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Proton Transfers from ZCH_3 to ZCH_2^- (Z = F, Cl, Br, OH, SH, SeH). An *ab Initio* Investigation

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Energy profiles for the identity-reaction carbon-to-carbon proton transfers from carbon acids of the type ZCH_3 to their conjugate bases ZCH_2^- have been studied by *ab initio* methods. Gas-phase acidities of ZCH_3 species are reproduced well at MP2/6-31+G*//MP2/6-31+G*. The barriers to proton transfer relative to the separated reactants (ΔH_{TS}) in kcal mol^{-1} are F (2.2), Cl (−4.2), Br (−8.2), OH (−2.1), SH (−5.7), SeH (−11.0) at MP2/6-31+G*//MP2/6-31+G*. Values at MP4/6-31+G**//MP2/6-31+G* are very similar. The orders of acidities and barrier heights suggest that the polarizability of Z is the dominant effect on both. That two or more ion−dipole complexes of similar energy exist for each system implies that the complexes will be fluxional. It is doubtful that these proton transfers could be observed experimentally. The dominant process for $HYCH_2^-$ + CH_3YH would almost certainly be the transfer of the YH proton, and calculations on the S_N2 reactions $ZCH_2^- + CH_3Z \rightarrow ZCH_2CH_3 + Z^-$ (Z = F, Cl, Br) reveal them to be strongly exothermic with barriers 6−10 kcal mol^{-1} below those for the corresponding proton transfer processes.

Introduction

Identity reactions are valuable because they remove the effect of endo- or exothermicity on barrier height and thus enable one to examine the intrinsic factors affecting barrier heights. They are, unfortunately, difficult to study experimentally because isotopic labeling is required to distinguish products from reactants. This difficulty does not exist in computational chemistry, and there are consequently many cases in the literature of *ab initio* studies of identity reactions.

A particularly important class of identity reactions are those involving proton transfers to and from carbon, a process which is a part of many organic reactions. Pioneering work on simple systems was reported by Scheiner and his coworkers.[1−4] Later, Gronert applied the G2 method[5] to methane and other simple first and second row hydrides.[6] Evidence that acids yielding delocalized anions showed high barriers to deprotonation was found by work on acetaldehyde,[7−9] acetonitrile,[10,11] and propene.[11] That the barriers for identity reactions of two of these species are unusually high was shown by the fact that a plot of acidity vs barrier height for identity reactions of three-carbon acids yielding localized anions, methane, ethylene, and acetylene, was linear, whereas the points for acetaldehyde and propene fell well above the line.[11]

Intriguingly, the point for acetonitrile fell slightly below the line. That this point was not also well above the line was attributed to lesser delocalization by the cyano group than by the vinyl or carbonyl groups. Polarizability of the cyano group was suggested as the reason the point fell slightly below rather than slightly above the line. In order to test this point, two sets of carbon acids with substituents showing a graded range of polarizabilities were chosen: fluoromethane, chloromethane, and bromomethane, and methanol, methanethiol, and methaneselenol. The reaction examined in all cases was

$$ZCH_2^- + ZCH_3 \rightarrow ZCH_3 + ZCH_2^- \qquad (1)$$

In early work, Wolfe[12] examined four reactions (Z = H, F, Cl, and SH) at the 3-21G(3-21G*) level and reported that the barrier was "essentially constant". Actually it varies over a range of nearly 4 kcal, and it is now also known that 3-21G does not give an accurate account of proton-transfer barriers, so we decided to proceed with studies using more elaborate basis sets (6-31+G* and 6-31+G**) and correlation corrections (MP2 to MP4), which we had shown gave good values of gas-phase acidities and satisfactory agreement with experimental results.[7,11,13]

Computational Methods

The calculations utilized Gaussian 92[14] and Gaussian 94.[15] Most of the work utilized the standard basis sets 6-31+G* and 6-31+G**.[16,17] The calculations on the

