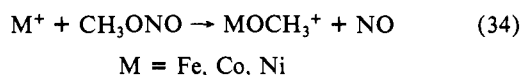


however, ethene coordination activates the complex by the ML^+ -ethene bond energy. This activation can effect β -hydride shifts generating hydrido-metal complexes. For exchange to take place the metal-olefin complex must be coordinatively unsaturated. In addition, the metal-olefin complex must be reasonably stable, and competing reactions such as displacement, dehydrogenation, condensation, olefin oligomerization, etc., must be slow relative to the insertion/elimination process, reaction 2. Ethene- d_4 yielded excellent results for $M(\text{propene})^+$ and $M(\text{isobutene})^+$ for $M = \text{Fe, Co, and Ni}$ and $M(1,3\text{-pentadiene})^+$, $M(2\text{-methylbutadiene})^+$, $M(\text{cyclopentadiene})^+$, and $M(\text{cycloheptatriene})^+$ for $M = \text{Fe, Co, Ni, and Rh}$. Only for $\text{Rh}(\text{propene})^+$ and $\text{Rh}(\text{isobutene})^+$ is deuterium superior to ethene- d_4 for H/D exchange due to complicating processes with ethene. For $M(\text{propene})^+$ species the rate of exchange with ethene- d_4 was found to decrease in the following order: $\text{Rh}^+ > \text{Co}^+ > \text{Fe}^+ > \text{Ni}^+$. It is interesting to note that more H/D scrambling has been observed for reactions of Co^+ with selectively deuterated alkanes than for either Fe^+ or Ni^+ .^{13,68}

The dynamics of a variety of metal-ligand species, where the ligand is not an olefin, may also be studied. For example, MOCH_3^+ ions are generated by reaction with methyl nitrite, reaction 34.⁶⁹ Collisional activation yields elimination of CH_2O



(68) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1983**, *2*, 1818.

in high efficiency, indicating that the ion has rearranged to a hydrido-formaldehyde complex prior to fragmentation. The hydrido-formaldehyde species may, however, be in dynamic equilibrium with the methoxy species, eq 35. The product of



reaction 34 undergoes three rapid H/D exchanges with ethene- d_4 .⁶⁹ This clearly indicates that the equilibrium in reaction 35 is occurring.

Propene- d_6 may be a useful reagent for investigating dynamic H/D exchanges for metal-olefin complexes which contain no labile hydrogens. For example, $M(\text{butadiene})^+$ and $M(\text{trimethylene methane})^+$ complexes could be studied. The butadiene complex should undergo only 4 exchanges, whereas all 6 hydrogens should be exchangeable in the trimethylene methane species.

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Registry No. C_2D_4 , 683-73-8; $n\text{-C}_5\text{H}_{12}$, 109-66-0; $\text{neo-C}_5\text{H}_{12}$, 463-82-1; C_2H_4 , 74-85-1; $\text{iso-C}_4\text{H}_{10}$, 75-28-5; $c\text{-C}_5\text{H}_8$, 142-29-0; $c\text{-C}_7\text{H}_{12}$, 628-92-2; H_2 , 1333-74-0; Fe^+ , 14067-02-8; Co^+ , 16610-75-6; Ni^+ , 14903-34-5; Rh^+ , 20561-59-5; cyclobutanone, 1191-95-3; *trans*-1,3-pentadiene, 2004-70-8; 1-butene, 106-98-9; *trans*-2-pentene, 646-04-8; 2-methylbutadiene, 78-79-5; 2-methylbutane, 78-78-4.

(69) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

Methyl Substituent Effects in the Gas-Phase Acidities of Halosubstituted Oxygen Acids. A Realignment with Substituent Effects in Solution

G. Caldwell,[†] T. B. McMahon,^{*††} P. Kebarle,^{*†} J. E. Bartmess,[‡] and J. P. Kiplinger[‡]

Contribution from the Departments of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, and Indiana University, Bloomington, Indiana 47405.

