

hydrogen atoms at idealized positions) gave $R = 0.041$ and $R_w = 0.042$ and 1.12 for the standard deviation for an observation of unit weight. The highest peak in a final difference electron density map had a height of only $0.20 \text{ e } \text{Å}^{-3}$.

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Supplementary Material Available: Table 1, atomic coordinates for the non-hydrogen atoms; Table 2, bond lengths; Table 3, bond angles; Table 4, anisotropic thermal parameters; Table 5, hydrogen atom coordinates; a copy of Figure I (6 pages). Ordering information is given on any current masthead page.

Effect of Central Substituents on the Gas-Phase Acidities of Propenes

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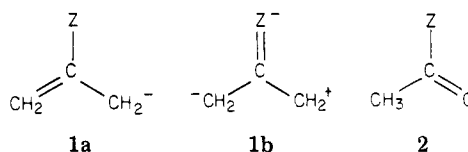
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The gas-phase acidities of a number of 2-substituted propenes have been measured by using ICR spectrometry. The acidities are rationalized in terms of structural effects on both acid and anion forms. MNDO calculations reproduce the acidities to $\pm 4.2 \text{ kcal/mol}$ and provide information on the interaction of the π orbitals of substituent and acid.

Electron-acceptor groups such as the carbonyl and nitro functionalities are known to stabilize adjacent anions by a mixture of resonance (π acceptor) and polar (σ acceptor) properties.¹ When various structural frameworks are placed between the substituent and the reactive group, then the differing mixtures of π and σ interactions can operate, the classic case being the difference between para- and meta-substituted benzene systems. There have been numerous ingenious attempts to separate the π and σ contributions to such stabilization such as by sterically constraining the geometry of the π systems of the substituent and the reactive site to reduce overlap of the orbitals.² Recent efforts have focused on the use of linear free-energy relationships to separate σ and π effects, primarily through the use of dual substituent parameter equations.³ There are now substituent constants that represent the polar and resonance properties of the more common substituent groups in both solution⁴ and gas phase,⁵ allowing mathematical separation of the two types of interactions.

One juxtaposition of π -interacting substituent and negatively charged group that has not been extensively investigated is that exemplified by the 2-substituted allyl-type anion 1. In formal valence bond terms, the negative charge cannot be delocalized into the substituent Z without involving charge-separated resonance structures



such as 1b. This is, however, a "Y-delocalized" system⁶ where any substituent, either π donating or π accepting, can result in stabilization of the anion.

The highest occupied molecular orbital (HOMO) of 1 involves little or no overlap between the π orbitals of the substituent and those of the allyl anion, due to the node at the central carbon. Thus, we might expect the acidities of the C2-substituted propenes to be largely determined by polar effects, although the lower orbitals should introduce some π interaction between the allyl moiety and the substituent.

Carboxylic acids provide anions analogous to 1, and a vast body of acidity data exists for such compounds.⁷ Unfortunately, the substituents of most interest in this work, strong π donors such as NR_2 and OR , and π acceptors such as NO_2 and $\text{C}\equiv\text{N}$, result in compounds in this series that hydrolyze too readily in aqueous solution for the $\text{p}K_{\text{a}}$ s to be measured. In addition, the lone pairs on the carbonyl and hydroxy oxygens result in the Y-delocalized π system being present in both acid and anion forms, so any effect on acidity due to it will be attenuated. Substituted carbonyl compounds such as 2 do not have the Y-delocalized π system in the neutral and have acidities accessible in dimethyl sulfoxide as solvent.⁸ Only a limited number have been measured, however, and none with the stronger π -acceptor groups such as NO_2 or $\text{C}\equiv\text{N}$. To avoid all problems with counterions, differential solvation, and solvolytic reactions, we have investigated the anionic reactions of a series of 2-substituted propenes in the gas phase using ion cyclotron resonance (ICR) mass spec-

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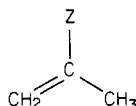
trometry.⁹ In addition, to provide further insight into the nature of the substituent-reactive site interactions, we have performed MNDO semiempirical calculations¹⁰ on all acids and anions investigated here, as well as for some substituted propenes not readily accessible experimentally.