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species containing bromine and selenium utilized the basis sets of Binning and Curtiss[18] for these atoms and the standard basis sets for the others. A few acidity calculations utilized the G2(MP2) method.[19] Correlation corrections utilized the Møller–Plesset method.[20–24] The enthalpies (ΔH) reported in the tables are corrected to constant pressure and for zero-point-energy differences from MP2/6-31+G*//MP2/6-31+G* calculations scaled to 0.95 to account for the overestimation of frequencies by Hartree–Fock methods.[25,26] The enthalpies were further corrected to 298 K for the contributions of the translational, rotational, and vibrational partition functions.[27] The vibrational contribution is not based on scaled frequencies, because inspection of numerous frequency calculations makes it doubtful that low-lying calculated frequencies (the only ones that contribute significantly to the vibrational partition functions) bear a predictable relation to experimental frequencies.[28]

Results and Discussion

As in our previous work, our criterion for the adequacy of the level of the calculations was their ability to reproduce experimental gas-phase acidities. Although the present systems are small enough that they could have been studied at higher levels than those chosen, we wanted to be able to compare them with results from our earlier studies.[7,11] The results are given in Table 1. It is immediately apparent that the results at MP2/6-31+G*//MP2/6-31+G* agree better with experiment than those at MP4/6-31+G**//MP2/6-31+G*. Two of the acids, CH_3F and CH_3Cl, have been studied by the G2 method.[5,29] These acidities agree well with experiment and also with the MP2/6-31+G*//MP2/6-31+G* values. Evidently there are compensating errors in the latter that are not as well balanced in the MP4/6-31+G**//MP2/6-31+G* values. As a double check, the G2(MP2) method[19] was used to calculate four of the acidities, shown in the last column of Table 1. The agreement of the MP2/6-31+G*//MP2/6-31+G* values with G2, G2(MP2), and the experimental results is excellent, leaving little doubt that the MP4/6-31+G**//MP2/6-31+G* values are too high. It is also obvious that the high-level calculations agree better with the CH_3Cl and CH_3Br experimental acidities of Hierl et al.[30] than with those of Ingemann et al.[31]

Table 1. Observed and Calculated Enthalpies for $ZCH_3 \rightarrow ZCH_2^- + H^+$

	ΔH			
Z	expt[a]	MP2/6-31+G*//MP2/6-31+G*	MP4/6-31+G**//MP2/6-31+G*	G2(MP2)
F	409.0[b]	409.0	412.6	410.9[f]
Cl	399.6,[c] 396.1[d]	400.5	404.5	397.9[g]
Br	396.7,[c] 392.8[d]	396.3	400.3	–
HO	–	413.3	417.7	414.8
HS	394.1[e]	397.5	403.1	396.0[h]
HSe	–	393.4	399.3	–

[a] ΔH of ionization in kcal mol^{-1}. [b] Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517–2529. [c] Reference 30. [d] Reference 31. [e] Reference 32. [f] The G2 method gives 410.4 (ref 29). [g] The G2 method gives 398.2 (ref 29). [h] A value of 398.1 at MP4/6-311+G**//6-311+G** has been reported by Downard, K. M.; Sheldon, J. C.; Bowie, J. H.; Lewis, D. E.; Hayes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8112–8115.

Table 2. Enthalpies[a] of Stationary Points in the ZCH_3 to $^-CH_2Z$ Proton Transfer

Z, level	ΔH_{well}	$\Delta H^{\ddagger}$ [b]	ΔH_{TS}[c]
F, MP2/6-31+G*//MP2/6-31+G*	−10.9	13.1	2.2
F, MP4[d]/6-31+G**//MP2/6-31+G*	−11.2	12.3	1.0
Cl, MP2/6-31+G*//MP2/6-31+G*	−11.3	7.1	−4.2
Cl, MP4[d]/6-31+G**//MP2/6-31+G*	−11.3	6.9	−4.3
Br, MP2/6-31+G*//MP2/6-31+G*	−15.8	7.6	−8.2
Br, MP4[d]/6-31+G**//MP2/6-31+G*	−15.6	7.5	−8.1
HO, MP2/6-31+G*//MP2/6-31+G*	−17.4	15.2	−2.1
HO, MP4[d]/6-31+G**//MP2/6-31+G*	−16.9	14.3	−2.6
HS, MP2/6-31+G*//MP2/6-31+G*	−7.2	1.5	−5.7
HS, MP4[d]/6-31+G**//MP2/6-31+G*	−7.3	1.6	−5.7
HSe, MP2/6-31+G*//MP2/6-31+G*	−13.4	2.4	−11.0
HSe, MP4[d]/6-31+G**//MP2/6-31+G*	−13.5	2.6	−10.9

[a] In kcal mol^{-1}. [b] $H_{TS} - H_{complex}$. [c] $H_{TS} - H_{reactants}$. [d] MP4SDTQ, frozen core approximation.

