interaction between the BF_4^- and the trityl cation.[28] The broad peak for $R^+BF_4^-$ is consistent with the BF_4^- being in an asymmetric environment with broadening resulting from increased B–F coupling and quadrupole relaxation by boron.[24a] Complete line-shape analysis shows that the broadening cannot be due to exchange of fluorine between ^{11}B and ^{10}B. Ion pairing alone might be sufficient to account for the broadening; however, the single broad peak observed in the mixture of trityl and Pr_4N^+ salts suggests that more extensive aggregation may exist. Thus, the BF_4^- is in a time-averaged environment (only one peak) but is nevertheless as broad as in the absence of Pr_4N^+. In a rapid time average, the peak would be of weighted average width (4.5 Hz). The broadening is probably not due to an intermediate exchange rate, since the peak shape remained essentially unchanged when the temperature was lowered by 40°. The simplest explanation of these results is that the Pr_4N^+ salt has been incorporated into the aggregate. Thus, we believe that the ^{19}F nmr results support our hypothesis of association.

The measured "activation energy" of 6.5 kcal/mol is a composite quantity, being the sum of E_a and $\Delta H°$ for the aggregation equilibria. It is, thus, difficult to assign any simple interpretation to it, although it is rather similar to some values measured previously.[5]

The apparently faster rate of reaction 2 in MeCN compared to water may be the result of a number of factors. Ritchie[6] has stressed the importance of solvent reorganization contributions to free energies of activation. In a solvent such as MeCN which is less structured than water,[29] such reorganization effects may well be smaller. In particular, the nucleophile, water, is not the solvent in this case and reaction with it need not cause disruption of any "iceberg-like" structure. Studies by Winstein[30] suggest that nucleophilic contributions from MeCN itself are unimportant. Because the ether peak is not appreciably broadened, reversible reaction of carbonium ions with ether to produce oxonium ions cannot be an important process under our conditions. In the absence of water, any exchange between cation and carbinol is slow.

Although there are difficulties in interpreting this work, it nevertheless provides considerable insight into the behavior of carbonium ions.[31] Furthermore, the low-order dependence on cation provides evidence of aggregation for ions of this type in MeCN. Finally, the rate constant itself provides a complement to those measured for reactions in more stable systems.

Acknowledgment. We thank Dr. T. M. Cole for a preliminary gift of triphenylcarbinol-d_9. We are pleased to acknowledge support from the National Science Foundation (GP 6736, GP 10621) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (2917-A4).

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[28] In addition, Taft has observed that chemical shifts in the cationic moiety of trityl salts in MeCN are dependent upon the anion employed. R. W. Taft, personal communication.

[29] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969), and references therein.

[30] A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 5010 (1964).

[31] H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 809 (1967), measured the rate of reaction of methyl oxocarbonium ion with water, but his result is not readily compared with ours.

Gas-Phase Acidities of Alcohols

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Abstract: Relative acidities in a series of aliphatic alcohols have been determined by ion cyclotron resonance spectroscopy. The order of acidities is $(CH_3)_3CCH_2OH > (CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH > H_2O$ and $(CH_3)_3COH \approx n\text{-}C_5H_{11}OH \approx n\text{-}C_4H_9OH > n\text{-}C_3H_7OH > CH_3CH_2OH$. Phenol was found to be considerably more acidic than any of the alcohols; toluene has an acidity between that of methanol and ethanol.

Structure and reactivity relationships remain as one of the bases of physical organic chemistry. Interpretation of both rates and equilibria in terms of molecular structure permits us to explain relative reactivities as well as to predict the behavior of yet unknown compounds. Acid dissociation lies at the heart of many of these correlations for two reasons. First, acid dissociation is relatively easy to measure, and second, the proton remains a constant element in comparing a wide variety of acids. Thus, both the Hammett[2] and Branch and Calvin[3] techniques make use of acidities. It is these methods which allow us to put structure–reactivity relationships on a quantitative basis and evaluate, for example, inductive effects.

These relationships presumably deal with the intrinsic behavior of the molecules of interest. Nevertheless, it is clear that other effects may be of great importance. That this is so can be seen from examination of many phenomena in various solvents. Thus, ionization potentials, relative acidities, etc., can be changed markedly by change of solvent or removal to the gas phase.[4] The relative acidities of alcohols and hydrocarbons in various solvents serve as an example of this, although many more exist. That the solvent may play

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

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.

[3] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1941.

[4] For some interesting comments see C. D. Ritchie and R. Uschold, *J. Amer. Chem. Soc.*, **90**, 2821 (1968).

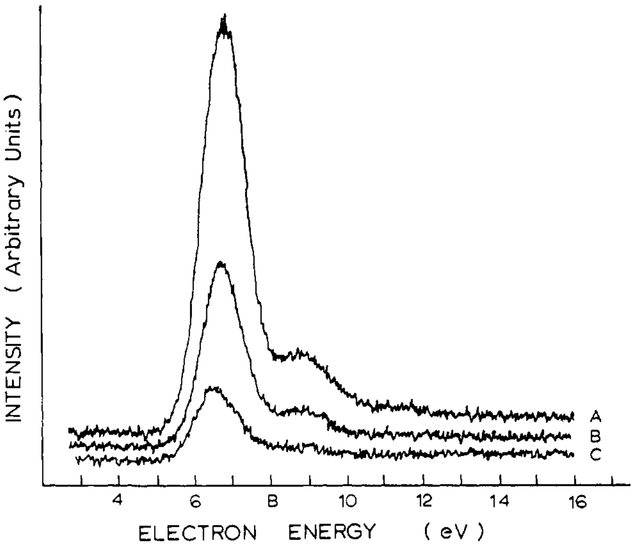

Figure 1. Ion intensities of $C_2H_5O^-$ (curve A), CH_3O^- (curve B), and OH^- (curve C) *vs.* electron energy in a mixture of ethanol, methanol, and water ($\sim 10^{-6}$ Torr). These plots indicate that all the negative ions are coupled chemically to the initially formed H^- from water. (Electron energy scale, uncorrected.)

