atoms. The stabilizing effect is generally greater the larger the number of hydrogens, and the amount of excess charge residing on the oxygen is correspondingly reduced. From the rules deduced above, the proximity of the alkyl group hydrogens to the basic atom also appears to be a factor in the stabilizing effect.

These conclusions may be demonstrated in the following analysis, which shows more quantitatively the source of the stabilization energy. The CNDO/2 energy is first written in terms of atom energies and bond energies. For the alcohol

$$E = \sum^{\mathrm{A}} E_{\mathrm{A}} + \sum_{\mathrm{A}>\mathrm{B}}^{\text{pairs}} E_{\mathrm{AB}} \tag{1}$$

where E_{A} is the energy of atom A and E_{AB} is the energy of the A–B atom pair, which may or may not be a formal chemical bond.

In order to facilitate the comparison of energy terms of the alcohol with its anion, eq 1 is rewritten and the terms are grouped so that the hydrogen atom and its interactions are separated from other atoms and their interactions. The atoms are numbered so that the acid hydrogen atom is number 1.

$$E = E_1 + \sum_{\mathrm{A}>1}^{\mathrm{A}} E_{\mathrm{A}1} + \sum_{\mathrm{A}\neq 1}^{\mathrm{A}} E_{\mathrm{A}} + \sum_{\substack{\mathrm{A}>\mathrm{B}\\ \mathrm{B}\neq 1}}^{\text{pairs}} E_{\mathrm{AB}} \tag{2}$$

where

$$E_{\mathrm{A}} = \sum_{\mu}^{\mathrm{A}} P_{\mu\mu}U_{\mu\mu} + {}^1\!/_2 \sum_{\mu}\sum_{\nu}^{\mathrm{A}} (P_{\mu\mu}P_{\nu\nu} - {}^1\!/_2 P_{\mu\nu}{}^2)\gamma_{\mathrm{AA}} \tag{3}$$

$$\begin{aligned} E_{\mathrm{AB}} = \sum_{\mu}^{\mathrm{A}}\sum_{\nu}^{\mathrm{B}} [2P_{\mu\nu}\beta_{\mathrm{AB}}{}^0 S_{\mu\nu} - {}^1\!/_2 P_{\mu\nu}{}^2\gamma_{\mathrm{AB}}] + {}\\ Z_{\mathrm{A}}Z_{\mathrm{B}}R_{\mathrm{AB}}{}^{-1} - Z_{\mathrm{B}}P_{\mathrm{AA}}\gamma_{\mathrm{AB}} - {}\\ Z_{\mathrm{A}}P_{\mathrm{BB}}\gamma_{\mathrm{BB}} + P_{\mathrm{AA}}P_{\mathrm{BB}}\gamma_{\mathrm{AB}} \end{aligned} \tag{4}$$

The notation is that of Pople and Segal.[10] The quantities $P_{\mu\nu}$ are elements of the charge density–bond order matrix, γ_{AB} is the repulsion energy between an electron on atom A and one on atom B, Z_{A} is the number of valence electrons in the neutral atom, β^0 is a parameter, and $U_{\mu\mu}$ is the local core matrix element, which is in turn a function of an ionization potential.

In the case of the anion, the atoms are numbered as in the alcohol so the subscripts A and B do not take on the value 1. If $\mathbf{P}_{\mu\nu}'$ ($\mu \neq 1, \nu \neq 1$) represents the charge density–bond order matrix of the anion, then the energy of the anion is

$$E' = \sum_{\mathrm{A}\neq 1}^{\mathrm{A}} E_{\mathrm{A}}' + \sum_{\substack{\mathrm{A}>\mathrm{B}\\ \mathrm{B}\neq 1}} E_{\mathrm{AB}}' \tag{5}$$

where

$$\begin{aligned} E_{\mathrm{A}}' = \sum_{\mu}^{\mathrm{A}} P_{\mu\mu}'U_{\mu\mu} + {}^1\!/_2 \sum_{\mu}\sum_{\nu} [P_{\mu\mu}'P_{\nu\nu}' - {}\\ {}^1\!/_2 (P_{\mu\nu}')^2]\gamma_{\mathrm{AA}} \end{aligned} \tag{6}$$