The $HYCH_2^-$ species exist in two stable conformations, one with the H–Y bond syn to the unshared pair and the other with it anti. The syn conformation is more stable for Y = O while the anti conformation is more stable for the other two species. The differences between the two conformations range from 1.3 to 4.9 kcal mol^{-1}, indicating that the less stable species makes only minor contributions to the equilibrium mixture. The acidities quoted thus refer to the more stable anion. It should also be noted that we found all $HYCH_2^-$ species to be stable with no tendency to rearrange spontaneously on optimization to the more stable CH_3Y^- species. Kass[32] has presented experimental evidence for the stability of $HSCH_2^-$.

Next the enthalpies of the stationary points in reaction 1 were calculated and are reported in Table 2. For these species, discrepancies between the MP2/6-31+G*//MP2/6-31+G* and the MP4/6-31+G**//MP2/6-31+G* enthalpies are much less than with the acidities, exceeding 1 kcal in just a single case. The well depths are in a range characteristic of anion–dipole complexes. With the exception of the oxygen species, the more stable complexes are those for the bromine and selenium species.

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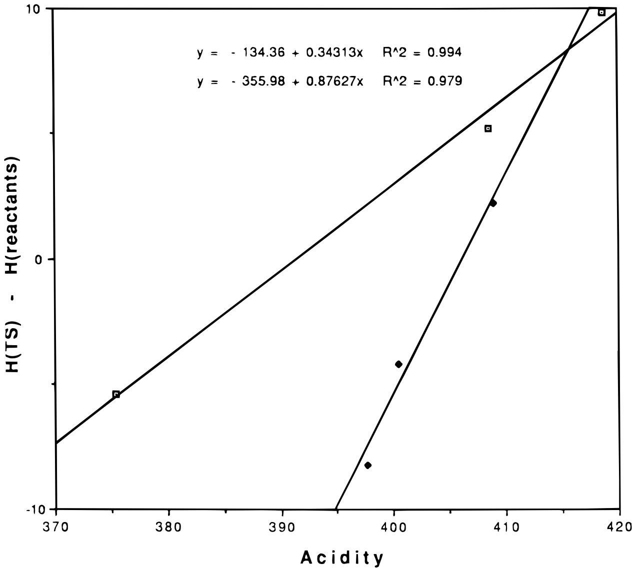

Figure 1. Plots of H(TS) − H(reactants) (= ΔH_{TS}) for identity-reaction proton transfers vs acidity (kcal mol^{-1}) at MP2/6-31+G*//MP2/6-31+G*. Open squares: Points for acetylene, ethylene, and methane. Closed diamonds: Points for bromomethane, chloromethane, and fluoromethane.

The barriers show a gratifyingly wide variation with substituent. The F−Br range is ca. 5 kcal in $\Delta H^\ddagger$ and 10 kcal in ΔH_{TS}. The corresponding O−Se range is ca. 12 kcal in $\Delta H^\ddagger$ and 9 kcal in ΔH_{TS}. The variation in ΔH_{TS}, which is a better measure of transition structure stability than $\Delta H^\ddagger$, is quite regular; it decreases monotonically in the order F > Cl > Br and HO > HS > HSe. The acidities increase (ΔH decreases) in this order.

Examination of substituent effects based on solution-phase data casts little light on these orders; σ_I values run F (0.50), Cl (0.46), Br (0.44), OH (0.25), and SH (0.25).[33] The order of our results is the reverse of that expected if the electronegativity of the substituent were the controlling factor: F (4.0), Cl (3.0), Br (2.8) and O (3.5), S (2.5), Se (2.4).[34] The order is, however, entirely consistent with polarizability as the controlling factor. Polarizabilities of the halogens, which are related to molar refractivity, are given as F (0.38), Cl (2.28), and Br (3.34).[35] Group molar refractivities run HO (2.85), HS (9.22), CH_3S (13.82), CH_3Se 17.03.[36] Though a complete set for HY is not to be found, these figures leave no room for doubt as to the order. It is thus clear that there is a convincing parallelism between increasing polarizability on the one hand and increasing acidity or decreasing proton-transfer barrier on the other.