Experimental Section

The ICR spectrometer and the techniques used have been previously described.¹¹ The chemicals used were obtained commercially except for 2-nitropropene, which was prepared by literature methods.¹² All compounds were purified by distillation or preparative gas chromatography, and the purity of each was checked by the ICR positive mass spectrum. Negative ions were generated by electron impact on NH₃ (NH₂⁻ at 6.3 eV), H₂O (H⁻, thence HO⁻ at 6.2 eV), and various alkyl nitrites (RO⁻ at 0 eV). All reactions proposed were confirmed by double resonance.⁹

Results

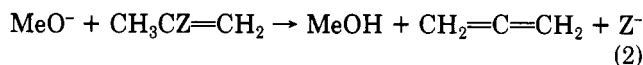
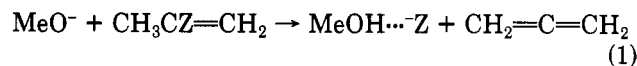
The gas-phase anionic chemistry of 3a-1 has been examined in the ICR spectrometer. Of these, only those with



3a, Z = H	h, Z = CF ₃	o, Z = OH
b, CH ₃	i, NO ₂	p, SiH ₃
c, CH=CH ₂	j, CO ₂ Me	q, Ph ₂
d, C ₆ H ₅	k, CHO	r, SH
e, OCH ₃	l, Br	s, Cl
f, F	m, BH ₂	
g, C≡N	n, NH ₂	

Z = H, CH₃, C≡N, and CF₃ give proton-transfer reactions sufficiently free from side reactions in their own vapor to allow exact determination of the $\Delta G^\circ_{\text{acid}}$ by the usual equilibrium techniques.¹¹ Propene is equal to water in acidity,¹¹ while 2-methylpropene is 1.1 kcal/mol more acidic. Methacrylonitrile (3g) can be equilibrated with both benzyl alcohol ($\delta\Delta G^\circ_{\text{acid}} = 1.2$ kcal/mol, alcohol less acidic) and with methoxyacetonitrile ($\delta\Delta G^\circ_{\text{acid}} = -0.1$, propene less acidic) to give $\Delta G^\circ_{\text{acid}} = 364.0$ and $\Delta H^\circ_{\text{acid}} = 371.6$ kcal/mol, consistent with the data of Dawson and Nibbering.¹³ Propionitrile and the trifluoromethylpropene 3h are equal in acidity, for $\Delta G^\circ_{\text{acid}} = 366.1$ kcal/mol and $\Delta H^\circ_{\text{acid}} = 371.0$ kcal/mol. For all the propenes in this work, we use the same $\Delta S^\circ_{\text{acid}}$ as for the parent.⁴ While there is undoubtedly some difference in change of internal rotation of the Z group upon proton loss in the various species here, it cannot be estimated easily and probably results in $T\Delta S^\circ_{\text{acid}}$ changes of at most a few tenths of a kcal/mol. The uncertainties in these are ± 2.3 kcal/mol absolute and ± 0.2 kcal/mol relative to the other acids in the gas-phase acidity scale.

A variety of side reactions interfere with the exact acidity determination for other systems. For 2-fluoropropene (3f), it is reported that reaction with methoxide gives both an (M - 1)⁻ ion and MeOH...F. The latter ion is through to arise from 1,2-elimination to give allene as in reaction 1.¹⁴ Such reactions are well-known in the gas



phase and occur when simple elimination to give a free anionic leaving group is endothermic, but less so than the hydrogen-bond strength of the cluster ion MeOH...Z⁻. The presence of both deprotonation product and clustered elimination product here is evidence for the deprotonation being just barely exothermic. For bases weaker than methoxide, such as the larger alkoxides, only the elimination product F⁻ is observed as in reaction 2. We thus place $\Delta G^\circ_{\text{acid}}$ for 3f between that of methanol and ethanol or at 371.7 ± 3 kcal/mol.

The methoxy compound 3e gives an (M - 1)⁻ ion on reaction with hydroxide but no such ion with methoxide, bracketing the acidity at 379 ± 6 kcal/mol for $\Delta G^\circ_{\text{acid}}$. The major peaks for reaction with methoxide are *m/z* 57 from displacement on methyl to give acetone enolate and *m/z* 63 from the clustering elimination reaction 1. Weaker alkoxide bases behave similarly to methoxide. Isoprene (3c) and α -methylstyrene (3d) are similarly deprotonated by hydroxide but not by methoxide. Unlike Squires and co-workers¹⁵ who observed eight exchanging hydrogens when the anion of the styrene was reacted with D₂O in the flowing afterglow, we observe only the four allylic hydrogens undergoing deuterium exchange in the ICR. We are unsure of the reason for this discrepancy and can only suggest that the slightly larger number of reactive collisions in the flowing afterglow spectrometer and the presence of a thermalizing helium bath gas may contribute to the different reactivity observed there.