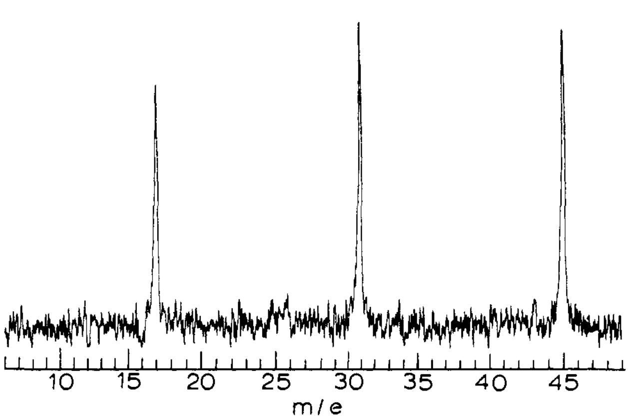

Figure 2. Negative ions present in a mixture of water, methanol, and ethanol. Total pressure, $\sim 10^{-5}$ Torr. This spectrum was obtained by using an electron energy modulation scheme.

an important, if not overwhelming, role is particularly obvious in the case of acidities, since the energy required to dissociate even strong acids in the gas phase is prohibitively high.[5]

It is therefore clearly desirable to know something about gas-phase acidities in order to correlate structure and reactivity as well as to evaluate solvent effects. While it is possible in principle to evaluate gas-phase acidities by a thermodynamic cycle, the relevant thermodynamic quantities are not available for most molecules. In particular, electron affinities of radicals are only known for a very small number of species. Consequently, this method cannot be generally used. As far as direct measurements are concerned, practically none exist. Little information is available for negative ions in the gas phase; even less is known regarding proton transfer to negative ions.

With the recent development of ion cyclotron resonance (icr) and double resonance spectroscopy, it has become possible to study ionic gas-phase reactions conveniently.[6] In this paper we report, in detail, on our studies[7] of alcohol acidities by icr spectroscopy. Gas-phase proton transfer reactions of type 1 involving simple aliphatic alcohols and their corresponding anions were examined. Both the forward and reverse reactions were probed, and the predominant direction of proton transfer was determined.

$$\mathrm{ROH} + \mathrm{R'O^-} \rightleftharpoons \mathrm{RO^-} + \mathrm{R'OH} \qquad (1)$$

Results

Generation of Ions. Single Resonance Spectra. In the icr spectrometer, ions are generated by an electron beam in the source region of the icr cell and are drifted into the analyzer region where they are detected.[8] Alkoxide ions were not readily generated directly from alcohols. Therefore, water was added to the alcohols to serve as a primary source of negative ions which subsequently reacted with alcohols by proton transfer to yield alkoxide ions. The principle primary negative ion formed from electron interaction with water is H^- (at 6.5 eV) by the well-known[9] dissociative resonance capture reaction, eq 2. In addition, the rapid reaction 3 is known[10] to occur with the unusually large cross section of 160 Å^2. Since reaction 4 occurs,[11,12] it is probable that reaction 5 is also an important one for the

$$\mathrm{H_2O} + e^- \longrightarrow \mathrm{H^-} + \mathrm{OH}\cdot \qquad (2)$$

$$\mathrm{H^-} + \mathrm{H_2O} \longrightarrow \mathrm{OH^-} + \mathrm{H_2} \qquad (3)$$

$$\mathrm{OH^-} + \mathrm{ROH} \longrightarrow \mathrm{RO^-} + \mathrm{H_2O} \qquad (4)$$

$$\mathrm{H^-} + \mathrm{ROH} \longrightarrow \mathrm{RO^-} + \mathrm{H_2} \qquad (5)$$

production of RO^- in a mixture of alcohols and water. Under the conditions of this study, H^- was not observed directly; however, a plot, Figure 1, of ion intensity for HO^-, CH_3O^-, and $C_2H_5O^-$ *vs.* electron energy for a mixture of water, methanol, and ethanol is very similar to the plot obtained at low pressure for H^- from water,[9] and suggests that H^- is the precursor, either directly or indirectly, of all the negative ions studied in this work. However, one cannot easily determine which ion, H^- or OH^-, is more efficient for the production of alkoxide ions from alcohols. A reasonable explanation for the inability to observe H^- directly is that the H^- intensity is depleted by rapid reaction in the source region with water and/or alcohol. Attempts to lower the pressure to observe H^- were unsuccessful; however, an exhaustive investigation was not undertaken.

A typical single resonance spectrum showing the negative ions present in a mixture of H_2O, CH_3OH, and C_2H_5OH at $\sim 10^{-5}$ Torr and an electron energy of 6.5 eV is shown in Figure 2. The major contributions occur at *m/e* 17, 31, and 45 for the M − 1 anions of water, methanol, and ethanol, respectively.