Plots of barrier height (ΔH_{TS}) vs acidity are given in Figure 1 for the CH_3X series and in Figure 2 for the CH_3YH series, where they are compared in each case with the corresponding plot for CH_4, C_2H_4, and C_2H_2. The correlation in Figure 1 is excellent, showing a substantially steeper dependence of barrier height on acidity than for the hydrocarbon acids. Comparisons of the CH_3X values with the hydrocarbon values at constant acidity (the difference between the CH_3X barrier and a point read from the hydrocarbon line at the same acidity) reveals stabilizations of the transition structures range from 3.6 kcal for CH_3F to 10.3 kcal for CH_3Br. The correlation in Figure 2 shows more scatter but, if the CH_3OH point is considered to be anomalous, the points for CH_3SH and CH_3SeH fit rather close to the line defined by the methyl halides in Figure 1. The CH_3OH system is anomalous in two other respects: an unexpectedly low acidity (compare the CH_3OH − CH_3SH difference with the CH_3F − CH_3Cl difference in Table 1), and an unusually stable ion−dipole complex. The stabilization of the transition structures in the CH_3YH series runs somewhat greater than in in the CH_3X series, 7.9 to 11.8 kcal, especially for CH_3OH (9.5 kcal).

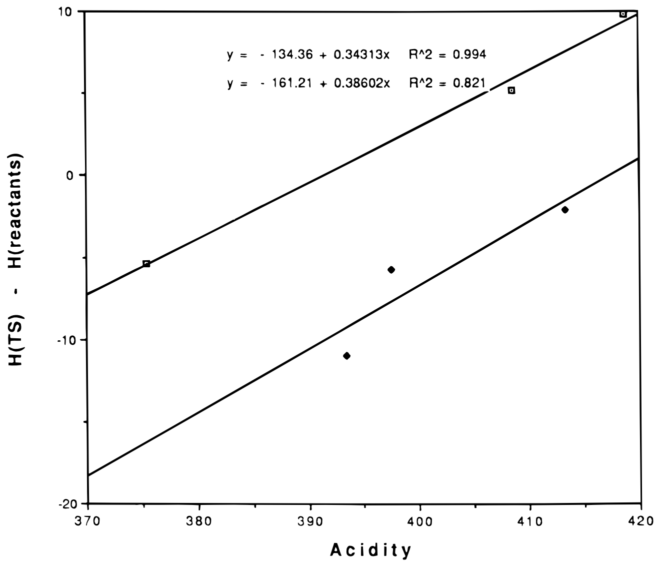

Figure 2. Plots of H(TS) − H(reactants) (= ΔH_{TS}) for identity-reaction proton transfers vs acidity (kcal mol^{-1}) at MP2/6-31+G*//MP2/6-31+G*. Open squares: Points for acetylene, ethylene, and methane. Closed diamonds: Points for methaneselenol, methanethiol, and methanol.

The obvious interpretation of these results is simply that the more polarizable the substituent, the more readily its electron cloud can deform to minimize repulsion between it and the electron cloud of an adjacent carbanion center. A more sophisticated statement of the same point can be based on the curve-crossing model of Shaik.[37] The transition structure can be regarded as a hybrid of the species **1**, **2**, and **3**. **1** and **2** must by symmetry contribute equally, but the contribution of **3**

$ZCH_2{:}^-\ H\text{-}CH_2Z \quad ZCH_2\text{-}H\ {}^-{:}CH_2Z \quad ZCH_2{:}^-\ H^+\ {}^-{:}CH_2Z$

1 **2** **3**

will depend on its energy, which will decrease steeply as the ability of Z to accommodate an adjacent negative charge increases. The contribution will thus increase steadily with polarizability, resulting in increasing stability of the transition structures and lower barriers. This argument will hold whatever the source of the stabilizing ability of Z, but we believe that polarizability is the most logical explanation.