Methoxide reacts with 2-nitropropene to give a small amount of (M - 1)⁻ anion, but the principal reaction channels give the radical anion *m/z* 86 and nitrite ion, *m/z* 46. Electron transfer from methoxide to nitroethylene¹⁶ and nitro aromatics¹⁷ has previously been observed. While nitrite ion is always observed when alkyl nitrites are used as the source of alkoxide ions in the ICR due to displacement and elimination reactions,¹⁸ the nitrite signal observed here is much larger than that seen for the other propenes. Double-resonance indicates that its source is methoxide. The thermochemistry in Table I indicates that the 1,2-elimination reaction (2) to allene should be exothermic. This would account for the low abundance of (M - 1)⁻ ion in spite of it being accessible thermochemically from methoxide. There are also small peaks in the unquenched spectrum attributable to slow condensation of the (M - 1)⁻ ion with the neutral nitropropene followed by loss of HONO and to simple addition of nitrite to the propene.

Methyl methacrylate (3j) gives no (M - 1)⁻ ion with any alkoxide base although such a reaction is expected to be exothermic. The parent peak in all cases is *m/z* 85, corresponding to displacement on methyl to give the carboxylate anion. This reaction should be ca. 35 kcal/mol exothermic for methoxide. Such reactivity of esters has been observed to be fast and often the principal reaction channel in the gas phase.¹⁹ A small amount of (M + 1)⁻

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Table I. Gas-Phase Acidities and Thermochemistry for 2-Substituted Propenes

Z ^a	$\Delta H^\circ_{\text{acid}}{}^b$	$\Delta H^\circ_{\text{acid}}{}^c$	$\sigma_1(\text{Z})^d$	EA(AH) ^e	EA(A ⁻) ^f	DH ^g	$\Delta H^\circ_{\text{H}^-}{}^{h,j}$	$\Delta H^\circ_{\text{elim}}{}^{i,j}$
H	390.8 ± 0.2	388.1	0.0	26	14	89	18	51
CH ₃	390.2 ± 0.2	388.1	-0.04	22	16	91	21	59
CH=CH ₂	385.0 ± 5	386.4	0.05	20	20	92	38	> 43
Ph	385.0 ± 5	381.5	0.10	-2	25	93	33	68
perp ^l		382.0		6	25			
OMe	385.0 ± 5	384.2	0.27	24	23	90	<10	26
F	378.0 ± 3	377.7	0.50	12	26	91	27	22
CHO	374.0 ± 3	378.1	0.31	-1	26	91	61	68
C≡N	371.6 ± 0.2	374.0	0.56	-1	32	92	56	24
CF ₃	371.0 ± 0.2	369.0	0.45	-4	36	91	67	29
NO ₂	<371.0	360.0	0.65	-23	44	90	81	-4
perp ^l		358.2		8	46			
CO ₂ Me		376.3	0.30	-3	27	90	60	
perp ^l		374.7		8	29			
BH ₂		383.8	-0.1 ^k	-3	20	90	68	
perp ^l		384.3		22	20			
NH ₂		383.8	0.12	23	19	90	<28	31
perp ^l		383.2		21	19			
OH		382.2	0.25	26	21	90	<10	37
SiH ₃		383.7	-0.10	5	27	97		45
PH ₂		381.5	0.04 ^k	13	24	92		40
SH		379.2	0.25	10	27	92		10
Cl		372.8	0.46	13	33	93		-9

^a Substituent on the 2-carbon of propene. ^b Experimental, see text, kcal/mol. Uncertainty is relative to other propenes. ^c From MNDO calculations, kcal/mol. ^d Reference 4. ^e Vertical electron affinity of the propene (LUMO energy), from MNDO calculations, kcal/mol. ^f Vertical electron detachment energy of the allyl anion (HOMO, energy), from MNDO calculations, kcal/mol. ^g For CH₂=CZCH₃ → CH₂=CZCH₂· + H·, calculated from eq 4. ^h For (CH₃)₂C=Z⁻ → CH₂=CZCH₃ + H⁻, kcal/mol. For CH₃O⁻ → CH₂=O + H⁻, $\Delta H^\circ = 43$ kcal/mol, ref 11. ⁱ For CH₂=CZCH₂· → CH₂=C=CH₂ + Z⁻, kcal/mol. ^j Calculated from known thermochemistry, ref 11. Blank indicates insufficient data to estimate $\Delta H^\circ_{\text{f}}$ for one of the species. ^k Estimated by the authors on the basis of electronegativity trends. ^l Previous substituent rotated 90°.