Deuterium labeling showed that it is the hydroxylic proton which is removed from the alcohols and that

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(5) The dissociation energy for HCl in the gas phase is *ca.* 333 kcal/mol endothermic.

(6) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(7) See J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968), for a preliminary report.

(8) (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. I. Brauman and L. K. Blair, *ibid.*, 90, 5636 (1968).

(9) See R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967), and references cited therein.

(10) J. A. D. Stockdale, R. N. Compton, and P. W. Reinhardt, *ibid.*, **184**, 81 (1969).

(11) V. L. von Trepka, *Z. Naturforsch.*, *A*, **18**, 1122 (1968).

(12) D. Vogt and H. Neuert, *Z. Phys.*, **199**, 32 (1967).

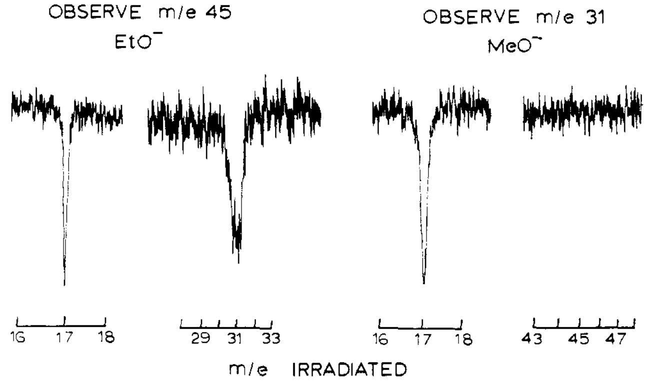

Figure 3. Alkoxide ion double resonance results for a mixture of water, methanol, and ethanol (electron energy, 6.5 eV uncorrected; total pressure, 10^{-5} Torr). The signal intensities of *m/e* 45 ($C_2H_5O^-$) and 31 (CH_3O^-) are displayed as a function of the frequency of the irradiating oscillator. Thus, irradiation of *m/e* 17 (OH^-) causes a decrease in the intensity of both $C_2H_5O^-$ and CH_3O^-. Irradiation of 31 causes a decrease in $C_2H_5O^-$, but irradiation of 45 has no effect on CH_3O^-.

the negative ions are, in fact, alkoxide ions. For example, the single resonance spectrum of a mixture of D_2O and CH_3OD contains peaks only at *m/e* 18 and 31. In addition, single-resonance spectra of mixtures containing $(CD_3)_2CHOH$ show only an *m/e* 65 contribution which indicates that the methyl protons are not being transferred.

Proton Transfer Reactions. Double Resonance Spectra. When ion cyclotron pulsed double resonance studies[13] were made on a mixture of H_2O, CH_3OH, and C_2H_5OH the following results were obtained. Irradiation of *m/e* 17 and 31 resulted in a decrease in the intensity of *m/e* 45. Similarly, irradiation of *m/e* 17 caused a decrease in the intensity of *m/e* 31, Figure 3. In addition, the intensity of *m/e* 17 was not changed when *m/e* 31 and 45 were heated. These double resonance results provide evidence that the following reactions are occurring in the icr cell and that the corresponding reverse reactions are not occurring, at least within the limits of measurability.[14,15] This conclusion

$$HO^- + C_2H_5OH \longrightarrow C_2H_5O^- + H_2O$$
$$HO^- + CH_3OH \longrightarrow CH_3O^- + H_2O$$
$$CH_3O^- + C_2H_5OH \longrightarrow C_2H_5O^- + CH_3OH$$

results from the argument that perturbation of one ion can cause a *decrease* in the concentration of another ion only if the two ions are coupled chemically in the absence of perturbation. That is, a concentration could only be decreased if the perturbation in some way inhibited a reaction which had previously been occurring. Thus, for example, perturbation of kinetic energy of HO^- reduces the abundance of CH_3O^-; consequently HO^- must be reacting with CH_3OH to produce CH_3O^-. The observations taken together result in the following order of ability to transfer a proton: $C_2H_5OH > CH_3OH > H_2O$.

Results for ion cyclotron pulsed double resonance experiments similar to the H_2O, CH_3OH, C_2H_5OH example for a number of alcohol mixtures with water are compiled in Table I. The following generalizations can be made from examination of the tabulated results. (1) In all cases, the reaction $OH^- + ROH \rightarrow RO^- + H_2O$ is observed, and in no case is the reverse reaction observed. (2) In general, for reaction $R'O^- + ROH \rightleftarrows R'OH + RO^-$, proton transfer is preferred in the direction which yields the alkoxide ion with the larger alkyl group. (3) In those cases where the alkyl groups of both alcohols are large and similar in size, proton transfer is observed in both directions.

By the same type of reasoning and interpretation applied to the example, the following order of ability to transfer a proton results: $(CH_3)_3CCH_2OH > (CH_3)_3COH > (CH_3)_2CHOH > C_2H_5OH > CH_3OH > H_2O$ and $(CH_3)_3COH \approx n\text{-}C_5H_{11}OH \approx n\text{-}C_4H_9OH > n\text{-}C_3H_7OH > C_2H_5OH$.

In addition to the alcohols, the double resonance results for toluene have been included in Table I. Initially, it was observed that OH^- abstracted a proton from toluene in a mixture of toluene and water, and that benzyl anion did not abstract a proton from water. By investigation of a number of mixtures of toluene and water with alcohols, it was found that toluene lies between methanol and ethanol in its ability to transfer a proton. (Transfer of the benzylic hydrogen from toluene was inferred from the observation that in mixtures of water and toluene with excess benzene, only $C_7H_7^-$ and no $C_6H_5^-$ was observed.)