Group charges calculated from NPA (natural population analysis) charges are given in Table 3.[38,39] The

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Table 3. Group Charges (NPA) at MP2/6-31+G*[a]

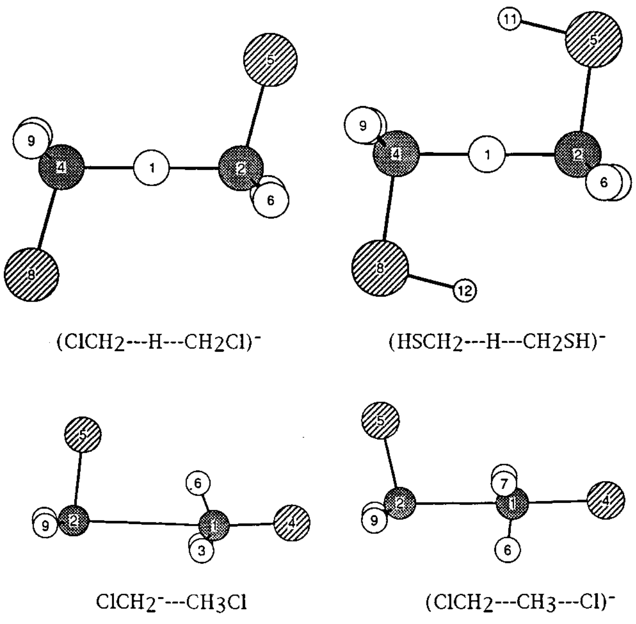
species	CH_2	Z^b	H^c
FCH_2^-	−0.409	−0.591	–
TS	−0.092	−0.544	0.272
$ClCH_2^-$	−0.616	−0.384	–
TS	−0.395	−0.270	0.329
$BrCH_2^-$	−0.616	−0.384	–
TS	−0.420	−0.247	0.333
$HOCH_2^-$	−0.542	−0.458	–
TS	−0.212	−0.413	0.250
$HSCH_2^-$	−0.854	−0.146	–
TS	−0.604	−0.055	0.319
$HSeCH_2^-$	−0.868	−0.132	–
TS	−0.635	−0.028	0.327

[a] Using the SCF density. [b] For the $HYCH_2^-$ species and TS, this is the charge on the HY group. [c] The proton in transit.

distribution of charge between Z and CH_2 in both the anions and the transition structures is clearly governed by the electronegativity of Z. That the F to Cl differences are greater than the Cl to Br differences, and the HO to HS differences greater than the HS to HSe differences, is not surprising, for the major changes in electronegativity are from F to Cl and from HO to HS (*vide supra*). While a dominance of electronegativity would seem to contradict our argument that polarizability determines the acidities and the barrier heights, closer examination shows that the charges actually support the interpretation in terms of the Shaik treatment. In the transition structures, the negative charge on CH_2 increases in the order F < Cl < Br and HO < HS < HSe, while the positive charge on the proton in transit increases in the same order. This is just as would be expected from a steadily increasing contribution of structure **3** to the resonance hybrid. Similarly, the negative charge on CH_2 in the anions increases in the same order as in the transition structures. In both cases this reflects the greater ease with which CH_2 accommodates a negative charge as Z becomes more polarizable.

The geometries of the transition structures do not vary much with the nature of the group Z, apart from the expected differences in C−Z bond lengths. The partial bond to the proton in transit decreases slightly from 1.433 to 1.415 Å from F to Br, and runs 1.397 to 1.410 to 1.405 Å along the series O, S, Se. Transition structures for Z = Cl and Z = SH are shown in the top line of Figure 3. The corresponding transition structures for the other Z's are almost the same as these. In particular, the Y−H bonds are syn to the partial C---H bonds in the transition structures of all three CH_3YH reactions.

The ion−dipole complexes show an interesting range of structures. The $CH_3X-^-CH_2X$ complexes show at least two stable structures for each X, one in which the $^-CH_2$ group is close to a proton of CH_3X, and the other in which it is aligned nearly linearly with the C−X bond so as to be in position for an S_N2 displacement. The energy differences between these two forms are at most 0.9 kcal (Table 4), so the actual structures must be fluxional. The "S_N2" complex for X = Cl is shown in Figure 3, and a direct comparison of the two types of complexes for X = Br is in the top line of Figure 4.