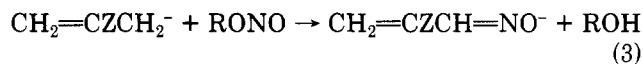
ion is also observed, arising from *m/z* 31, which we believe to be hydride transfer from HNO⁻ or CH₃O⁻.²⁰ Formation of an *M* + 1 ion is also observed for the aldehyde **3k** and for **3h**. The pertinent thermochemistry is given in Table I. It is evident that only those propenes with hydride affinities greater than that of CH₂=O undergo this reaction, with the exception of the nitropropene. This same pattern of reactivity has been observed for the corresponding ethylenes.¹⁶

Methacrolein (**3k**) gives a small amount of (*M* - 1)⁻ ion (3% of the parent peak) on reaction with methoxide, but none with neopentoxide. We thus place its acidity between these two alcohols at $\Delta G^\circ_{\text{acid}} = 374 \pm 3$ kcal/mol. The (*M* + 1)⁻ ion, as mentioned above, is prominent, but the major products are peaks at *m/z* 109 and 111. Double resonance indicate that these arise from the (*M* - 1)⁻ ion, explaining its small abundance at long times. These also do not appear on reaction with neopentoxide, since deprotonation of the propene does not occur there. No deuterium exchange is observed for either *m/z* 109 or 111 with CH₃OD or D₂O, and they are not shifted in mass when CD₃O⁻ is used as the primary anion. The *M* + 1 anion does increase in mass by 1 amu when the latter ion source is used as expected. These two signals correspond to condensation of the (*M* + 1)⁻ ion with the neutral propene followed by loss of CO or H₂CO. A similar addition product, followed by loss of HF, is seen for the trifluoro compound **3h**; there is precedent for such additions and losses.¹³ Small amounts of *m/z* 93 and 121 are also formed from methacrolein. It may be that the acidic site in the aldehydic case is not the hydrogen leading to the allyl anion but rather the formyl proton. These appear to be similar in acidity to the alcohols, in terms of the Riveros reaction of formate esters.²¹

We do not observe deuterium exchange into the (*M* - 1)⁻ of methacrolein with MeOD²² but believe this to be due to the rapid formation of the *m/z* 109/111 condensation products from the (*M* - 1)⁻ ion rather than a lack of equal exchangeable hydrogens. Both ab initio and MNDO calculations²³ indicate that the formyl hydrogen is at least 7 kcal/mol less acidic than the methyl group.

The bromide **31** gives only Br⁻ upon treatment with any of the anionic bases used here. As with the nitro substituent, the thermochemistry in Table I indicates that for 2-chloropropene, elimination from the (*M* - 1)⁻ ion to give allene and chloride should be exothermic. While the MNDO program used to obtain these data does not include the parameters to calculate the analogous values for the bromo compound, it is likely that such an elimination should be even more favored for **31**.

For all propenes giving (*M* - 1)⁻ ions with CH₃ONO, small amounts of the *M* + 28 peak are observed, especially if the alkyl nitrite pressure is allowed to rise above 1 × 10⁻⁷ torr. This ion corresponds to a Claisen-type condensation of the (*M* - 1)⁻ ion with the nitrite ester as in reaction 3.²⁴



Discussion

As noted in the introduction, the 2-substituted propenes investigated in this work are isoelectronic with carboxylic acids and methyl ketones. Taft^{5b} has shown that, for a limited number of substituents *Z*, the gas-phase acidities