In a more elaborate sequence of experiments, phenol was shown to be a substantially stronger acid than any of the alcohols. This was demonstrated by a set of pairwise comparisons which gave the order of proton transfer ability: phenol > hydrogen cyanide > nitromethane > acetone > *t*-butyl alcohol.

In order to check the double resonance technique as a method for ordering the ability to transfer protons, a system was chosen for which the energetics for proton transfer are known. Therefore, the following reaction was investigated for a mixture of dry HCl and HBr. The forward reaction was confirmed by pulsed double

$$HBr + Cl^- \longrightarrow HCl + Br^-$$

resonance, and no reverse reaction was observed. In addition, both of the isotopic proton transfer reactions, $^{79}Br^- + H^{81}Br \rightleftarrows H^{79}Br + {}^{81}Br^-$, and $^{35}Cl^- + H^{37}Cl \rightleftarrows H^{37}Cl + {}^{35}Cl^-$ were also observed.

Discussion

Acidities from Proton Transfers. An ideal approach to the determination of gas-phase acidities would be to measure the equilibrium concentrations of ions and neutrals for a general system $HA + B^- = HB + A^-$. However, with present mass spectrometers, it is experimentally difficult to trap ions for sufficient time for them to relax both thermally and chemically. Nevertheless, considerable success has been met in obtaining "thermochemical" quantities such as proton affinities of neutrals and heats of formation of ions under non-

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(13) See ref 6 and 8c for a discussion of the double resonance technique. Basically, the method depends upon applying radiofrequency energy at the resonance frequency of the reactant ion, thereby increasing its kinetic energy, while at the same time the intensity of the product ion is monitored. The experiment is actually done with a pulsed signal and phase-sensitive detection. A decrease in product ion intensity has generally been associated with exothermic or thermoneutral reactions.

(14) A decrease in the apparent rate constant with increasing kinetic energy is often observed for exothermic reactions.[15] Simple theory predicts no dependence of the rate constant on kinetic energy if the interaction is an ion-induced dipole one. Theories incorporating other effects, such as hard-sphere interactions, generally predict a negative dependence. Furthermore, loss of reactant ions from the cell or the increasing importance of new reaction pathways at higher energy would result in a negative dependence of rate constant on kinetic energy.

(15) See *Advan. Chem. Ser.*, No. **58** (1966), especially the articles by J. H. Futrell and F. P. Abramson and by L. Friedman for reviews, discussions, and relevant comments.

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

Reaction	F	R
$OH^- + CH_3OH = H_2O + CH_3O^-$	$-$	0
$OD^- + CH_3OD = D_2O + CH_3O^-$	$-$	0
$OH^- + C_2H_5OH = H_2O + C_2H_5O^-$	$-$	0
$OH^- + n\text{-}C_3H_7OH = H_2O + C_3H_7O^-$	$-$	*
$OH^- + i\text{-}C_3H_7OH = H_2O + i\text{-}C_3H_7O^-$	$-$	0
$OH^- + n\text{-}C_4H_9OH = H_2O + n\text{-}C_4H_9O^-$	$-$	0
$OH^- + t\text{-}C_4H_9OH = H_2O + t\text{-}C_4H_9O^-$	$-$	*
$OH^- + n\text{-}C_5H_{11}OH = H_2O + n\text{-}C_5H_{11}O^-$	$-$	*
$OH^- + (CH_3)_3CCH_2OH = H_2O + (CH_3)_3CCH_2O^-$	$-$	*
$CH_3O^- + C_2H_5OH = CH_3OH + C_2H_5O^-$	$-$	0
$C_2H_5O^- + n\text{-}C_3H_7OH = C_2H_5OH + n\text{-}C_3H_7O^-$	$-$	0
$CH_3O^- + i\text{-}C_3H_7OH = CH_3OH + i\text{-}C_3H_7O^-$	$-$	0
$C_2H_5O^- + i\text{-}C_3H_7OH = C_2H_5OH + i\text{-}C_3H_7O^-$	$-$	0
$n\text{-}C_3H_7O^- + (CD_3)_2CHOH = n\text{-}C_3H_7OH + (CD_3)_2CHO^-$	$-$	$-$
$n\text{-}C_3H_7O^- + n\text{-}C_4H_9OH = n\text{-}C_3H_7OH + n\text{-}C_4H_9O^-$	$-$	0
$i\text{-}C_3H_7O^- + n\text{-}C_4H_9OH = i\text{-}C_3H_7OH + n\text{-}C_4H_9O^-$	$-$	$-$
$i\text{-}C_3H_7O^- + t\text{-}C_4H_9OH = i\text{-}C_3H_7OH + t\text{-}C_4H_9O^-$	$-$	0
$C_2H_5O^- + n\text{-}C_5H_{11}OH = C_2H_5OH + n\text{-}C_5H_{11}O^-$	$-$	0
$i\text{-}C_3H_7O^- + n\text{-}C_5H_{11}OH = i\text{-}C_3H_7OH + n\text{-}C_5H_{11}O^-$	$-$	$-$
$n\text{-}C_4H_9O^- + n\text{-}C_5H_{11}OH = n\text{-}C_4H_9OH + n\text{-}C_5H_{11}O^-$	$-$	$-$
$t\text{-}C_4H_9O^- + n\text{-}C_5H_{11}OH = t\text{-}C_4H_9OH + n\text{-}C_5H_{11}O^-$	$-$	$-$
$t\text{-}C_4H_9O^- + (CH_3)_3CCH_2OH = t\text{-}C_4H_9OH + (CH_3)_3CCH_2O^-$	$-$	+
$OH^- + C_6H_5CH_3 = H_2O + C_6H_5CH_2^-$	$-$	*
$CH_3O^- + C_6H_5CH_3 = CH_3OH + C_6H_5CH_2^-$	$-$	0
$C_6H_5CH_2^- + C_2H_5OH = C_6H_5CH_3 + C_2H_5O^-$	*	+
$C_6H_5CH_2^- + i\text{-}C_3H_7OH = C_6H_5CH_3 + i\text{-}C_3H_7O^-$	$-$	0
$C_6H_5CH_2^- + t\text{-}C_4H_9OH = C_6H_5CH_3 + t\text{-}C_4H_9O^-$	$-$	0

