however, ethene coordination activates the complex by the ML
– ethene bond energy. This activation can effect 18–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–d4 yielded
excellent results for M(propene) and M(isobutene) for M =
Fe, Co, and Ni and M(1,3-pentadiene), M(2-methylbutadiene)
M(cyclopentadiene), and M(cycloheptatriene) for M = Fe, Co,
Ni, and Rh. Only for Rh(propene) and Rh(isobutene) is
deuterium superior to ethene–d4 for H/D exchange due to complica-
tion processes with ethene. For M(propene) species the rate of
exchange with ethene–d4 was found to decrease in the following
order: Rx > Co > Fe > Ni.2 It is interesting to note that more H/D
scrambling has been observed for reactions of Co2+ with
selectively deuterated alkynes than for either Fe2+ or Ni2+.3,8

The dynamics of a variety of metal–ligand species, where the
ligand is not an olefin, may also be studied. For example,
MOCH3+ ions are generated by reaction with methyl nitrite,
reaction 34.9

\[
M^+ + CH_3ONO \rightarrow MOCH_3^+ \rightarrow NO \quad (34)
\]

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

\[
H-M^+OH_2 \rightarrow M^+OCH_3 \quad (35)
\]

reaction 34 undergoes three rapid H/D exchanges with ethene–d6.
This clearly indicates that the equilibrium in reaction 35 is
occurring.

Propene–d6 may be a useful reagent for investigating dynamic
H/D exchanges for metal–olefin complexes which contain no labile
hydrogens. For example, M(butadiene) and M(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. C2H2, 50-81-7; C2H4, 74-85-1; iso-C3H6, 109-66-0;
C4H8, 75-28-5; C2H4, 142-29-0; C5H10, 628-92-2; HH2, 1333-74-0; Fe2+, 14067-02-8; Co2+, 16610-75-6; Ni2+, 14903-35-8; H2*,
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.


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

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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 sp3 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-C4H9OH > iso-C4H9OH > C2H5OH >
CH3OH > H2O) 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
alkoxide anions, these are overcome 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,
CH3CH2CO2H has a gas-phase acidity 1.2 kcal/mol greater than
CH3CO2H, and CH3CH2CH=CH2CH=CH2 has 1.3 kcal/mol more acidic than
CH3CH=CH.4 However, when methyl for hydrogen substitution
occurs at the sp2 or sp carbon an overall acid weakening effect
is observed. For example, CH3CO2H is 3.3 kcal/mol less acidic
than HCO2H and CH3CH=CH is 4.2 kcal/mol less acidic than
HC=CH.5 These latter results have been interpreted, using perturbation molecular orbital theory, as being due to a stabiliz-

(1968).
(2) F. W. Baker, R. C. Parish, and L. M. Stock, J. Am. Chem. Soc., 89,
5677 (1967), and references cited therein.
Bartmess, R. T. McIver, Jr., In "Gas Phase Ion Chemistry", Bowers, M. T.,
Gas-Phase Acids of Halosubstituted Oxygen Acids

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 K) $\approx$ $\Delta G^\circ$ (300 K) $\approx$ $\Delta H^\circ$. On the basis of the HPMS and ICR 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 halosubstituted 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 (Table I) produces somewhat more complex gas-phase acidity changes. Methyl for hydrogen substitution in the fluorinated alcohols (Table I) produces somewhat more complex gas-phase acidity changes. Methyl for hydrogen substitution in the mono-trifluoroacetyl-methyl-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. However, considering that methyl

Table I. Free Energies $\Delta G^\circ$ (600 K) for Several Proton Transfer Equilibria: $A^-BH = AH + B^-$