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Abstract: The gas-phase acidities of a number of chloro-, bromo-, and trifluoromethyl-substituted carboxylic acids and alcohols have been measured by using pulsed electron beam high-pressure mass spectrometry and in several cases pulsed ion cyclotron resonance spectroscopy. The results show that in situations where a methyl group is substituted (at sp^3 carbon) in a carboxylic acid or alcohol, a net acid weakening effect is observed. This is in contrast to normal aliphatic carboxylic acids and alcohols where methyl substitution leads to an increase in acid strength. The reversal of the methyl substituent effect is interpreted as due to a diminished charge-induced polarization stabilization in the species substituted with electronegative groups.

Brauman and Blair's discovery¹ of the gas-phase aliphatic alcohol acidity order ($t\text{-C}_4\text{H}_9\text{OH} > \text{iso-C}_3\text{H}_7\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{OH} > \text{H}_2\text{O}$) was a landmark event in the interpretation of intrinsic alkyl substituent effects.¹ This ordering, which is an exact reversal of that observed in aqueous solution,² demonstrated for the first time that alkyl groups have the ability to stabilize negative charge via a through-space polarization interaction. With more quantitative data, Taft has shown that while alkyl groups do in fact exert substantial destabilizing, field/inductive effects in alkoxy anions, these are overwhelmed by the stabilizing ion-induced polarization interaction which may be from three to seven times greater in magnitude.³ This type of net anionic stabilization is observed for other acidic functional groups as well. For example,

$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ has a gas-phase acidity 1.2 kcal/mol greater than $\text{CH}_3\text{CO}_2\text{H}$, and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ is 1.3 kcal/mol more acidic than $\text{CH}_3\text{C}\equiv\text{CH}$.⁴ However, when methyl for hydrogen substitution occurs at the sp^2 or sp carbon an overall acid weakening effect is observed. For example, $\text{CH}_3\text{CO}_2\text{H}$ is 3.3 kcal/mol less acidic than HCO_2H and $\text{CH}_3\text{C}\equiv\text{CH}$ is 4.2 kcal/mol less acidic than $\text{HC}\equiv\text{CH}$.⁴ These latter results have been interpreted, using perturbation molecular orbital theory, as being due to a stabili-

(1) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 5636, 6501 (1968).

(2) F. W. Baker, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.* **89**, 5677 (1967), and references cited therein.

(3) R. W. Taft, M. Taagepera, J. L. M. Abboud, J. F. Wolf, D. J. De Frees, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **100**, 7765 (1978); R. W. Taft, *Prog. Phys. Org. Chem.*, **14**, 287 (1984).

(4) J. B. Cummings and P. Kebarle, *Can. J. Chem.*, **56**, 1 (1978); J. E. Bartmess, R. T. McIver, Jr., in "Gas Phase Ion Chemistry", Bowers, M. T., Ed., Academic Press, New York, 1979, Vol. 2, Chapter 11.

[†]University of Alberta.

[‡]Present address: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

[‡]Indiana University.

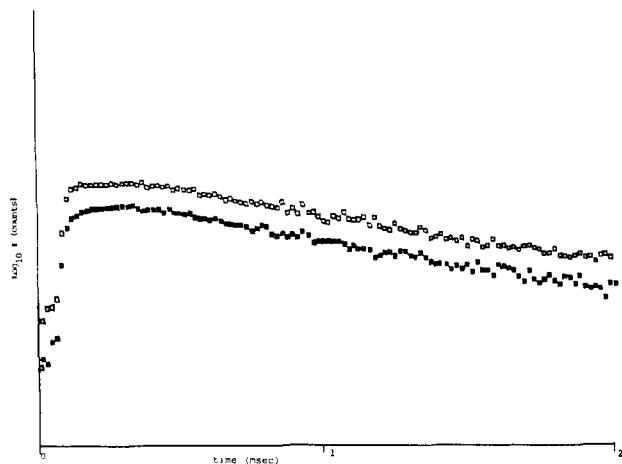


Figure 1. $\log I$ (counts) vs. time (ms) profile for the reaction $(\text{CF}_3)_2\text{C}-\text{HO}^- + (\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OH} = (\text{CF}_3)_2\text{C}(\text{CH}_3)\text{O}^- + (\text{CF}_3)_2\text{CHOH}$ where \blacksquare represents $(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{O}^-$ and \square represents $(\text{CF}_3)_2\text{CHO}^-$. HPMS conditions were as follows: neutral ratio $(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OH}/(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{O}^- = 0.6$, buffer gas CH_4 at 4 torr, NF_3 at ~ 10 mtorr (source of F^-), temperature $T = 600$ K, and equilibrium constant $K = 33$.