[a] The sign of the double resonance signal is given. A negative sign ($-$) means that the product ion concentration diminished when the reactant was irradiated. A negative sign ($-$) is generally associated with an exothermic or thermoneutral reaction. A positive sign (+) is generally associated with endothermic reactions.[8c] 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 the reaction was not investigated.

equilibrium conditions where the general approach to interpretation has been to consider the energetics of the reaction of an isolated ion and neutral molecule.

The simple criterion of the occurrence or nonoccurrence of an ion–molecule reaction has been employed for determining whether a reaction is exothermic or endothermic. This criterion is expected to be more reasonable for reactions involving simple atom transfer or proton transfer than for those reactions involving considerable structural rearrangements. For the proton transfer studies reported here involving alkoxide ions and alcohols, we have investigated both forward and reverse reactions, and have assumed that the occurrence or nonoccurrence of a reaction is a reflection of the energetics for the proton transfer. That is, we assume that for a reaction to occur the reactants must have sufficient energy to form the products in their ground states. A reaction might not occur either because it is endothermic, or because it has an unusually large activation energy. However, when a reaction is observed to occur in one direction, but not the reverse, considerations of microscopic reversibility make it clear that, provided the reactants are in their ground states, only thermodynamic quantities are important. For reactions of type 1, $\Delta H° = \Delta E°$, thus the predominant direction of reaction provides evidence regarding the sign of $\Delta H°$. Finally, it is certain that $\Delta S°$ must be approximately zero for these reactions, since contributions to the entropy are essentially identical for both reactants and products.[16] Consequently, we feel that the observed order of ability to transfer a proton is an accurate reflection of the sign of $\Delta G°$, and thus represents a true gas-phase acidity.

We wish to emphasize the importance of examining reactions in both directions, since it is possible that the presence of internally excited reactant ions can lead to incorrect results about ground-state energetics when only a single reaction is considered. Equally important, the internal consistency of sets of pairwise experiments makes it highly unlikely that excited states are responsible for the results. As an example, the observation that $C_2H_5O^-$ abstracts a proton from propanol but not from methanol provides strong evidence that propanol is a stronger acid than methanol, regardless of the structure or energetics of $C_2H_5O^-$. (The observation of the reverse proton transfer from ethanol to CH_3O^- suggests that there is no unusual activation barrier for this reaction.) Although our observations of proton transfer in both directions for some of the larger alcohols can be explained by the presence of internally excited ions, they are more likely the result of these reactions being nearly thermoneutral for the ground-state ions. We have assumed that for those cases in which proton transfer is observed in both directions, the two alcohols are approximately equal in acidity. In any event, the general trend of increased acidity on going from small alkyl substituents to large ones is maintained.

Analysis of Gas Phase Acidities. We have chosen to consider the energetics of acid dissociation, $HA \rightarrow A^- + H^+$, as the sum of three fundamental processes which include (eq 6) the bond dissociation energy of HA, (eq 7) the electron affinity of $A\cdot$, and (eq 8) the ionization potential of $H\cdot$.[17]

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[16] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

$$\begin{array}{llr} \mathrm{HA} \longrightarrow \mathrm{H}\cdot + \mathrm{A}\cdot & DH^\circ(\mathrm{HA}) & (6) \\ \mathrm{e}^- + \mathrm{A}\cdot \longrightarrow \mathrm{A}^- & -EA(\mathrm{A}\cdot) & (7) \\ \mathrm{H}\cdot \longrightarrow \mathrm{H}^+ + \mathrm{e}^- & IP(\mathrm{H}\cdot) & (8) \\ \hline \mathrm{HA} \longrightarrow \mathrm{H}^+ + \mathrm{A}^- & \Delta H^\circ & \end{array}$$