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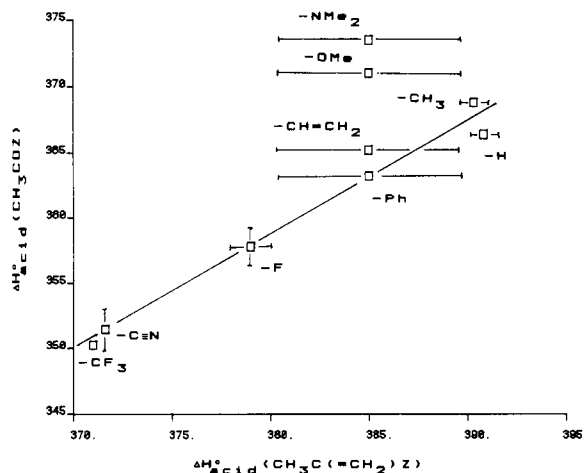


Figure 1. $\Delta H^\circ_{\text{acid}}$ values for the 2-substituted propenes $\text{CH}_3\text{C}(\text{Z})=\text{CH}_2$ vs. the acetyl compounds $\text{CH}_3\text{C}(\text{Z})=\text{O}$. The line is a least-squares fit to all points except save NMe_2 and OMe . Acetyl acidities are from ref 5. Scales are in kcal/mol, uncertainty bars are relative values.

of ZCO_2H and ZCOCH_3 parallel each other, with the acidities of the carboxylic acids ca. 30% more sensitive to substituent effects than for the acetyl compounds. This increased sensitivity in ZCO_2H is attributed to "the more central position of the charge"^{5b} in the carboxylate anion, since it would be more directly in the line of the dipolar field of the substituent Z than when the charge is on the oxygen in the enolate. For the 2-substituted allyl anions investigated in this work, it might be expected that saturation effects²⁵ arising from the relatively weak acidity of the propenes, plus the average central position of the negative charge due to the symmetry of the allyl anion, would result in the largest sensitivity to the substituent of all. Instead, Figure 1 reveals that the propene acidities are less sensitive to substituent effects than those for the carboxylic acids and comparable in sensitivity to those for the acetyl compounds, except for the good π -donor groups OMe and NMe_2 .

An explanation of this requires a more detailed orbital analysis involving interactions in both the acid and anionic forms. Substituents capable of π donation or acceptance would be expected to have a relatively small effect on the energy of the allyl anion via that interaction, since the group is located on a carbon that is a node in the HOMO of the π system, "inactive" in PMO terminology.²⁶ Thus σ (polar) effects should predominate in the anion. For the neutral propenes with substituents such as NR_2 and OR , however, a three-atom four-electron system exists, where the presence of the electronegative atom will stabilize the π orbitals.²⁶ A similar argument applies for those substituents such as $-\text{CH}=\text{O}$ where the four-electron system extends over four atoms. The net effect in all cases is stabilization of the acid form, with a reduction in acidity, for both π -donor and π -acceptor substituents. The size of this effect is consistent with the 3 to 7 kcal/mol stabilizations found by Hine and Skoglund for such substituents on double bonds.²⁷

Figure 1 indicates that the amino and alkoxy groups are less acidifying for the acetyl compounds than for the propenes, relative to π -donor groups. This is ascribed to

the substituent effect on the neutral acid form: the four-electron three-atom π system in the neutral acetyl compound contains two electronegative atoms, so its π orbitals are lower in energy and the molecule is stabilized, relative to the propenes with only one electronegative atom.²⁶ The methyl group as substituent is less capable of π interactions due to lack of a lone pair or π system. In both the carboxylic acid and acetyl series, methyl is acid-weakening compared to hydrogen, while the opposite is true for the propenes. The first effect has been attributed to the polar effects of methyl vs. hydrogen when attached to sp^2 carbon in both acid and anion.³ The inversion for the propenes may be rationalized as a polarizability effect. The acidity of the propenes is so low that the anion will utilize any stabilizing interaction available and the polarizability interaction is enhanced to where it exceeds the polar effect.