zation exerted by methyl on the neutral acid. The stabilization is due to a π -type donation from the functional group to the empty π^* orbital of the methyl group.⁵

It has thus generally been expected that methyl for hydrogen substitution at sp^3 carbon in oxygen acids will be stabilizing by virtue of the alkyl group polarization effect on the anionic center. We report in the present work the first examples of acidity decreases produced by methyl for hydrogen substitution at the sp^3 carbon of oxyacids and also provide a rationalization of the effects observed.

Experimental Section

Measurements were carried out with a pulsed electron beam high-pressure mass spectrometer (HPMS).⁶ Briefly, the equilibrium constants, K , were determined by measuring the ion intensities observed in a gas mixture of about 4 torr of methane containing known concentrations of the neutral acids of interest and 10 mtorr of NF_3 (source of F^-). Equilibrium was established rapidly, i.e., the observed ion intensity ratio became constant in less than 100 μs after the initiating electron pulse. The equilibrium constant K was determined from the steady-state ionic abundances and the known concentrations of the neutral acids. The equation $\Delta G^\circ = -RT \ln K$ was used to evaluate the free energy change where $T = 600$ K. A typical example of experimental data obtained is shown in Figure 1 for a 1:1.8 mixture of $(\text{CF}_3)_2\text{CHOH}$ and $(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OH}$.

Several of the equilibria were also examined by using trapped-ion ion cyclotron resonance spectroscopy (ICR).^{7,8} These results were obtained at neutral acid pressures of up to 5×10^{-6} torr, trapping times of up to 1 s, and $T = 298$ and 307 K.

Chemicals were all commercially available and purified prior to use.

Results and Discussion

The results obtained from the proton transfer equilibria, measurements are given in Table I. The agreement between the HPMS results obtained at 600 K with the ICR results obtained at near room temperature indicates that there are no significant entropy changes involved in the proton transfer reactions, i.e., $\Delta G^\circ_{600} \approx \Delta G^\circ_{300} \approx \Delta H^\circ$. On the basis of the HPMS and ICR

Table I. Free Energies ΔG°_{600} for Several Proton Transfer Equilibria: $\text{A}^- + \text{BH} = \text{AH} + \text{B}^-$

RCO_2H	$\Delta G^\circ (600\text{K})^{a,b}$	ROH	$\Delta G^\circ (600\text{K})^{a,b}$
$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CO}_2\text{H}$	(334.8)	$\text{CF}_3\text{CH}_2\text{OH}$	(356.8)
$\text{HCH}(\text{Cl})\text{CH}_2\text{CO}_2\text{H}$	(333.8)	$\text{CF}_3\text{CH}(\text{CH}_3)\text{OH}$	(356.4)
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$	(330.5)	$\text{CF}_3\text{C}(\text{CH}_3)_2\text{OH}$	(356.2)
$\text{CH}_3\text{CH}(\text{Cl})\text{CO}_2\text{H}$	(330.4)	$(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OH}$	(342.0)
$\text{HCH}(\text{Cl})\text{CO}_2\text{H}$	(329.0)	$(\text{CF}_3)_2\text{CHOH}$	(339.7)
$\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CO}_2\text{H}$	(329.4)		
$\text{CH}_3\text{CH}(\text{Br})\text{CO}_2\text{H}$	(329.2)		
$\text{HCH}(\text{Br})\text{CO}_2\text{H}$	(328.2)		