The lack of data for electron affinities of radicals[18] is primarily the reason for the difficulty in calculating ΔH° for acid dissociation in the gas phase. Sufficient data are available however, to compare the acidities of the halogen acids.[19] Our observation that the reaction, $\mathrm{HBr} + \mathrm{Cl}^- \rightarrow \mathrm{HCl} + \mathrm{Br}^-$, occurs while the reverse does not is consistent with these data and provides a verification of the technique for a case where the energetics are well known. It is important to notice that the relative acidities in the HX series are due to HX bond strengths rather than electron affinities of X. The dissociation of these halogen acids is a very endothermic process in the gas phase, which points out the fact that dissociation of any acid in solution is due almost entirely to solvation of ions. Consequently, the dissociation reaction, $\mathrm{HA} \rightarrow \mathrm{H}^+ + \mathrm{A}^-$, is not experimentally observed in the gas phase. Thus, for the reaction actually observed, $\mathrm{HA} + \mathrm{B}^- \rightarrow \mathrm{HB} + \mathrm{A}^-$, which establishes the relative acidities of HA and HB, the above energy scheme is reduced to a consideration of differences in bond strengths of HA and HB and differences in electron affinities of A and B. Since the O–H bond strength is approximately 104 kcal/mol for all the simple alcohols,[22] the relative acidity order is due to differences in electron affinities of the alkoxyl radicals. The alcohol acidity order is such that the electron affinity of the alkoxyl radicals in general increases with the size of the alkyl group. This order is consistent with the electron affinity values reported recently by Hamill,[23] and consistent at least with the relative order reported by Page.[24] However, the absolute values of Page are too low and are not consistent with the reaction, $\mathrm{ROH} + \mathrm{OH}^- \rightarrow \mathrm{RO}^- + \mathrm{H_2O}$. From this reaction one can calculate the lower limit, $EA(\mathrm{RO}) >$ 28 kcal/mol, given $EA(\mathrm{OH}) = 43$ kcal/mol[25] and O–H bond strengths of 119 and 104 kcal/mol for water and alcohol, respectively.[20] However, one cannot obtain the relative electron affinities of OH· and RO· from this reaction, since the O–H bond strength of water is greater than that for alcohols.

In view of the substantial resonance stabilization to be expected in the phenoxyl radical and phenoxide ion, it is not at all surprising to find phenol a much stronger acid than are the aliphatic alcohols. Thus, when comparing acids of this type, we find that the usual intuitive organic chemical approach is satisfactory. On the other hand, toluene, which lies between methanol and ethanol in acidity presents a problem. The unexpectedly high acidity of toluene can be attributed to its weak (85 kcal/mol) benzylic C–H bond,[20,26] some 19 kcal/mol weaker than the O–H bond in the alcohols. In the case of ethanol, this is only just compensated by the higher electron affinity of the ethoxy radical: $EA(\mathrm{EtO}\cdot) - EA(\mathrm{C_6H_5CH_2}\cdot) \approx 19$ kcal/mol.[27] Thus, the acidities of alcohols are clearly enhanced by the electron attracting power of the oxygen, but this effect is largely reversed by the increased O–H bond energy.

It has been customary to associate the acidity of an acid with the "stability" of its conjugate base. To the extent that the "stability" is associated with electron affinity, it is clear from the foregoing arguments that such correlations can be misleading. For example, HBr is a stronger acid than HCl, although Cl· has a greater electron affinity than does Br·. The difference in bond strengths more than compensates in this case.[28]

Effects of Alkyl Groups. The nature of the polar effect of alkyl groups has received considerable attention and has generated a variety of explanations for its properties.[29] In fact, considerable debate has been generated regarding its direction relative to hydrogen in some cases. The evidence of the charge-stabilizing or -destabilizing properties of the alkyl group relative to hydrogen differs in cationic and anionic systems, and in saturated and unsaturated systems. Most of the data comes from solution studies, although some data are available for cations in the gas phase. As far as we know, no data have been available on the effect of alkyl groups in anions in the gas phase prior to our work.

A great deal of the evidence for the widely accepted belief that alkyl groups are electron releasing and hence stabilizing toward positive charge comes from studies involving carbonium ions which support the stability order tertiary > secondary > primary. Classic experiments which support this view include enhanced rates of solvolysis as substitution increases in alkyl halides, orientation in ionic addition to unsymmetrical olefins, and skeletal rearrangements in which more highly substituted carbonium ions are formed preferentially. These carbonium ion studies can be classified in the unsaturated cationic group since they involve alkyl groups attached to an sp^2 center. The explanation that the alkyl group is electron releasing in these cases is attractive, since an sp^2 carbon is more electronegative than an sp^3 carbon.[30]

Evidence for the electron releasing inductive effect of alkyl groups in saturated cationic systems is not as strong as in the cases involving carbonium ions, and the

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

(18) However, see J. I. Brauman and K. C. Smyth, *J. Amer. Chem. Soc.*, **91**, 7778 (1969).

(19) For HCl, $DH^\circ = 103$,[20] $EA = 83$,[21] $\Delta H^\circ = 333$; for HBr, $DH^\circ = 88$,[20] $EA = 78$,[21] $\Delta H^\circ = 323$. (All quantities in kilocalories per mole.)

(20) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(21) R. S. Berry and C. W. Riemann, *J. Chem. Phys.*, **38**, 1540 (1963).

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

(23) J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968).

(24) F. M. Page, U. S. Department of the Army Report No. DA-91-591-EVC-6-3206, 1965, quoted by Hamill.[23]

(25) L. M. Branscomb, *Phys. Rev.*, **48**, 11 (1966); J. Kay and F. M. Page, *Trans. Faraday Soc.*, **62**, 3081 (1966).

(26) R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 650 (1966). Propylene is also a strong acid, falling between methanol and water, probably for the same reason—a weak C–H bond.

(27) From the reaction: $\mathrm{C_6H_5CH_3} + \mathrm{OH}^- \rightarrow \mathrm{C_6H_5CH_2}^- + \mathrm{H_2O}$ we calculate $EA(\mathrm{C_6H_5CH_2}\cdot) \geqslant 9$ kcal/mol.

(28) See J. I. Brauman and L. K. Blair, manuscript submitted for publication, for a general discussion of periodic trends.