<table>
<thead>
<tr>
<th>$\text{RCO}_2\text{H}$</th>
<th>$\Delta G^\circ$ (600 K)</th>
<th>$\Delta G^\circ$ (300 K)</th>
<th>$\Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CO}_2\text{H}$</td>
<td>334.8</td>
<td>336.8</td>
<td></td>
</tr>
<tr>
<td>$\text{HCH(\text{Cl})CH}_2\text{CO}_2\text{H}$</td>
<td>338.6</td>
<td>341.1</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}(\text{Cl})\text{CO}_2\text{H}$</td>
<td>330.5</td>
<td>342.0</td>
<td></td>
</tr>
<tr>
<td>$\text{HCH(CI)CO}_2\text{H}$</td>
<td>339.0</td>
<td>342.0</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta G^\circ$ values between double arrows relate to the measured proton transfer equilibrium $A^-BH = AH + B^-$ 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. The numbers in parentheses are the $\Delta G^\circ_{600}$ for the gas-phase acid dissociation $AH = A^- + H^+$. These were obtained by referencing the relative values from the proton transfer equilibria to the absolute gas-phase acidity scale: ref 4, Caldew, Renneboog, and Kebarle, unpublished results, and Bartmess unpublished results. ICR equilibrium measurements obtained at 307 K, Bartmess. Reference 10. Larson and McMahon. ICR equilibrium measurements obtained at 298 K McMahon.

Figure 1. log J (counts) vs. time (ms) profile for the reaction (CF$_3$)$_2$C-H$^+$ + (CF$_3$)$_2$C(C$_x$H$_y$)OH = (CF$_3$)$_2$C(C$_x$H$_y$)O$^-$ + (CF$_3$)$_2$CHOH where □ represents (CF$_3$)$_2$C(C$_x$H$_y$)O$^-$ and ■ represents (CF$_3$)$_2$CHOH. HPMS conditions were as follows: neutral ratio (CF$_3$)$_2$CHOH/(CF$_3$)$_2$C(C$_x$H$_y$)OH = 0.6, buffer gas CH$_4$ at 4 torr, NF$_3$ at ~10 mtorr (source of F$^-$), temperature $T$ = 600 K, and equilibrium constant $K = 33$.

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 oxycarids 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). 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 0.6, buffer gas CH$_4$ at 4 torr, NF$_3$ at ~10 mtorr (source of F$^-$), temperature $T$ = 600 K, and equilibrium constant $K = 33$. It is due to a $\pi$-type donation from the functional group to the empty $\pi^*$ orbital of the methyl group.

For a more detailed explanation of experiment see Experimental Section (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, the observed very small changes observed for methyl substitution in CF3CHOH 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 C1 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 oxianionic groups. The resulting charge dispersal in the anionic moiety is the factor responsible for the acidifying effect of these substituents. For example, CICH2CO2H has a gas-phase acidity 12.5 kcal/mol greater than CH3CO2H and (CF3)2CHOH is 27.8 kcal/mol more acidic than (CH3)2CHOH.4 In fact (CF3)2CHOH has approximately the same gas-phase acidity as CH3CO2H. 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 
\[ V(r) = -\frac{\alpha^2}{2\epsilon(r)} \]
Since \( V \) depends on the square of the ionic charge \( \epsilon \), a much smaller stabilization is obtained when the charge is distributed over more than one center. For example, splitting of a single charge at distance \( r \) into three charges of \( 1/3e \) at distances \( r \) leads to a stabilization 
\[ -V(r) = \frac{\alpha^2}{2r^2} \]
which is only \( 1/9 \) of the \( -V(r) \) of the single charge. Thus, the spreading of the charge by the charge-dispersed anion 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 Taft11) 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 donor group such that the conjugation stabilizing the neutrals cannot occur.

One can expect that a reversal of the methyl-substituent effect will occur only after sufficient charge dispersal in the anion by electron-negative 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. alpha 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 CF3 groups. The fact that the charge dispersal caused by the two CF3 groups is very large is indicated by the acidity of the bis(CF3-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 NO2. 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. CH3CH(CI)CH2CO2H, 1951-12-8; HCh(CI)CH2CO2H, 107-94-8; CH3CH2CH(CI)CO2H, 1470-24-5; CH3CH2CH(CI)CO2H, 598-75-7; HCh(CI)CO2H, 79-11-8; CH3CH2CH(Br)CO2H, 80-58-0; CH3CH(Br)CO2H, 598-72-1; HCh(Br)CO2H, 79-08-3; CF3CH2OH, 75-89-8; CF3CH(OH), 374-01-6; CF3CCH3OH, 597-52-8; (CF3)2C(CH3)OH, 1515-14-6; (CF3)2CHOH, 920-66-1.