^a ΔG° values between double arrows relate to the measured proton transfer equilibrium $\text{A}^- + \text{BH} = \text{AH} + \text{B}^-$ and were obtained from $-\Delta G^\circ = RT \ln K$. For each pair of acids connected by double arrows the more acidic one is at the bottom. HPMS at 600 K was used for all measurements except where otherwise indicated. Units in kcal/mol with an estimated error of ± 0.3 kcal/mol. ^b The numbers in parentheses are the ΔG°_{300} for the gas-phase acid dissociation $\text{AH} = \text{A}^- + \text{H}^+$. These were obtained by referencing the relative values from the proton transfer equilibria to the absolute gas-phase acidity scale: ref 4, Caldwell, Renneboog, and Kebarle, unpublished results, and Bartmess unpublished results. ^c ICR equilibrium measurement obtained at 307 K, Bartmess.¹⁵ ^d Reference 10. ^e Larson and McMahon.¹⁴ ^f ICR equilibrium measurements obtained at 298 K McMahon.¹⁵

results, entropy changes between 1 to 3 eu are estimated for the proton transfer reactions involving the fluorinated alcohols. We are therefore confident that the acid-weakening effects observed in the present study relate directly to electronic energy changes and are not due to entropy effects.

Examining the results in Table I one finds that in every case where CH_3 is substituted for H at the sp^3 carbon in the halo-substituted carboxylic acids a decrease in the gas-phase acidity is observed. Within the carboxylic acids methyl for hydrogen substitution has an acid-weakening effect of about 1 kcal/mol which decreases somewhat as the halo substituent is moved away from the acidic site.⁹ Ethyl for methyl substitution causes no further destabilization of the carboxylic acids.¹⁰ Methyl for hydrogen substitution in the fluorinated alcohols (Table I) produces somewhat more complex gas-phase acidity changes. Methyl for hydrogen substitution in $(\text{CF}_3)_2\text{CHOH}$ causes a decrease in gas-phase acidity similar to that observed for the halosubstituted carboxylic acids. Methyl for hydrogen substitution in the mono-trifluoromethyl-substituted alcohols produces a very small change in gas-phase acidity, the two ICR determinations being unfortunately in disagreement on the direction of the change for the first methyl substitution.¹⁵ However, considering that methyl

(9) R. Yamdagni and P. Kebarle, *Can. J. Chem.*, **52**, 861 (1974). Yamdagni and Kebarle originally reported these effects but did not comment on the unusual alkyl effects in the carboxylic acid series.

(10) The free energy difference between α -chlorobutyric and α -chloropropionic acids has been reported to be approximately 1 kcal/mol with $\text{EtCH}(\text{Cl})\text{CO}_2\text{H}$ less acidic than $\text{CH}_3\text{CH}(\text{Cl})\text{CO}_2\text{H}$.⁹ Here we report the pair to be approximately equal in acidity. The reason for the discrepancy is not clear even though the proton transfer reactions were determined in the same laboratory. The bromo analogues gave a similar result.

(11) The energetics of acid ionization can be considered as the sum of three thermodynamic processes: electron affinity of the radical, ionization potential of the hydrogen atom (313.6 kcal/mol),⁴ and homolytic bond dissociation energy. It has been noted that the bond dissociation energies of the carboxylic acids are close regardless of the nature of the substituent.¹² This constant bond dissociation energy is to be expected since the methyl for hydrogen substitution is far removed from the O-H acidic proton. A similar argument will apply to the alcohols. Therefore, the stabilizing or destabilizing effect of the methyl for hydrogen substitution manifests itself in the electron affinity of the alkoxy or carboxylic radical.

(5) A. Pross and L. Radom, *J. Am. Chem. Soc.*, **100**, 6572 (1978). The stabilization of the neutral acid is due to a π -type donation from the lone pair of the functional group to the empty π^* orbital of the methyl group. For an identical effect influencing the basicities of methyl-substituted amines see Table V in: S. Ikuta and P. Kebarle, *Can. J. Chem.*, **61**, 97 (1983).

(6) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 2222 (1977). For a more detailed explanation of experiment see Experimental Section therein.

(7) J. E. Bartmess, R. L. Hays, H. N. Khatri, R. N. Misra, and S. R. Wilson, *J. Am. Chem. Soc.*, **103**, 4746 (1981). For a description of the ICR spectrometer see the Experimental Section therein.