In order to provide further information on the substituent-reactive center interactions seen in these systems and to yield some information for those cases where other reactivity prevents experimental determination of acidities, MNDO semiempirical calculations¹⁰ have been performed on a number of these acids and their anions. The MNDO method has been shown to reproduce gas-phase acidities of compounds giving delocalized anions fairly reliably, though acids giving localized anions are calculated to be 5–20 kcal/mol less acidic than found experimentally, for second-row anions.²³ All geometric variables in both the acid and anion forms were allowed to vary in the geometry optimization, with certain exceptions. It was found that the compounds with NH_2 , Ph , CO_2H , and NO_2 groups optimized to a conformation where the π systems of the substituent and of the propene or allyl anion were perpendicular to each other. Such a geometry is counter to experimental data²⁸ and ab initio calculations.²⁹ When the p orbitals of these substituents are constrained to be parallel to the π orbitals of the three-carbon fragment, the calculated acidities change by only 1.8 kcal/mol for the worst case. This is due to parallel effects on the heats of formation of the acid and anion forms. For example, for the phenyl compound 3d the perpendicular form is calculated to be more stable than the planar form by 7.7 kcal/mol for the acid and by 7.2 kcal/mol for the anion. The carbomethoxy and nitro groups show similar, though smaller, effects.²⁹ This is not a universal problem, in that planar geometries are preferred for the CHO and BH_2 groups. The amino group is of special interest, in that geometry optimization from several different starting geometries results in a pyramidal amino group, with the lone pair perpendicular to the π system of both the acid and anion, as if NH hyperconjugation were preferred. When the amino group's lone pair is constrained to be parallel to the π system of the C3 fragment, however, the resulting geometry optimization results in lower enthalpies for both forms, by 0.6–1.2 kcal/mol. Other than for these specific rotations, the bond lengths and angles of the acids are as expected, within the known variances of the MNDO method.¹⁰ Removal of the acidic proton results in a shortening of the propene $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^2}$ bond by $0.15 \pm 0.05 \text{ \AA}$ in all cases and a lengthening of the $\text{C}=\text{C}$ bond in the allylic moiety by $0.01-0.02 \text{ \AA}$. The bond between the substituent and the central carbon likewise increases in length by $0.01-0.04 \text{ \AA}$ in all cases upon proton removal. This is in

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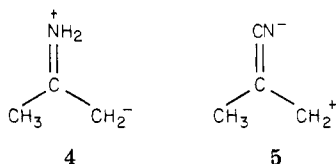
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contrast to the cases where the substituent is directly conjugated to the anionic site in carbon acids, and a shortening of the C-Z bond occurs on proton removal.^{2e-h} The three-carbon portion on the allylic anions are planar in all cases.³⁰

The calculated acidities are given in Table I. For those propenes where experimental equilibrium acidities are available (Z = H, CH₃, C≡N, CF₃), the calculated values are within ±4.2 kcal/mol of the experimental value. For the acids where only a bracketing of the acidity could be achieved due to lack of standard acids (Z = OMe, Ph, CH=CH₂) or due to interfering side reactions (Z = F, CHO, NO₂), the calculated acidities are consistent with the observed reactivities. The only propene that experimentally gives a stable radical anion, 2-nitropropene, is the only case in the calculations where the lowest unoccupied molecular orbital is appreciably bound (electron affinity = 22.6 kcal/mol by Koopman's theorem). The lowest unoccupied molecular orbitals are calculated to be bound by 1–3 kcal/mol for Z = CF₃, C≡N, CO₂Me, and BH₂, but this is within the uncertainty of the method, and such weakly bound radical anions probably would not stand up to experimental conditions. The expected decrease in substituent–double bond overlap on proton loss is seen in the calculations as a lengthening of the C₂–Z bond by 0.01–0.04 Å in all cases upon deprotonation. In addition, those second-row substituents capable of π-electron donation (CH₃, NH₂, OH, F) are calculated to have an excess negative charge of –0.01 to –0.10 unit on the methylene carbon in the neutral propene, consistent with structures such as 4, while the resonance-withdrawing groups (BH₂, CF₃, CHO, CO₂Me, NO₂, C≡N) all exhibit +0.01 to +0.08 charge on the methylene as in 5.



If the substituent effect on the anions is primarily polar in nature, then the acidity data should correlate with the polar parameter σ_1 .⁴ Figure 2 reveals a general trend of the calculated and experimental acidities following this parameter, with second- and third-row substituents on separate but parallel lines. The calculated acidities are in the expected polar order: CH₃ < NH₂ < OH < F and SiH₃ < PH₂ < SH < Cl, with the third-row substituents more acidic than the second by about 5 kcal/mol, though without experimental verification, this could be an artifact of the MNDO method. Both electronegativity and various measures of polar effects such as σ_1 predict that the third-row groups should be less electron accepting than the corresponding second-row substituents. The calculated increase in acidity with the larger groups can be attributed either to the increased polarizability interactions in the anion for the third-row substituents or to greater resonance stabilization of the neutral acid relative to the anion due to structures such as 4 and 5 by the second-row elements. The second-row groups are more comparable in size to the propene system and will overlap better.