$(ClCH_2---H---CH_2Cl)^-$ $(HSCH_2---H---CH_2SH)^-$

$ClCH_2^----CH_3Cl$ $(ClCH_2---CH_3---Cl)^-$

Figure 3. Top row: Transition structures for identity-reaction proton transfers of chloromethane and methanethiol at MP2/6-31+G*//MP2/6-31+G*. Bottom row: Ion−dipole complex and transition structure for the S_N2 reaction of $ClCH_2^-$ and CH_3Cl at MP2/6-31+G*//6-31+G*.

Table 4. Enthalpies[a,b] of Stationary Points in the Reaction $ZCH_2^- + CH_3Z \rightarrow ZCH_2CH_3 + Z^-$ at MP4[c]/6-31+G*//6-31+G*

Z	ΔH_{well1}	$\Delta H^{\ddagger\,d}$	$\Delta H_{TS}{}^e$	$\Delta H_{well2}{}^d$	$\Delta H_{prod}{}^f$
F	−11.0 (−11.0)	4.0 (13.6)	−7.0 (2.6)	−78.5	−63.2
Cl	−10.6 (−10.8)	1.2 (7.1)	−9.4 (−3.7)	−91.0	−80.5
Br	−15.9 (−15.0)	−0.9 (7.8)	−16.8 (−7.1)	−94.0	−79.3

[a] In kcal mol^{-1}. [b] Figures for the corresponding proton transfer reactions from CH_3Z to ZCH_2^- are given in parentheses. [c] MP4SDTQ, frozen core approximation. [d] $H_{TS} - H_{complex}$. [e] $H_{TS} - H_{reactants}$. [f] $H_{products} - H_{reactants}$.

The $CH_3YH-^-CH_2YH$ complexes show more varied behavior. At least three stable structures exist for each Y. The most stable of each of the three complexes are shown in the second and third lines of Figure 4. The oxygen species is obviously oriented so as to take advantage of hydrogen bonding between the oxygen (atom 4) of $^-CH_2OH$ and the proton (atom 1) of CH_3OH. That this complex is more stable than the complexes from the sulfur and selenium species (Table 2) is very probably a consequence of this hydrogen bonding. The sulfur and selenium species are proton-transfer-like and S_N2-like, respectively. There is more variation in energy between the different complexes for each Y. For Y = O, the range is 3.5 kcal; for Y = S, it is 0.9 kcal; and for Y = Se, it is 1.9 kcal. In each case the two lowest structures are close enough (0.1−0.6 kcal) to ensure fluxional behavior.

It is interesting to ask whether any of these identity proton transfers might be observable in gas-phase experiments. In the case of the CH_3YH reactions, it is almost certain that the $HYCH_2^-$ ion would preferentially attack the YH proton of CH_3YH, which is not only more acidic but which should also show a lower intrinsic barrier to deprotonation than a CH proton. This problem does not exist with the CH_3X reactions, but another one does. The XCH_2^- ion can attack the methyl *carbon* instead of a methyl hydrogen, leading to the S_N2 reaction 2:

$$XCH_2^- + CH_3X \rightarrow XCH_2CH_3 + X^- \quad (2)$$

Although the intrinsic barrier to this displacement reaction is expected to be substantial, the results in Table 4 show clearly that the actual barriers for the S_N2 reactions are well below the corresponding barriers for

