petitive, intramolecular H^+ transfer and Dieckmann cyclization with loss of CH_3OH. The relative amounts of these two termination reactions were strongly dependent on the structure of the initiator anion. Several other minor reactions were observed when $NCCH_2^-$ and $C_3H_5^-$ were used as initiators.

Acknowledgment. We gratefully acknowledge support of this research from the U.S. Army Research Office and the National Science Foundation (equipment grant), discussions with Professor Donald Setser, and efforts by Mike Jones to computer simulate the oligomerization data using $C_3H_5^-$ as the initiator anion.

Registry No. $H_2C{=}CHCO_2CH_3$, 96-33-3; F_3C^-, 54128-17-5; $C_3H_5^-$, 1724-46-5; $NCCH_2^-$, 21438-99-3.

Gas-Phase Acidity of Aliphatic Alcohols

Geneviève Boand, Raymond Houriet, and Tino Gäumann*

Contribution from the Institute of Physical Chemistry, Federal Institute of Technology, CH-1015 Lausanne, Switzerland. *Received July 26, 1982*

Abstract: The gas-phase acidities of aliphatic alcohols containing up to nine carbon atoms have been determined by the method of dissociation of proton-bound dimers. Alkyl substituent effects on acidity are discussed in terms of dipolar, polarizability, and hyperconjugation effects. The latter seems to account for the unexpected higher acidity observed for secondary alcohols with respect to the isomeric tertiary alcohols. The influence of through-space dipolar interactions is involved to account for the increasing acidity of the higher linear homologues.

Introduction

The dissociation of proton-bound dimer ions results in the formation of two products according to reaction 1. It has been

$$A_1HA_2^- \xrightarrow{k_1} A_1^- + A_2H \qquad (1a)$$

$$A_1HA_2^- \xrightarrow{k_2} A_2^- + A_1H \qquad (1b)$$

shown[1] that thermodynamic properties related to the acidities of A_1H and A_2H can be obtained from the relative intensities of A_1^- and A_2^- according to

$$\ln I(A_1^-)/I(A_2^-) = \ln k_1/k_2 = \Delta(\Delta G^\circ_{ac})/RT \qquad (2)$$

where $I(A_1^-)$ stands for the measured intensity of A_1^- and $\Delta(\Delta G^\circ_{ac})$ is the difference in gas-phase acidities between A_1H and A_2H, ΔG°_{ac} being defined as the change in free energy for the heterolytic cleavage reaction (3). Recently, there has been a

$$AH \rightarrow A^- + H^+ \qquad (3)$$

growing interest in the determination of molecular properties in isolated systems, and information on gas-phase basicities and acidities has become available, mostly from measurements of proton-transfer equilibria either in ion cyclotron resonance (ICR) or high-pressure mass spectrometric experiments (HPMS; see ref 2 for a recent review). The effects of alkyl groups on acidity have been considered in terms of inductive and polarization substituent effects.[3,4] It is now established that the stabilization of anions by alkyl substituents is due mostly to the role played by polarization forces between the charged center and the alkyl group. Destabilizing inductive effects operate at longer molecular distances and thus influence the stability of anions of a lesser extent. The possible role played by resonance effects such as hyperconjugation has also been considered in order to explain stabilization and isotope effects in anions.[5] However, some results[6] indicate that the effect of methyl groups on acidity seems to be difficult to predict also because there are relatively few data available on the acidic properties in the gas phase as compared to known basic properties.

In the course of recent studies of the reactions of alkoxide anions[7] we became interested in the acidities of aliphatic alcohols. We have applied the method of dissociation of proton-bound dimers to the determination of their relative acidities. The method of dissociation of proton-bound dimers was originally developed by Cooks and collaborators (see literature cited in ref 1), and it can represent a useful alternative to the ICR and HPMS methods. The method is based on the possibility for sampling decomposition products in a well-defined time domain of metastable decays given by the experimental parameters of a double-sector mass spectrometer operated in the MIKES mode.[8] It is assumed that the relative intensities of the products of metastable unimolecular decompositions can be directly related to their respective reaction rate constants of formation as represented in eq 2. Actually, this is based on the assumption that both rate constants k_1 and k_2 behave in an identical manner as a function of the internal energy in the system (see ref 1). Given the narrow time domain (hence corresponding to a narrow energy domain) sampled by the MIKES experiment and considering the similarities between the bonds being broken in the dissociation of proton-bound dimers, the above assumption can certainly be justified in these systems. However, competitive rearrangements and/or dissociation processes may alter the quantitation of the results: this has been reported in ref 1 for cases involving aliphatic ketones. The method of dissociation of proton-bound dimers can be the method of choice to study cases in which steady pressures required for equilibrium measurements

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(1) McLuckey, S. A.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1313.