$$\begin{aligned} E_{\mathrm{AB}}' = \sum_{\mu}^{\mathrm{A}}\sum_{\nu}^{\mathrm{B}} [2P_{\mu\nu}'\beta_{\mathrm{AB}}{}^0 S_{\mu\nu} - {}^1\!/_2 (P_{\mu\nu}')^2\gamma_{\mathrm{AB}}] + {}\\ Z_{\mathrm{A}}Z_{\mathrm{B}}R_{\mathrm{AB}}{}^{-1} - Z_{\mathrm{B}}P_{\mathrm{AA}}'\gamma_{\mathrm{AB}} - {}\\ Z_{\mathrm{A}}P_{\mathrm{BB}}'\gamma_{\mathrm{AB}} + P_{\mathrm{AA}}'P_{\mathrm{BB}}'\gamma_{\mathrm{AB}} \end{aligned} \tag{7}$$

The energy of removing the proton is by convention the negative of the total CNDO/2 electronic energy difference ΔE

$$-\Delta E = E' - E \tag{8}$$

The redistribution of electron density when the proton is removed may be written as

$$D_{\mu\nu} = P_{\mu\nu}' - P_{\mu\nu} \tag{9}$$

The elements $D_{\mu\nu}$ represent the loss of density from the proton and the gain in density of the remainder of the molecule.

Since there is the same number of electrons in the base as in the acid, the total difference electron density between the acid and the base is zero, and because of the zero differential overlap approximation this is represented by

$$\sum_{\mu} D_{\mu\mu} = 0 \tag{10}$$

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[8] W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1961).

[9] S. W. Benson and R. Shaw, *Advan. Chem., Ser.*, **No. 75**, 288 (1968).