For the second-row substituents, those propenes with π-acceptor substituents are considerably more acidic, both

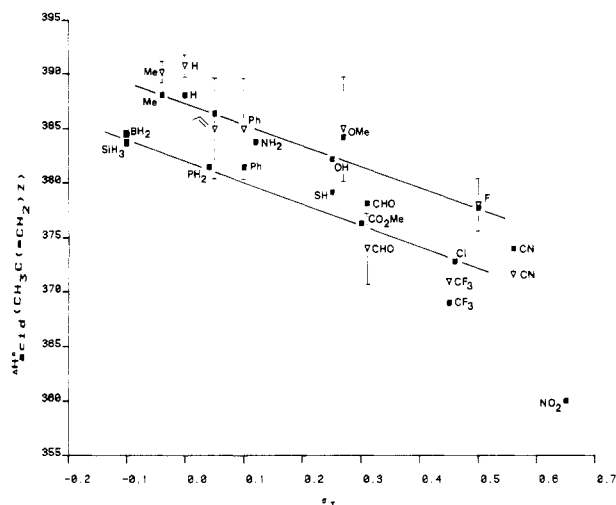


Figure 2. $\Delta H^\circ_{\text{acid}}$ for $\text{CH}_3\text{C}(\text{Z})=\text{CH}_2$ acidities, experimental (∇) and MNDO (\blacksquare). The σ_1 values are from ref 4, except PH_2 , estimated from data in Rakshys, J. W.; Taft, R. W., Jr.; Sheppard, W. A. *J. Am. Chem. Soc.* 1968, 90, 5236, and BH_2 , estimated as –0.1. The upper line is a least-squares fit to the MNDO values for CH_3 , NMe_2 , OMe , F ; the lower line, to the third-row groups. Uncertainty bars are relative values.

experimentally and by the calculations, than expected from the polar effect alone. This is contrary to the arguments advanced above concerning π interactions in the acid form, but examination of the π MOs from the calculations provides a rationale for this. The allyl anions with second-row hydrides as substituents can be taken as perturbations of an allyl anion by a p orbital on the heteroatom. For the electronegative substituents, the HOMO, nonbonding to the substituent, is not perturbed, but the higher and lower MOs are appreciably lowered in energy. There are thus three bound orbitals for the six electrons to go into. The MNDO calculations show all these π orbitals becoming increasingly lower in energy as the π-accepting ability of the substituent increases, as in the series $\text{CH}=\text{CH}_2$, $\text{C}\equiv\text{N}$, $\text{CH}=\text{O}$, NO_2 . This order parallels the deviations of these acids from the line of the second-row hydride groups in Figure 2. For BH_2 , one of the degenerate orbitals is raised in energy, and the four electrons go into only two bound orbitals. There is still stabilization of the anion, due to the lower π orbital, as seen in the deviation of the calculated BH_2 acidity from the line in Figure 2. The deviation is relatively small, however, because the borane substituent cannot use its ability as the strongest π-acceptor group known³¹ (σ_{R} of ca. 1.4) to stabilize the allyl anion by direct overlap in the HOMO.

The structure of the anions suggest that a relationship might exist between the propene acidities and σ_{m} , another case where there are no direct π interactions with the reactive site but polar effects can operate. The experimental data give a relatively poor correlation ($r = 0.971$) with $\rho = -27 \pm 4$. There are reversals for Z = H and CH_3 and for trifluoromethyl and cyano from the ordering predicted by σ_{m} . The experimental data are too few and not of sufficient precision for a proper dual substituent parameter analysis,⁴ but for σ_1 and $\sigma_{\text{R}} - (g)$,⁵ ρ_1 of –23 and ρ_{R} of –8 are obtained ($f = 0.12$ and 0.25, respectively). The polar effects are clearly much more important than π interactions. Other σ_{R} parameters gave even worse correlations.

The rotation of the substituent with respect to the propenyl or allylic moieties should allow separation of π

(30) The 2-nitroallyl anion, unlike all other cases here, does not remain planar in the C3 fragment upon geometry optimization. The NO_2 group rotates 90° to the C3 group, and the terminal CH_2 groups also rotate 23° in a conrotatory fashion. The MNDO method is known to give larger errors in calculations involving N–O bonds, as noted in ref 10.

