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Negative Ion Hyperconjugation in Fluorocarbanions and the Nature of the Borderline between E1cB and E2 Mechanisms. An ab Initio Study

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Ab initio calculations at the MP2/6-31+G*//MP2/6-31+G* level on the 2,2-difluoroethyl (**7**), 1,2,2-trifluoroethyl (**8**), 1,1,2-trifluoroethyl (**9**), 2,2,2-trifluoroethyl (**10**), 1,1,2,2-tetrafluoroethyl (**11**), 1,2,2,2-tetrafluoroethyl (**12**), and 1,1,2,2,2-pentafluoroethyl (**13**) carbanions show that the bond to the anti-β-fluorine is significantly weakened with respect to both the C−F bonds of the conjugate acids and the gauche-β- fluorine(s) of the carbanion. The extent of bond weakening decreases with increasing fluorination of the carbanion, but even **13** shows some evidence of weakening. The criteria are the carbon−fluorine bond length, the charge on fluorine, and the ^{18}F/^{19}F equilibrium isotope effect (EIE). The TS for proton abstraction by hydroxide ion from 1,1,1-trifluoroethane (**3**) to give **10** hydrated at the carbanion center shows bonding changes at all centers of a sort normally associated with E2 TSs, judging from isotope effects, bond lengths, and charges. The carbon-hydrated **10** collapses to elimination products only as the water molecule is migrated from carbon to fluorine. Calculations on the E2 reaction of hydroxide ion with ethyl fluoride result in an E1cB-like E2 TS very similar to that for the proton-transfer step in the E1cB reaction of **3**. It is suggested that E1cB reactions can show a spectrum of TSs from carbanion-like to E2-like as the stability of the carbanion decreases.

Introduction

Some time ago, I proposed that the E2 and E1cB(irrev) mechanisms could be distinguished by the observation of a leaving-group isotope effect or element effect in the former but not in the latter case.[1] This proposal depended on the assumption that there is no weakening of the bond to the leaving group in the rate-determining proton transfer of the E1cB(irrev) reaction. It was shortly pointed out by Thibblin and Ahlberg[2] that if there is negative ion hyperconjugation in the carbanion resulting from proton abstraction, such hyperconjugation might also weaken the bond to the leaving group in the proton-transfer transition state and thus cause a leaving-group isotope effect.

The computational evidence at the time for negative ion hyperconjugation was based on qualitative MO arguments[3] and a semiempirical calculation on the 2-fluoroethyl ion,[4] but calculations at higher levels soon followed. Apeloig[5] reported STO-3G and 4-31G calculations on 2-fluoroethyl and 2,2,2-trifluoroethyl anions. A particularly important paper by Schleyer and Kos[6] pointed out that the 2-fluoroethyl anion loses fluoride at 3-21+G and 4-31+G, whereas the 2,2,2-trifluoroethyl anion shows distinct shortening of the C−C bond and lengthening of the C−F bond anti to the unshared pair. A more recent paper by Dixon, Fukunaga, and Smart[7] used a double-ζ basis set with d polarization functions on carbon and a diffuse orbital to investigate a number of fluorocarbanions. They found, interestingly, that the changes in the C−C and anti C−F bonds of 2,2,2-trifluoroethyl anion were less than reported by Schleyer and Kos, though still sufficient to point to hyperconjugation. No reports of high-level calculations with correlation corrections could be found in the literature, so an investigation in which all species were optimized at MP2/6-31+G*, and some at higher levels, was undertaken. A preliminary report of this investigation has been published.[8]

Computational Methods

The calculations utilized Gaussian 92[9] and Gaussian 94.[10] Most of the work utilized the standard basis sets 6-31+G* and 6-311+G**.[11,12] The acidity calculations

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Table 1. Acidities of Fluoroethanes

fluoroethane	ΔH(acid) MP2/6-31+G*//MP2/6-31+G*	ΔH(acid) G2(MP2)
H-CH_2CHF_2 (**1**)	*a*	*a*
H-$CHFCHF_2$ (**2**)	382.4	388.9
H-CF_2CH2F (**2**)	380.3	387.7
H-CH_2CF_3 (**3**)	381.6	387.8
H-$CHFCF_3$ (**4**)	375.9	382.6
H-CF_2CHF_2 (**5**)	373.0	380.2
H-CF_2CF_3 (**6**)	365.7	374.0[b]