[10] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

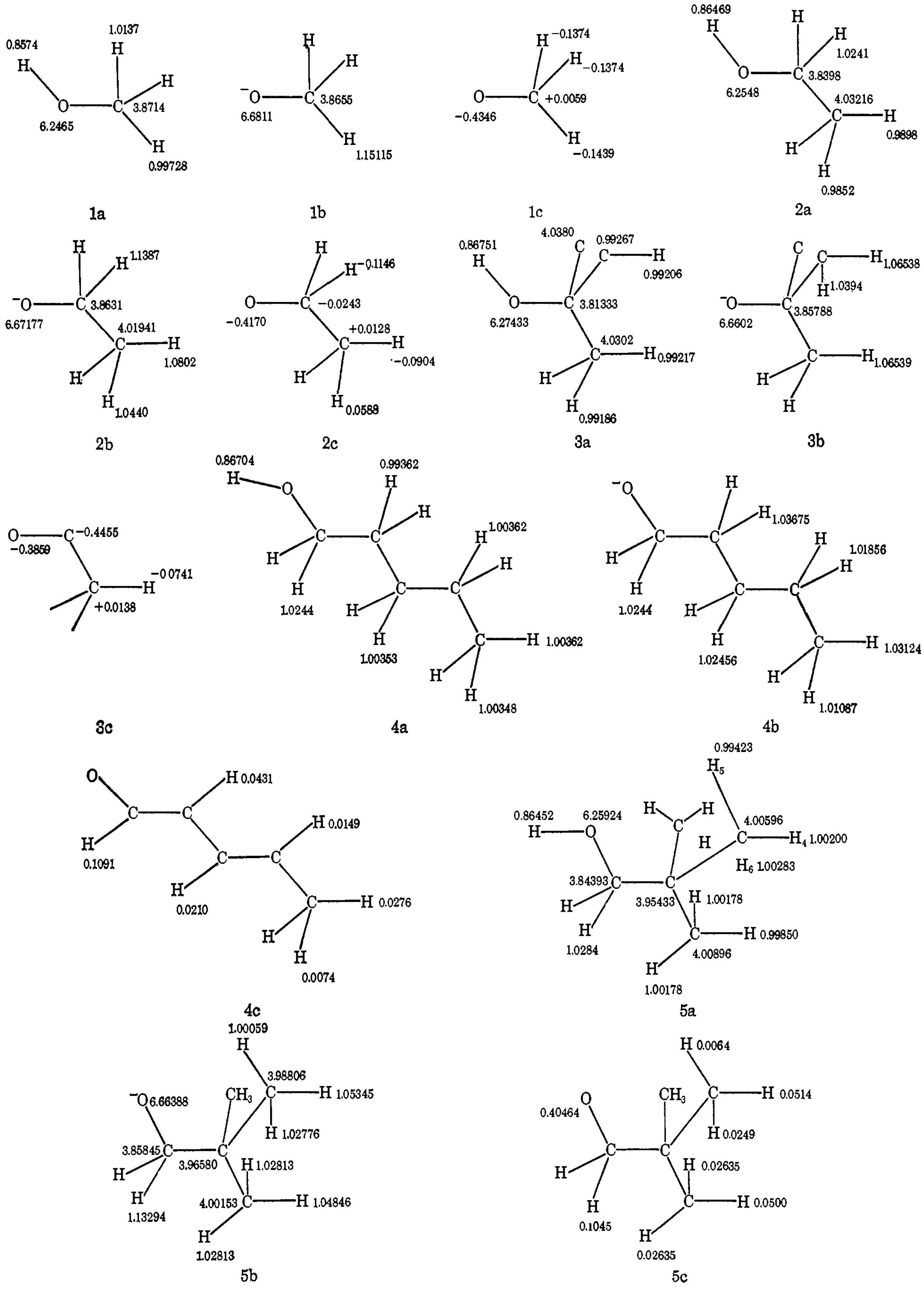

Figure 1. Electron atomic populations for selected alcohols and anions, and the corresponding difference populations: 1, methanol; 2, ethanol; 3, *t*-butyl alcohol; 4, 1-pentanol; 5, neopentyl alcohol. The letters a, b, and c refer to the acid, base, and difference-density structure, respectively.

Since $P_{\mu 1} = 0$, $D_{\mu 1} = -P_{\mu 1}$ for all μ. Then the proton ionization energy $-\Delta E$ can be written exactly in terms of the difference density $D_{\mu\nu}$ and the acid density $P_{\mu\nu}$

$$-\Delta E = -E_1 + -\sum_{A \neq 1}^{A} E_{A1} + \sum_{A \neq 1}^{A} \Delta E_A + \sum_{\substack{A>B \\ B \neq 1}}^{A,B} \Delta E_{AB} \quad (11)$$

where

$$E_1 = P_{11}U_{11} + {}^1/_4 P_{11}{}^2\gamma_{11} \quad (12)$$

$$E_{A1} = \sum_{\mu}^{A}(2P_{\mu 1}\beta_{A1}{}^0 S_{\mu 1} - {}^1/_2 P_{\mu}{}^2\gamma_{A1}] + Z_A R_{A1}{}^{-1} - P_{AA}\gamma_{A1} - Z_A P_{11}\gamma_{A1} + P_{AA}P_{11}\gamma_{A1} \quad (13)$$

$$\Delta E_A = \sum_{\mu}^{A} D_{\mu\mu}U_{\mu\mu} + {}^1/_2 \sum_{\mu}^{A}\sum_{\nu}^{A}[D_{\mu\mu}D_{\nu\nu} - ({}^1/_2 D_{\mu\nu})D_{\mu\nu}]\gamma_{AA} + {}^1/_2 \sum_{\mu}^{A}\sum_{\nu}^{A}(P_{\mu\mu}D_{\nu\nu} + D_{\mu\mu}P_{\nu\nu} - D_{\mu\nu}P_{\mu\nu})\gamma_{AA} \quad (14)$$

$$\Delta E_{AB} = \sum_{\mu}\sum_{\nu}\{2D_{\mu\nu}\beta_{AB}{}^0 S_{\mu\nu} - {}^1/_2[(2P_{\mu\nu})D_{\mu\nu} + D_{\mu\nu}{}^2]\}\gamma_{AB} - (D_{AA}Z_B + D_{BB}Z_A - P_{AA}D_{BB} - P_{BB}D_{AA} - D_{AA}D_{BB})\gamma_{AB} \quad (15)$$

As can be seen from Table II, which lists the results for a representative portion of the series, namely, methanol, ethanol, 2-propanol, *n*-butyl alcohol, *t*-butyl alcohol, and neopentyl alcohol, the charge density q_H of the acid proton is, in general, constant around -0.857 to -0.870. In fact, the first two terms of eq 11, representing the sum of energy contributions in which the hydrogen atom appears, are constant for the series to within about 1 kcal (column 2). Thus, the last two terms of eq 11, representing the energy of the 0.86 electronic charge which has moved onto the remainder of the molecule, are the terms almost entirely responsible for the differences in acidities. Numerical values for the sum of these last two terms are tabulated for several alcohols in column 3. Differences among these values parallel closely differences among total ΔE values for the alcohols considered.