(29) See M. J. S. Dewar, *Tetrahedron*, **17**, 123 (1962); P. von R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, **90**, 6528 (1968), and references cited therein. Also, see E. M. Arnett and J. W. Larsen, *ibid.*, **91**, 1438 (1969); W. M. Schubert and D. F. Gurka, *ibid.*, **91**, 1443 (1969); A. Himoe and L. M. Stock, *ibid.*, **91**, 1452 (1969).

(30) (a) See, for example M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962; (b) see J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); M. D. Newton and W. N. Lipscomb, *ibid.*, **89**, 4261 (1967), for a different view of the origin of the dipole moment in methylacetylene.

apparent failure of trimethylamine to fall in the normal inductive order when the basicities of the methylamines were measured in solution generated considerable attention. Subsequently, gas-phase studies of Munson[31] and in these laboratories[7] showed that the methylamine basicities, in fact, do fall in the "normal inductive" order: trimethylamine > dimethylamine > methylamine > ammonia, and that the solution basicities are controlled by solvent effects. Additional studies of cationic-saturated systems in the gas phase support the "inductive" order of alkyl groups. For example, the basicities, $Et_2O > Me_2O$ and EtOH > MeOH.[31]

As far as anions are concerned, negative σ values,[32,33] although small, suggest that alkyl groups are "electron releasing" relative to hydrogen in unsaturated anionic systems. This behavior is also consistent with the difference in electronegativity properties of sp^2 and sp^3 carbons, although it may be a π-polarizability phenomenon.[30b] Recent work indicates that the effect is intrinsic and is maintained in the gas phase.[34]

Negative σ^* values[32,33] obtained from solution studies of saturated anionic systems support the inductive order of electron-releasing, and hence anion-destabilizing, property of alkyl groups. In fact, the solution order[35] of alcohol acidities, MeOH > EtOH > *t*-BuOH supports this view, and a $\sigma^*\rho^*$ correlation of +1.41 has been obtained.[36] The gas-phase order which we report is the reverse of the solution order, and shows that alkyl groups can stabilize anions in simple saturated systems in the gas phase. Thus, the solution order is probably an artifact, and does not represent any *intrinsic* property of the molecules. Most likely, the solution behavior results from steric hindrance to solvation in the larger alkoxides. As the free energies of solution of the ions are large compared to the differences in dissociation energies, reversal of order could easily occur in going from gas phase to solution. The generality of the property that alkyl groups stabilize anions in simple saturated systems in the gas phase is supported by our studies of the acidity of aliphatic amines which show behavior analogous to that of the alcohols.[37]

We postulate that the stabilization property of alkyl groups for both positive and negative saturated ions in the gas phase arises from the polarizability of the alkyl group and its proximity to the charged center.[38] A simple electrostatic model based on an ion-induced dipole potential can explain the lowering of the potential energy for a saturated system such as RO^- when the size of the alkyl group is increased.

The potential energy for an ion of charge e situated a distance, r, from a nonpolar molecule of polarizability, α, is given by

$$U(r) = -\frac{1}{2}\frac{\alpha e^2}{r^4}$$

An ion of unit charge situated 2–3 Å from methane which has $\alpha = 26 \times 10^{-25}$ cm^3 results in a value of $U(r) = -20$ to 24 kcal/mol. This type of interaction is thought to be the most important one in ion–molecule reactions for bringing ions and neutrals together, and it accounts appreciably for their rates.[39] It seems reasonable to assume that these induced dipole interactions may be important internally to lower the potential energy within ions, especially for the case where the charge is localized on a particular atom and where relatively nonpolar groups such as alkyl groups are situated close to the atom bearing the charge.

Since the polarizability of a molecule is an additive property, the sum of "bond" polarizabilities,[40] we can construct a simple electrostatic model by assuming that each C–C and C–H bond interacts with a charge localized on the oxygen atom. Using appropriate geometries and $\alpha_{\parallel}$ and $\alpha_{\perp}$ reported by Denbigh,[41] we estimate a difference in *EA* of *ca.* 12 kcal/mol between *t*-BuO· and MeO·. It is to be expected that these polarizabilities, which are determined at low field strengths, are quite likely inadequate in this context. Large field strengths exist within a fewn ågströms of a unit charge, and hyperpolarizability effects may be important.[42] In addition, polarization can occur through the bonds as well. Nevertheless, the order of magnitude of the effect appears consistent with the electron affinity differences determined by Hamill,[23] and our previous estimate.[37]

The value of this approach to effects of alkyl groups lies in its simple physical interpretation. As is the case with many other *ad hoc* explanations, it is based on a localized orbital model. Presumably, a full Hartree–Fock calculation would obviate approximations of this sort, but such calculations do not lend themselves to intuitive extensions. Recent CNDO type calculations predict the correct ordering of alcohol acidities,[43] but there is some reason to believe that calculations of this type overemphasize ionic contributions and may therefore be somewhat unreliable.[44]

It is likely that increasing the size of the alkyl group will generally tend to increase acidity even in unsaturated systems. However, the relative effect of methyl *vs.* hydrogen may well be to destabilize anions in unsaturated systems (*viz.* methylacetylene and xylene).[34] This is consistent with an intrinsic dipole effect superimposed upon the polarizability phenomenon.

The polarizability phenomenon may be thought of as a kind of internal solvation. The size of the effect is substantially less than the free energy of solvation in a protic solvent. Thus steric hindrance to solvation might well play a more important role in ionic stabilization in solution and thus swamp out the intrinsic acidity effect.