(2) "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(3) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.

(4) (a) Taft, R. W.; Taagepera, M.; Abboud, J. L. M.; Wolf, J. F.; DeFrees, D. J.; Hehre, W. J.; Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765. (b) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *Ibid.* **1979**, *101*, 6046.

(5) DeFrees, D. J.; Bartmess, J. E.; Kim, J. K.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 6451.

(6) For a recent review, see: Bartmess, J. E.; McIver, R. T., Jr., in ref 2, Chapter 11.

(7) Boand, G.; Houriet, R.; Gäumann, T. "Lecture Notes in Chemistry", Hartmann, H., Wanczek, K. P., Eds.; Springer-Verlag: New York, 1982; Vol. 31.

(8) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, R. G. "Metastable Ions"; Elsevier: Amsterdam, The Netherlands, 1973.

0002-7863/83/1505-2203$01.50/0

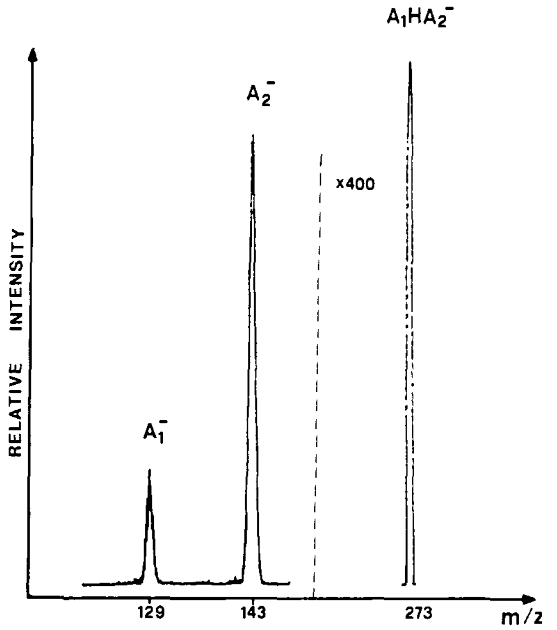


Figure 1. MIKE spectrum of the proton-bound dimer anion formed from 1-octanol (A_1H) and 1-nonanol (A_2H).

are difficult to obtain or when dealing with compounds containing a high level of impurities.

Experimental Section

The MIKE spectra[8] were determined on a double-sector mass spectrometer (ZAB-2F) of reverse geometry equipped with a high-pressure chemical ionization (CI) source. We used binary mixtures of alcohols in a 1:1 ratio at an approximate pressure of 10^{-2} torr, and the reactant gas N_2O was added up to pressures of about 1 torr. Source temperature was kept constant at 180 °C. The alcohol samples were obtained from commercial sources (Fluka) and used as received. The following isotopically labeled samples were synthesized by standard methods and purified by preparative gas chromatography before use: 2-isopropanol-*1,1,1-d*$_3$; 2-propanol-*1,1,1,3,3,3-d*$_6$; 2-butanol-*1,1,1,3,3-d*$_5$; 2-butanol-*1,1,1-d*$_3$.

In the course of the present investigation we found that the method of dissociation of proton-bound dimers is better suited to our problem than the trapped-ion ICR method.[9] In the latter, we found it difficult to trap negative ions over extended period of time (approximately 1 s) without appreciable ion loss (over 50%) even with a continuous ejection of electrons.

Results

An example of the MIKE spectrum of $A_1HA_2^-$ obtained in the 1-octanol (A_1H)/1-nonanol (A_2H) system is shown in Figure 1. It is seen that the only dissociation products are A_1^- and A_2^-, with intensities of about 0.4% of that of the parent peak $A_1HA_2^-$. The quantitation of the experimental data was performed in an analogous manner to that described in ref 1; peak areas were taken as a measure of ion intensities. We did not apply any correction for the possible discrimination effect from the electron multiplier detector.[10] In order to correlate the experimental values of ln $I(A_1^-)/I(A_2^-)$ = ln k_1/k_2 with $\Delta(\Delta G°_{ac})$ (see eq 2), we used a set of eight alcohols of known acidities. From the values of ln k_1/k_2 determined for each pair of acids, we constructed a scale of values for ln k_1/k_2 in which A_2H = 1-propanol is taken as a reference acid. By plotting this scale against the gas-phase acidity $\Delta G°_{ac}$, we obtained the calibration line represented in Figure 2.