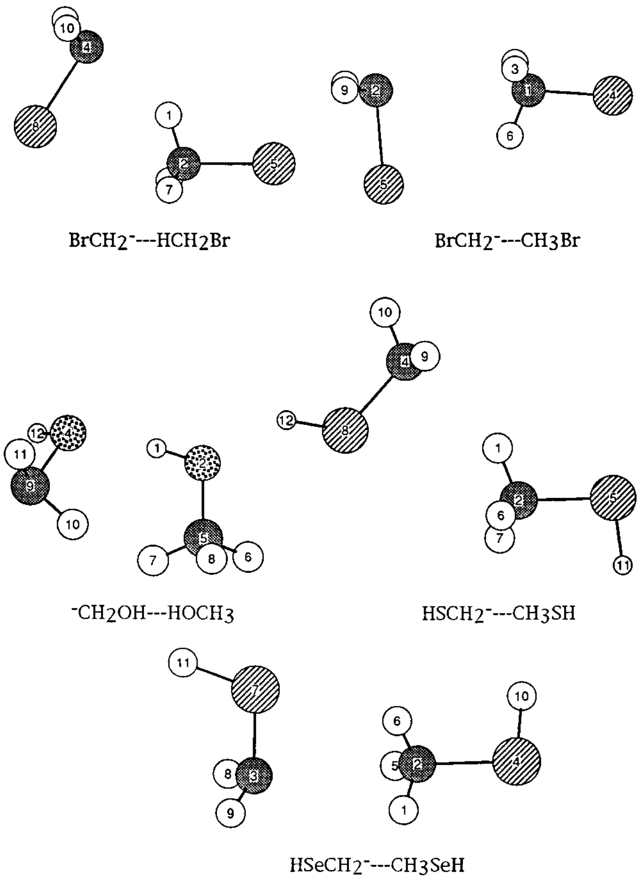


Figure 4. Ion−dipole complexes at MP2/6-31+G*//MP2/6-31+G*. Top row: proton-transfer-like and S_N2-like complexes of $BrCH_2^-$ and CH_3Br. Next two rows: most stable complexes of $HYCH_2^-$ and CH_3YH for Y = O, S, and Se, respectively.

the identity proton transfers, which are shown in parentheses below the barriers for the displacements. The differences are so great that this reaction was studied only up to MP4/6-31+G*//6-31+G*, since it appeared very unlikely that the differences would be reversed at a higher level.

The reason for the low barriers is apparent from the other figures in Table 4. The product ion−dipole complexes are lower in enthalpy than the reactants by 78 kcal or more, and the final products lower by 63 kcal or more. The consequences of this high exothermicity are illustrated in the lower line of Figure 3. The transition structure on the right is very similar to the ion−dipole reactant complex on the left and is thus quite reactant-like. A comment on the ion−dipole complex is in order. Note that in two cases in Table 4, the ion−dipole complex for the S_N2 reaction differs somewhat in energy from that for the proton transfer. This is because there are really at least two stable ion−dipole complexes, (*vide supra*) one with the carbon of the XCH_2^- ion closer to the methyl carbon as shown, and the other with it closer to a methyl hydrogen, the species optimized for the complexes leading to proton transfer.

Table 5. Thermochemical Contributions in kcal mol^{-1} to the Enthalpy Change of $XCH_2^- + CH_3X \rightarrow XCH_2CH_3 + X^-$ [a]

X	EA(XCH_2)	*D*(CX)	*D*(CC)	EA(X)	Δ*H*
F	4.6	112.8	90.0	78.4	−51.0
Cl	18.4	83.4	92.6	83.4	−74.2
Br	23.1	70.6	91.7	77.6	−75.6

[a] Data from refs 40 and 41.

At first sight the extreme exothermicity of the S_N2 reaction is unexpected, for the C-C bond being formed is actually weaker than the C-F bond and only ca. 10−20 kcal stronger than the C-Cl and C-Br bonds. A thermodynamic cycle (Scheme 1), however, shows that the *ab initio* thermochemistry is qualitatively entirely reasonable. From the Scheme, the overall enthalpy change of reaction 2 is given by

$$\Delta H = \mathrm{EA(XCH_2)} + \mathrm{D(CX)} - \mathrm{D(CC)} - \mathrm{EA(X)}$$

The information needed to apply this equation can be found in or derived from data in standard compilations.[40,41] The necessary values and the resulting enthalpy changes for reactions 2 are given in Table 5. The enthalpy changes run somewhat lower than the *ab initio* values in Table 4, but they are in the same order and are also strongly exothermic. The contributions from the CC bond energies and the electron affinities of X are the factors which make the reactions exothermic, while the most important contributor to the variability of Δ*H* is the CX bond energy.

Summary

The carbon acidity of ZCH_3 (Z = F, Cl, Br, HO, HS, and HSe) increases, and the barrier height for the identity proton transfer from ZCH_3 to ZCH_2^- decreases in the order of increasing polarizability of Z as determined by ab initio calculations at MP2/6-31+G*//MP2/6-31+G*. The calculated acidities compare favorably with experimental results where available. The proton transfers are unlikely to be observable under experimental conditions because of faster competing reactions: transfer of the YH rather than the CH proton of $HYCH_3$ to $HYCH_2^-$, and a highly exothermic S_N2 attack of XCH_2^- on CH_3X.

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Supporting Information Available: Potential energies in hartrees and *Z*-matrices (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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