[a] Anion unstable. Decomposes to ion−dipole complex of fluoride ion + fluoroethylene. [b] Lit. (expt, ref 23) 374.3 ± 3.3.

utilized the G2(MP2) method for comparison with results at lower levels.[13] Correlation corrections utilized the Møller−Plesset method.[14−18] 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.[19,20] The enthalpies were further corrected to 298 K for the contributions of the translational, rotational, and vibrational partition functions.[21] 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.[22]

Results and Discussion

To test the reliability of the levels of calculation used, comparisons of calculated and experimental gas-phase acidities of the fluoroethanes were chosen. Unfortunately, only one value, that for pentafluoroethane (**6**), could be found in a standard compilation.[23] Acidities of various fluoroethanes are reported in an ICR study[24] but are probably not reliable because of instability of many of the carbanions under the reaction conditions. Consequently, we chose G2(MP2)[13] results as benchmark values. The calculated acidities are listed in Table 1. The G2(MP2) value for **6** is in excellent agreement with the experimental value. The MP2/6-31+G*//MP2/6-31+G* values run consistently below the G2(MP2) values by around 6−8 kcal mol^{-1}. The relative values, however, are very similar in both sets of calculations. A linear least-squares fit of the MP2/6-31+G* to the G2(MP2) data has a slope of 1.10 and a correlation coefficient of 0.997. Optimization at MP2/6-31+G* was chosen for all of the fluorocarbons and fluorocarbanions. Although G2(MP2) would certainly give more accurate energies, it utilizes frequency calculations on a species optimized at HF/6-31G(d), which we have found unreliable for isotope effects. Isotope effects must be based on frequencies of an optimized species to be meaningful, so a basis set much larger than 6-31+G* and/or higher levels of correlation would be impractical for the more highly fluorinated species.

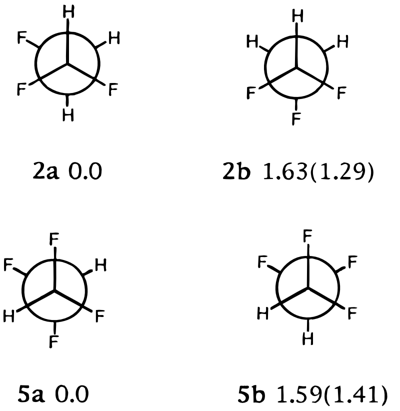

Figure 1. Conformations of fluorocarbons. Enthalpies in kcal/mol relative to the lowest conformation. MP2/6-31+G* values followed by G2(MP2) values in parentheses.

Formulas for the fluoroethanes examined are given in Table 1. The carbanions were **7**−**13**. Some of the species

$^-CH_2CF_2H$ **7** $^-CFHCF_2H$ **8** $^-CF_2CH_2F$ **9** $^-CH_2CF_3$ **10**

$^-CF_2CHF_2$ **11** $^-CFHCF_3$ **12** $^-CF_2CF_3$ **13**

had more than one staggered conformation. The conformations of the substrates and their enthalpies relative to the most stable one are given in Figure 1; corresponding information on the carbanions is given in Figure 2. The acidities reported in Table 1 are calculated from the most stable conformations of the fluoroethanes and the corresponding carbanions. Using weighted averages would make only trivial differences in the results. A minor departure from this practice was necessary for the data reported in Table 2. In the case of **11**, the most stable conformation, **11a**, has no fluorine anti to the unshared pair.

Table 2 summarizes the changes in going from the fluoroethane to the carbanion. The criteria for fluorine hyperconjugation were (1) the length of the C−F bond anti to the unshared pair in the carbanion vs the conjugate acid, ΔR, (2) the charge on the F anti to the unshared pair in the carbanion vs the conjugate acid, ΔQ, and (3) the $^{18}F/^{19}F$ equilibrium isotope effect (EIE) for the F anti to the unshared pair on ionization of the conjugate acid. Each of these three quantities was also calculated for the F gauche to the unshared pair so as to allow for inductive and other nondirectional effects.