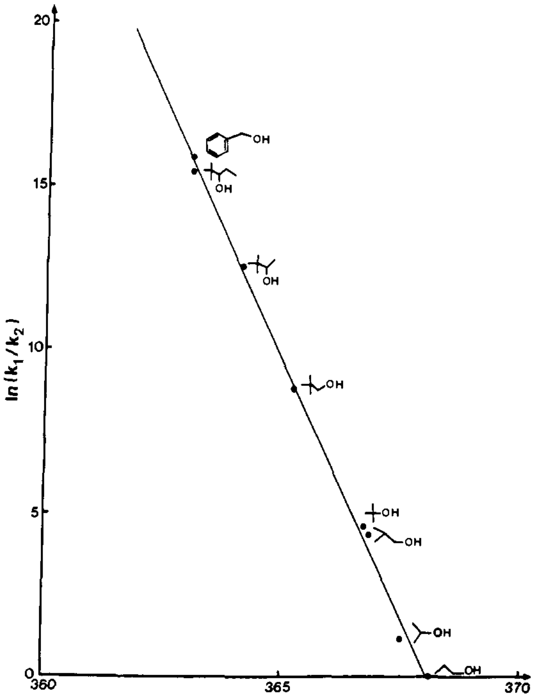
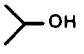
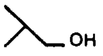
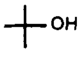
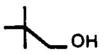
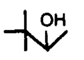
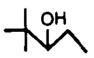
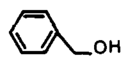


Figure 2. Calibration line, ln k_1/k_2 vs. gas-phase acidity. All rates are related to A_2H = 1-propanol (see text).

Table I. Reference Compounds Used for Establishing the Correlation of Figure 2. Values of ln k_1/k_2 All Refer to A_2H = 1-Propanol. Values for $\Delta G°_{ac}$ Are Taken from Ref 2[a]

	$\Delta G°_{ac}$	ln(k_1/k_2)
	368.1	0
	367.5	1.1
	366.8	4.3
	366.7	4.6
	365.2	8.8
	364.1	12.5
	363.0	15.4
	363.0	15.9

[a] ln $(k_1/k_2) = (1141 \pm 25) - (3.10 \pm 0.07)\Delta G°_{ac}$.

Least-squares treatment yielded the relationship ln $k_1/k_2 = (1141 \pm 25) - (3.10 \pm 0.07)\Delta G°_{ac}$ ($\Delta G°_{ac}$ in kcal/mol). The experimental values and literature values for the acidities of the reference compounds are given in Table I. Notice that the quantity ln k_1/k_2 has been plotted vs. the free-energy change $\Delta G°_{ac}$ rather than against the enthalpy change as reported in ref 1. Although entropy changes are negligible in the systems presently studied,[11] in many

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[9] McMahon, T. B.; Beauchamp, J. L. *Rev. Sci. Instrum.* **1972**, *43*, 509.

[10] In order to check the response of the electron multiplier detector as a function of ion kinetic energy, the MIKE spectra of $A_1HA_2^-$ dimers were recorded at different accelerating source voltages. We found that the $\Delta G°_{ac}$ values derived from experiments conducted at 8 and 6 kV were identical within the experimental error. See also: (a) La Lau, C. "Topics in Organic Mass Spectrometry"; Burlingame, A. L., Ed.; Wiley-Interscience: New York, 1970. (b) Cooks, R. G. "High Performance Mass Spectrometry: Chemical Applications"; Gross, M. L., Ed.; American Chemical Society: Washington, D.C., 1978; ACS Symp. Ser. 70.

[11] Cumming, J. B.; Kebarle, P. *Can J. Chem.* **1978**, *56*, 1.