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and σ effects.² For the substituents Ph, NH₂, BH₂, NO₂, and CO₂Me, MNDO calculations on the perpendicular form indicate little change in acidity, due to small and parallel effects on the heats of formation of the acid and anion forms, as shown in Table I. The small effect on the anion's enthalpy for the good π -acceptor groups BH₂ and CO₂H and good π -donor group NH₂, agrees with the conclusion above, that there is little π interaction between the allyl anion's π system and the substituent. The energy of the anion's HOMO (vertical electron affinity) is virtually unaffected by rotation of the substituent. For the neutral propenes, rotation of the substituent does not appreciably affect the heat of formation but does destabilize the HOMO and LUMO (vertical electron affinity) for the good π -acceptor groups.

Gas-phase acidities may be expressed as a function of the homolytic bond strength of the acidic hydrogen and the electron affinity of the radical thereby produced, as in eq 4.³² For the aliphatic alcohols, the RO-H bond

$$\Delta H^{\circ}_{\text{acid}}(\text{AH}) = \text{DH}(\text{AH}) + \text{IP}(\text{H}\cdot) - \text{EA}(\text{A}\cdot) \quad (4)$$

(32) Baughn, E. C.; Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* 1941, 37, 377.

strength is nearly constant and the variation in the alcohols' acidity is attributable to the difference in electron affinity of the alkoxy radicals.³³ If the binding energy of the HOMO of the allyl anions here is taken as the vertical electron affinity, by Koopman's theorem, then we can derive the C-H bond strength of the propenes by an inversion of eq 4. This data is presented in Table I. A nearly constant bond strength of 91 ± 2 kcal/mol is found for most propenes, even though the electron affinities range from 14 (Z = H) to 44 (Z = NO₂) kcal/mol. The experimental value for the parent propene bond strength is 86.3 ± 1.5 kcal/mol.³⁴ This small effect of the substituents on the allyl radical stability is consistent with the relatively small π interactions occurring in the allyl form and the lack of polar effects on radical stabilities.

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Transmission of Polar Substituent Effects in Bicycloalkane Systems. Synthesis and Nuclear Magnetic Resonance Study (Carbon-13 and Fluorine-19) of 4-Substituted Bicyclo[2.2.1]hept-1-yl Fluorides¹

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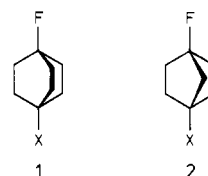
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A number of 4-substituted (X) bicyclo[2.2.1]hept-1-yl fluorides (2) have been synthesized, and their ¹³C and ¹⁹F NMR spectra have been recorded. The synthesis of all these compounds, except for the parent (2, X = H) of the series, has been accomplished from 4-fluorobicyclo[2.2.1]heptane-1-carboxylic acid (2, X = COOH) by, in the main, functionalization procedures previously employed for the synthesis of 4-substituted (X) bicyclo[2.2.2]oct-1-yl fluorides (1) from the corresponding acid (1, X = COOH). The key new precursor compound (2, X = COOH) was prepared by a new route to 1,4-disubstituted bicyclo[2.2.1]heptane derivatives. A standard multiple linear least-squares regression analysis of the ¹⁹F substituent chemical shifts (SCS) against polar substituent parameters reveals that these NMR substituent-probe parameters of system 2 are predominantly manifestations of electric field and electronegativity effects. Most importantly, the long-range electronegativity effects are found to be of opposite sign to those observed in system 1. A qualitative explanation for this striking phenomenon is advanced in terms of σ -electron delocalization mechanisms ("through-bond" and "through-space" effects). The implication of these results with respect to the transmission of polar substituent effects in saturated systems as monitored by chemical reactivity probes is noted.

Introduction

1,4-Disubstituted bicycloalkanes, being geometrically rigid aliphatic substrates in which the substituent and side-chain probe are located at sterically remote sites, are attractive model systems for investigating the nature of polar substituent effects without the concomitant encumbrances of stereochemical phenomena and π -resonance effects.²⁻⁴ In this connection, we recently presented a

systematic ¹³C and ¹⁹F NMR study of an extensive series of 4-substituted bicyclo[2.2.2]oct-1-yl fluorides (1).^{5,6}



Based on the results of a standard multiple linear least-squares regression analysis of the ¹⁹F substituent chemical shifts (SCS) of system 1 vs. polar substituent parameters^{7,8}

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