(8) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1973). For a description of the ICR spectrometer see the Experimental Section.

substitution in ethanol (leading to 2-propanol) increases the acidity by 2 kcal/mol,⁴ the observed very small changes observed for methyl substitution in $\text{CF}_3\text{CH}_2\text{OH}$ show clearly that the presence of the electron-withdrawing fluorines decreases the methyl acidifying effect to almost nothing or even reverses it.

The above results can be rationalized by a consideration of the probable shifts in electron density which occur in the alkoxide and carboxylate anions in the presence of a strongly electron-withdrawing group.¹¹ The Cl or Br groups in the carboxylic acid series and trifluoromethyl group(s) in the alcohol series will inductively withdraw appreciable negative charge away from the oxyanionic groups. The resulting charge dispersal in the anionic moiety is the factor responsible for the acidifying effect of these substituents. For example, $\text{ClCH}_2\text{CO}_2\text{H}$ has a gas-phase acidity 12.5 kcal/mol greater than $\text{CH}_3\text{CO}_2\text{H}$ and $(\text{CF}_3)_2\text{CHOH}$ is 27.8 kcal/mol more acidic than $(\text{CH}_3)_2\text{CHOH}$.⁴ In fact $(\text{CF}_3)_2\text{CHOH}$ has approximately the same gas-phase acidity as $\text{CH}_3\text{CO}_2\text{H}$. Thus rather than having a single (for alkoxides) or two (for carboxylates) dominant polarization interaction(s) between the methyl group and charge center(s) there will be polarization interactions with a number of centers at considerably less than unit negative charge.

The classical energy lowering due to a charge-polarizable group interaction is given by $V(r) = -\alpha e^2/2r^4$. Since V depends on the square of the ionic charge e , a much smaller stabilization is obtained when the charge is distributed over more than one center. For example, splitting of a single charge e at distance r into three charges of $1/3e$ at distances r leads to a polarization stabilization $-V(r)$ which is only $1/3$ of the $-V(r)$ of the single charge. Thus, the spreading of the charge by the chlorosubstituent in the carboxylic acids and by the trifluoromethyl-substituted alcohols reduces substantially the polarization stabilization provided by the methyl group. In the absence of this polarization stabilization the destabilizing field/inductive effect of the methyl group (see

Taft³) becomes dominant and methyl substitution leads to an acidity decrease.

We recognize that the present arguments may be simplistic in nature and that other factors may be involved.¹³ Thus, we have completely neglected the methyl substituent effect on the neutral acids. As mentioned in the introduction the decrease of acidity from acetylene to methylacetylene and from formic to acetic acid is due to methyl effects in the neutrals. It seems probable, however, that this particular effect should not be involved in the present systems since the methyl substitution in some of the present cases (the trifluoromethyl alcohols and acids) is removed from the π donor group such that the conjugation stabilizing the neutrals⁵ cannot occur.

One can expect that a reversal of the methyl-substituent effect will occur only after sufficient charge dispersal in the anion by electronegative groups has occurred. Groups that disperse the charge will cause only a decrease of the acidifying effect of the methyl substituent. This is borne out by experiment. For example, methyl substitution in methanol leads to an increase of acidity by 3.1 kcal/mol, while methyl substitution in acetic acid increases the acidity by only 1 kcal/mol.⁴ The lesser methyl acidifying effect in the carboxylic acids must be due to the dispersal of the anionic charge over the two oxygen atoms of the carboxylic group. Since the charge in the carboxylate anion is already dispersed, the addition of only one chloro substituent is sufficient to cause a reversal of the methyl-substituent effect (see chloroacetic acid vs. α chloropropionic acid (Table I)) while for the single oxygen center alcohols a clear reversal is observed only after the introduction of very strong electron withdrawal, i.e., two CF_3 groups. The fact that the charge dispersal caused by the two CF_3 groups is very large is indicated by the acidity of the bis(CF_3 -substituted) alcohols which is almost as high as that of the carboxylic acids (Table I).

Similar substituent effect arguments may apply to other gas-phase acids where strong electron-withdrawing groups are present, such as CN or NO_2 . This and the effect of alkyl substitution other than methyl groups are currently under investigation.