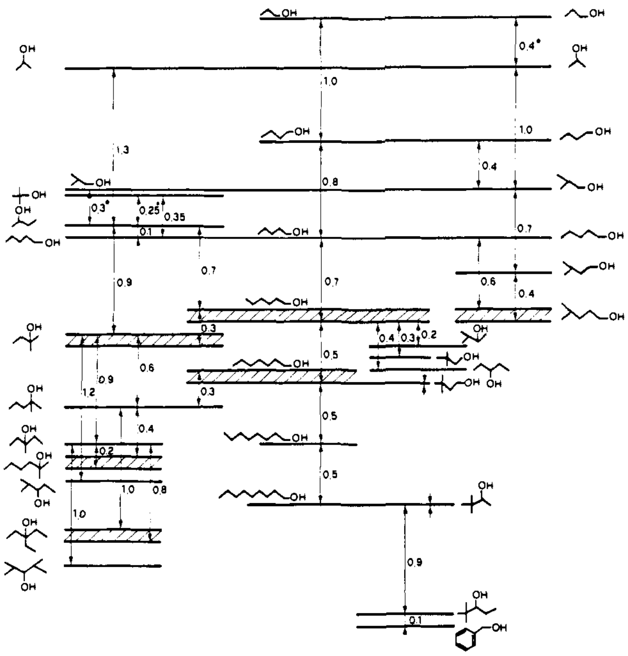


Figure 3. Multiple overlapping sequence used to determine relative acidities. Experiments performed with the different pairs of alcohols are indicated by the arrows. The asterisks designate values obtained with samples of D-labeled alcohols (see text).

cases significant entropic corrections have to be estimated by considering the rotational symmetry numbers of reactant and products (see also ref 2, chapters 9–11).

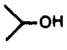
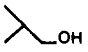
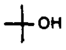
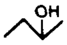
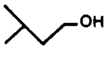
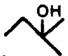
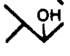
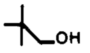
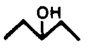
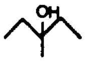
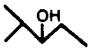
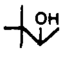
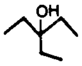
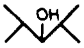
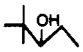
Figure 3 illustrates the results obtained with all binary alcohol mixtures studied. Experimental values of ln k_1/k_2 were converted into $\Delta(\Delta G)$ values according to the calibration line of Figure 2. For a given alcohol, multiple determinations show that the reproducibility on the acidity value is ±0.1 kcal/mol as indicated by the shaded area of Figure 3. The resulting acidity data for all compounds investigated are summarized in Table II.

For establishing directly the relative acidities of alcohol isomers (Figure 3) partially D-labeled molecules were used (see experimental part). Possible secondary isotope effects on acidity were evaluated by using d_0-, d_3-, and d_6-labeled samples of 2-propanol. It was found that deuteration in the β-position enhanced acidity with values of $\Delta(\Delta G)$ equal to −0.02 kcal/mol for the d_3/d_0 pair, −0.03 for d_6/d_3, and −0.08 for d_6/d_0. Thus this secondary isotope effect amounts to an average of about 10 cal/mol per C–D bond. In view of this small value, we applied no corrections to the values of ln k_1/k_2 in the deuterated isomers studied.

Discussion

In order to visualize the effects of substitution on the acidities of alcohols, the acidity differences are reported together with the structures of the neutrals in Figure 4. Inspection of the figure discloses substituent effects of methyl groups introduced at various positions in the alcohol molecules. It is seen that methyl groups stabilize the alkoxide anions with an efficiency depending upon the site of substitution. The effect is largest when the methyl is in the α-position with respect to the functional group, but it is not additive since its magntitude falls off rapidly when going from primary (3.1 kcal/mol) to secondary (1.8 kcal/mol) to tertiary (1.1 kcal/mol) structures. We can observe that this effect is qualitatively similar to the effect on the gas-phase basicity of alkylamines where respective values of 3.0, 2.3, and 1.9 kcal/mol have been found.[12] On the other hand, when methyl substitution occurs on a β-position, it shows a constant value (1.4 kcal/mol) in primary alcohols in contrast with the effect on the basicities of amines where values of 1.4, 1.0, and 0.7 kcal/mol are found for the relevant homologues.[12] These differences indicate that effects other than polar and polarization interactions may contribute to the acidity of alcohols (vide infra). The effect of methyl substitution at the β-positions shows a slightly decreasing value in secondary and tertiary alcohols. Positional effect can be visualized by considering substitution by a methyl group in 1-propanol: it is seen (Figure 4) that stabilization by 1.8, 1.4, and 1.0 kcal/mol occurs when the first methyl group is introduced respectively in the α-, β-, and γ-positions with respect to the

Table II. Acidity Data for Alcohols. Values of ln k_1/k_2 Refer to A_2H = 1-Propanol. ΔG°_{ac} in kcal/mol

	$\ln(k_1/k_2)$	ΔG°_{ac}
	0	368.1
	1.1	367.7
	3.1	367.1
	4.3	366.7
	4.6	366.6
	5.3	366.3
	5.8	366.2
	6.9	365.9
	7.7	365.6
	7.8	365.5
	8.1	365.4
	8.1	365.4
	8.8	365.2
	8.8	365.2
	9.4	365.0
	9.4	365.0
	10.3	364.8
	10.9	364.6
	11.0	364.5
	11.6	364.3
	11.9	364.2
	12.5	364.0
	12.5	364.0
	13.4	363.7
	13.8	363.6
	15.4	363.1
	15.9	363.0

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(12) Aue, D. H.; Bowers, M. T., in ref 2, Chapter 9, Table I.