These energies suggest that the stabilities of the bases are indeed due to the energies of the excess charge densities in the presence of the core. The core is here the acid itself, minus the proton and the 0.86 electron in the 1s orbital of the acid proton.

It can also be demonstrated that the precise form of the electron density distribution in the core plays a negligible part in the important energy differences. The core is first replaced by a rather arbitrary one in which the diagonal density matrix elements $P_{\mu\mu}$ are all 1.0 except for the oxygen atom where

$$P_{2s2s} = P_{2p_x2p_x} = P_{2p_y2p_y} = P_{2p_z2p_z} = 1.5$$

and all off-diagonal elements $P_{\mu\nu} = 0$ for $\mu \neq \nu$, so that each atom is electrically neutral. The result of the interaction of the difference charge density $D_{\mu\nu}$ with this new core is shown in column 4 of Table II. While the individual entries run higher than in the true core in column 3, the differences between any two entries are almost the same for the idealized core as for the true core. Therefore, the distribution D_{μ} itself is the important factor in the energy differences, and subtle differences in the electronic structure of different alkyl groups are not.

Discussion

The negative charge on alkoxy ions and presumably other negative ions is better stabilized by large bulky alkyl groups, where the charge density $D_{\mu\mu}$ can be thought of as spreading out under the influence of its own repulsive potential. Methyl groups and especially larger alkyl groups provide a region for the charge density to expand onto. Larger alkoxide ions, because of their larger peripheral region, are generally more stable than smaller ones, and such alcohols are correspondingly more acidic.

This effect of the charge distribution on the energy differences can be understood in terms of the electrostatic potential energy of the distribution. The total repulsive potential energy of the difference density for an anion is

$$V_R = \sum_{\mu \neq 1} \sum_{\nu \neq 1} D_{\mu\mu}\gamma_{\mu\nu}D_{\nu\nu} \quad (16)$$

The energy tends to be higher and the system more unstable if the electron density is concentrated in a smaller region of space, *i.e.*, on fewer hydrogen atoms. A large number of atoms in a molecule indicates more interatom repulsion contribution and less intraatom repulsion contribution. Since the interatom repulsion integrals $\gamma_{\mu\nu}$ ($\mu \neq \nu$) are smaller than any of the intraatom repulsion integrals $\gamma_{\mu\mu}$, and since $\Sigma_{\mu \neq 1}D_{\mu\mu}$ is approximately constant for all anions, there will be less repulsion energy V_R in large molecules.

For the same reason, as the charge spreads out more among the hydrogens of the larger alkyl groups, the oxygen atom can release more of its charge, and thereby contribute to the stability of the system. Hence, a correlation between charge density on the oxygen atom and the acidity is found, which is recorded in Table I, column 4.

From the rules deduced above in the results, it can be seen that hydrogen atoms some distance away from the basic atom are less effective in stabilizing the ion than are the hydrogen atoms of α or β alkyl groups. This is true even to the extent that the calculated acidity of the extended conformation of *n*-pentyl alcohol is less than the calculated acidity of a single conformation of *t*-butyl alcohol, which would not be predicted on the basis of alkyl group molecular weight only. This is probably because the sum of reciprocal distances between the hydrogen atoms is on the average less for a branched alkyl group than for a normal alkyl group (in an extended conformation) of equal size. V_R for a branched alkyl group would then be less than V_R for a normal alkyl group of equal size, and might even be less for a larger normal alkyl group.

Computer Programming. The computer programs were written by the author in Fortran IV for the CDC 6500. For the CNDO/2 calculations, convergence was considered complete when the energy difference between two successive iterations was 0.000001 au.

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