The observed decrease of gas-phase acidity with methyl substitution in oxygen acids containing electron-withdrawing groups is in the same direction as that observed in solution where it generally holds for all oxygen acids, i.e., also acids without additional electron-withdrawing groups. This realignment of gas-phase and solution methyl effects is not accidental. In solution, there is charge dispersal from the negative oxy center(s) of the anion to the solvent while in the gas phase it is the additional electron-withdrawing substituents that must provide the same function. Thus, the gas-phase methyl acidity effect has gone full circle; first Brauman and Blair¹ showed that the methyl effect is opposite to that in solution, now the present work finds that the effect is the same as in solution if the environment around the charge is modified to functionally resemble that present in solution. Brauman and Blair¹ attributed the reversal of solution-phase acidities to steric hindrance to solvation, an effect that undoubtedly is present. The charge dispersal effect described here is an additional effect acting in the same direction.

Registry No. $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CO}_2\text{H}$, 1951-12-8; $\text{HCH}(\text{Cl})\text{CH}_2\text{CO}_2\text{H}$, 107-94-8; $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$, 4170-24-5; $\text{CH}_3\text{CH}(\text{Cl})\text{CO}_2\text{H}$, 598-78-7; $\text{HCH}(\text{Cl})\text{CO}_2\text{H}$, 79-11-8; $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CO}_2\text{H}$, 80-58-0; $\text{CH}_3\text{CH}(\text{Br})\text{CO}_2\text{H}$, 598-72-1; $\text{HCH}(\text{Br})\text{CO}_2\text{H}$, 79-08-3; $\text{CF}_3\text{CH}_2\text{OH}$, 75-89-8; $\text{CF}_3\text{CH}(\text{CH}_3)\text{OH}$, 374-01-6; $\text{CF}_3\text{C}(\text{CH}_3)_2\text{OH}$, 507-52-8; $(\text{C}_2\text{F}_5)_2\text{C}(\text{CH}_3)\text{OH}$, 1515-14-6; $(\text{CF}_3)_2\text{CHOH}$, 920-66-1.

(12) D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, **33**, 493 (1982).

(13) For example, by analogy to the explanation of the relative acidities of HCO_2H vs. $\text{CH}_3\text{CO}_2\text{H}$ and $\text{HC}\equiv\text{CH}$ vs. $\text{CH}_3\text{C}\equiv\text{CH}$ with use of PMO theory,⁵ it may be the case that in situations where CH_3 is substituted for H in species where a strongly electron-withdrawing group is already present that the acid-weakening effect is due to a greater stabilization of the neutral acid relative to its conjugate anion. However, in the absence of accurate quantum-mechanical calculations, the validity of such a suggestion cannot be tested. For this and other reasons (see text), we prefer the simpler qualitative arguments advanced here.

(14) J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.*, **105**, 2944 (1983).

(15) Measurements of the gas-phase acidity of these alcohols at 307 K were carried out relative to *m*-fluoroaniline at Indiana University. Measurements of acidities between $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3\text{CH}(\text{CH}_3)\text{OH}$ at 298 K were carried out at the University of New Brunswick where the alcohols were examined directly relative to each other by using alcohol partial pressure ratios which varied by a factor of 10. In this case ion signals for deprotonated species decayed at long times due to formation of $2M - 1$ dimers by bimolecular radiative association reactions.¹⁶ As a result this determination may have the larger error. Note that the two ICR results give acidities of opposite order. Direct acidity measurements using HPMS could not be carried out due to the presence of more acidic impurities. However, earlier ICR results indicated that the relative gas-phase acidities of $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3\text{CH}(\text{C}_2\text{H}_5)\text{OH}$ were also approximately the same.¹⁷ The data for clustering a F^- and Cl^- to these alcohols, using HPMS, indicated that the CH_3 -substituted species were less acidic.¹⁸

(16) G. Caldwell and J. E. Bartmess, *J. Phys. Chem.*, **85**, 3571 (1981).

(17) J. H. J. Dawson and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, **25**, 47 (1977).

(18) J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.*, **106**, 517 (1984).