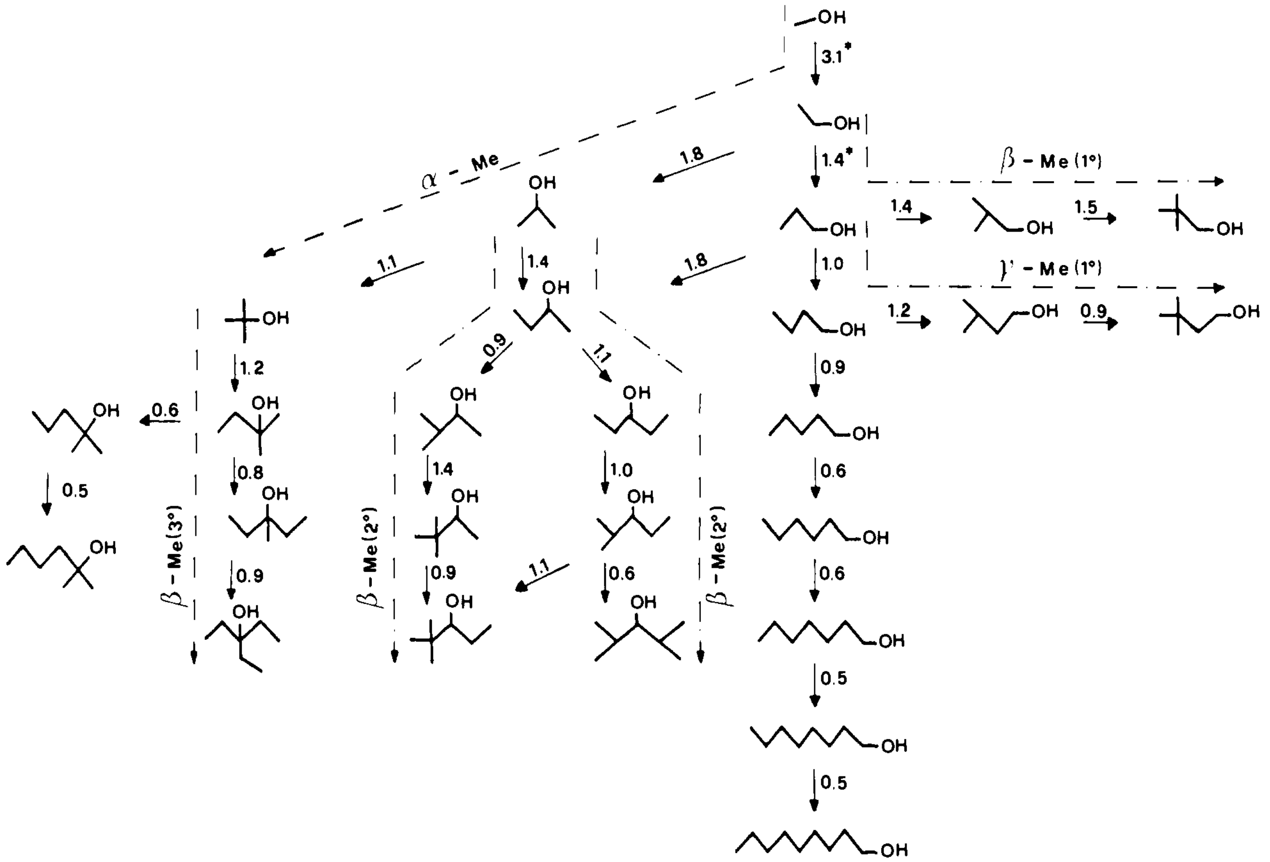

Figure 4. Substituent effects on the acidities of alcohols. The values of $\Delta(\Delta G^\circ_{ac})$ are taken from Table II except for those labeled with an asterisk, taken from ref 2.

hydroxyl group.