Experimental Section

Materials. Hydrogen chloride and hydrogen bromide were commercially available samples (Matheson) in lecture bottles.

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(32) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(33) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

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(38) This proposal has been suggested previously as an explanation for effects of alkyl groups. For example, see 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).

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(40) J. D. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1964, p 947.

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(43) T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969); N. C. Baird, *Can. J. Chem.*, **47**, 2306 (1969).

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Samples were degassed at −190°. Alcohols were generally reagent grade or 99+ mol % pure. Commercial grade toluene, *t*-butyl alcohol, *n*-butyl alcohol, and neopentyl alcohol were used as received. Deuterated 2-propanol, $(CD_3)_2CHOH$, >99% D was prepared by a standard procedure[45] from lithium aluminum hydride and acetone-d_6 (Stohler Isotopic Chemicals, >99.5% D). Methanol-O-*d* (>99%) was obtained as a gift from Professor C. Djerassi.

Preparation of Samples. All samples were prepared as gases or gas mixtures (22–28°) directly on a vacuum line, degassed by using 3–5 freeze–pump–thaw cycles, and trap distilled (−190°) directly into a 250-ml gas-sample bulb. The glass-sample bulb was fitted with a high-vacuum stopcock and ground-glass joint for direct introduction of the sample into the unheated inlet of the icr spectrometer. During the course of this study the single inlet of the icr instrument was replaced with a dual inlet which greatly facilitated the introduction of samples into the icr cell. In general the compound which was used as the source of negative ions (*e.g.*, water) was introduced through one inlet, and the other one or two components were introduced through the other inlet. The partial pressures of the neutrals in the icr cell usually were comparable and never exceeded a 5:1 ratio for any two species. The composition of the mixture could be determined by observing the positive ion mass spectrum at the same pressure at which the negative ion reactions were studied. In experiments where no double resonance signal was observed, care was taken to make sure that a sufficient partial pressure of neutral was present for collisions with the ion in question. The total pressure was generally maintained within the range 1–5 × 10^{-5} Torr measured at the Vac-Ion pump.

Instrumentation. The basic icr instrument used was the Syratron mass spectrometer (V-5900) (Serial No. 105) obtained commercially from Varian Associates, Palo Alto, Calif. Auxiliary equipment included a Princeton Applied Research lock-in amplifier (Model JB-4) for phase-sensitive detection, a Hewlett-Packard test oscillator (Model 650A) used as an auxiliary double resonance oscillator, the Varian Associates double resonance oscillator (Model V5918, Serial No. 110), a F. L. Moseley Model 7030A X–Y recorded, a Tetronix type RM 504 oscilloscope, a Hewlett-Packard 5321 B electronic counter, and a Hewlett-Packard 410 C voltmeter.

Single-resonance spectra were obtained by fixing the marginal oscillator frequency (153.5 kHz) and sweeping the magnetic field using, for the most part, a field-modulation phase-sensitive detection scheme. The pulsed double resonance technique[8c,e] was used for all reaction studies. For double resonance, irradiating radiofrequency amplitudes were kept to a minimum, and reactions were studied near the threshold for a double resonance signal. Typical amplitudes were 0.02–0.10 V (peak-to-peak measured externally at the base of the cell). Trapping voltages in the range 0.7–2.5 V were used. Analyzer drift voltages <0.10 V for both analyzer plates were typical. Source drift voltages <1.0 V for both source plates were typical. Trapping and drift voltages were measured at the console (peak-to-peak). The cross-sectional dimensions of the cell in this instrument are 2.54 × 2.54 cm. No special modification in cell design or instrumentation was made for observing negative ions.

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Protonated Cyclopropanes. V. The Treatment of 1-^{14}C-1-Chloropropane with Aluminum Chloride[1]

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Abstract: The isotopic scrambling during partial isomerization of 1-^{14}C-1-chloropropane (I-Cl-1-^{14}C) to 2-chloropropane (IV-Cl-^{14}C) induced by treatment with $AlCl_3$ at 0° has been investigated. When the isomerization to IV-Cl-^{14}C was 90%, the recovered I-Cl-^{14}C showed about 7 and 22% rearrangements of the label from C-1 to C-2 and C-3, respectively. Since some conversion of IV-Cl to I-Cl was found to take place under the conditions employed, reversible isomerizations between I-Cl and IV-Cl would contribute to some of the isotope position rearrangements from C-1 to C-3. To account for the scrambling to C-2, it is proposed that equilibrating protonated cyclopropane intermediates were involved, and these would collapse to I-Cl with the ^{14}C-label rearranging to both C-2 and C-3. Small amounts of ^{14}C activity (1.4–3.0%) were found at the C-2 position of the IV-Cl-^{14}C obtained in these experiments. It is suggested that the IV-Cl-2-^{14}C could have arisen from isomerizations involving isotopically scrambled I-Cl-2-^{14}C.

In reactions involving protonated cyclopropane as an intermediate, there is general agreement that the face-protonated structure is not the stable species[2] and that equilibrating edge-protonated cyclopropanes might be preferred over corner protonation.[2,3] Recently, Collins[4] has pointed out that in reactions with 1-propyl derivatives labeled with isotopic carbon at C-1 (*e.g.*, I-X-1-^{14}C), a differentiation between corner and edge protonation may be possible from isotopic scrambling data. If products were formed before equilibrium has

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