An interesting consequence of methyl substituent effect is to be found in 2-butanol, which is seen to be more acidic than 2-methyl-2-propanol by 0.3 kcal/mol. The weaker acidity of tertiary alcohols relative to the secondary isomers seems also to prevail for the pentyl, hexyl, and heptyl homologues, although the isomers studied in the latter cases also present structural differences in their hydrocarbon parts. In terms of substituent effects, the enhanced acidity of secondary alcohols relative to tertiary isomers reflects the larger stabilizing effect of a methyl group in the β-position relative to the α-position in secondary alcohols. This observation supports the possible role played by hyperconjugative stabilization in anions as proposed by DeFrees et al.[5] In the case of alkoxide anions, hyperconjugation may be described in terms of structures of the form

$$X_2HC{-}O^- \leftrightarrow X_2C{=}O + H^-$$

In the present systems, the role played by H hyperconjugation seems to account for the constant substituent effect of β-methyl groups in primary alcohols. It also appears to be a plausible reason for explaining the relatively low acidity of tertiary alcohols. The present results also indicate that H hyperconjugation in alkoxide anions prevails upon hyperconjugation by methyl groups.

Figure 4 reveals that the methyl group substituent effect decreases as the alkyl chain length is increased. However, this does not lead to a rapid leveling of acidities as would be anticipated from the ion-induced dipole potential, which falls off rapidly (r^{-4}) with distance r. The $\Delta(\Delta G^\circ_{ac})$ decreases slowly and seems to reach a constant value (0.5 kcal/mol) beyond 1-heptanol. This behavior is qualitatively similar to the effect of increasing chain length on the basicity of *n*-alkylamines,[12] but in the latter case, the constant increment in basicity, ΔGB, appears to be of only 0.2 kcal/mol. The latter result has been interpreted[12] as resulting from a coiling of the chain to bring the polarizable alkyl group in the proximity of the charged center. The present study suggests that this long-distance effect of the alkyl chain is more efficient at stabilizing negatively charged species. Through-space interactions can be rationalized in terms involving ion–dipole and ion-induced dipole potentials. In first approximation, the latter term can contribute equally at stabilizing both cations and anions. The ion–dipole interaction is also likely to contribute since it can operate at long distances (r^{-2} dependence). Moreover, ion–dipole interactions discriminate with respect to the sign of the charged center, which may cause the experimental differences in $\Delta(\Delta G^\circ_{ac})$, 0.5 kcal/mol, and ΔGB, 0.2 kcal/mol, cited above. We tentatively suggest that long-range alkyl substituent effects result both from polarization terms and from the interaction of the charge with bond dipole moments in the alkyl group. The enhanced stabilization of anions with respect to protonated amines containing the same alkyl group would thus indicate that the bond polarity in C–H involves partial negative charge on the carbon atom and partial positive charge on the hydrogen atom. This is in accordance with the electronegativity values for the carbon and hydrogen atoms, but a more elaborate description of these effects is beyond the scope of the present work.[13]

Registry No. Benzenemethanol, 100-51-6; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-methyl-1-propanol, 78-83-1; 2-methyl-2-propanol, 75-65-0; 2-butanol, 78-92-2; 1-pentanol, 71-41-0; 3-methyl-1-butanol, 123-51-3; 1-hexanol, 111-27-3; 4-methyl-1-pentanol, 626-89-1; 2-methyl-2-butanol, 75-85-4; 3-methyl-2-butanol, 598-75-4; 2,2-dimethyl-1-propanol, 75-84-3; 3-pentanol, 584-02-1; 1-heptanol, 111-70-6; 3,3-dimethyl-1-butanol, 624-95-3; 2-methyl-2-pentanol, 590-36-3; 3-methyl-3-pentanol, 77-74-7; 1-octanol, 111-87-5; 2-methyl-2-hexanol, 625-23-0; 1-nonanol, 143-08-8; 3,3-dimethyl-2-butanol, 464-07-3; 3-ethyl-3-pentanol, 597-49-9; 2-methyl-3-pentanol, 565-67-3; 2,4-dimethyl-3-pentanol, 600-36-2; 2,2-dimethyl-3-pentanol, 3970-62-5; propan-2-ol-*1,1,1*-d_3, 84809-71-2; propan-2-ol-*1,1,1,3,3,3*-d_6, 3976-29-2; butan-2-ol-*1,1,1,3,3*-d_5, 10307-14-9; butan-2-ol-*1,1,1*-d_3, 53716-61-3.

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(13) For a detailed discussion, see for instance: "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; ACS Monograph 167, Van Nostrand: New York, 1970.