Carbanions with fewer than three fluorines were not stable at MP2/6-31+G* with respect to loss of fluoride.

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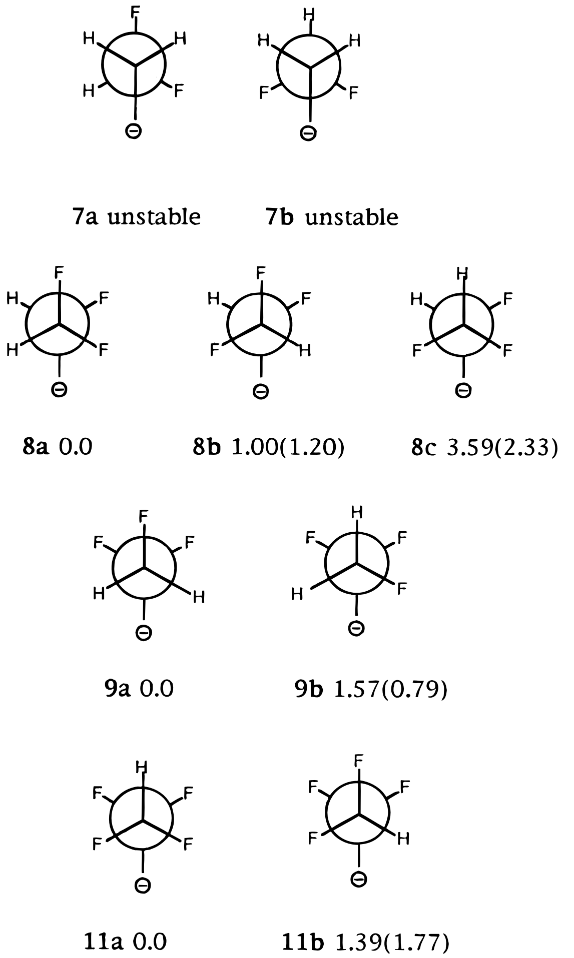

7a unstable **7b** unstable

8a 0.0 **8b** 1.00(1.20) **8c** 3.59(2.33)

9a 0.0 **9b** 1.57(0.79)

11a 0.0 **11b** 1.39(1.77)

Figure 2. Conformations of fluorocarbanions. Enthalpies in kcal/mol relative to the lowest conformation. MP2/6-31+G* values followed by G2(MP2) values in parentheses.

2-Fluoroethyl is already unstable at rather low HF levels,[6,25] as is **7**, which loses fluoride to give an ion−dipole complex of fluoride and fluoroethylene. The conformation **7b** is stable at HF/6-31+G*, but at MP2/6-31+G* it rotates toward **7a** and loses fluoride upon attempted optimization. In general, the more highly fluorinated the carbanion, the lower the three criteria for hyperconjugation. There is, however, some evidence for hyperconjugation even in **13**. The position of the fluorines relative to the carbanion center matters; carbanion **9**, which has two fluorines on the carbanionic carbon, shows less evidence for hyperconjugation than **8**, which has only one.

Although it is clear that fluorine hyperconjugation is significant in all the fluoroethyl carbanions examined, it will not necessarily be an important effect in the transition state for deprotonation of the corresponding fluoroethane. Consequently, the stationary points in the deprotonation of **3** by hydroxide ion and the subsequent loss of fluoride to give 1,1-difluoroethylene were determined.

The mechanism found is summarized in Figure 3. Although **15** is only 0.5 kcal above **14**, there is no doubt that it is a stationary point. The potential energy barrier is 3.9 kcal, and the imaginary frequency is 1187i. Once **16** is formed, it shows no tendency to lose fluoride by simple lengthening of the C−F bond. Hydrogen bonding of water to the unshared pair apparently reduces its ability to interact with the anti F. Two possible paths for completion of the elimination seem reasonable. One is removal of the water molecule from the carbanion center and reattachment to a fluorine. The resulting species loses fluoride as $FHOH^-$ upon attempted optimization. This path, however, involves an enthalpy barrier only 2.2 kcal below the separated reactants. A more likely path is migration of the water molecule from the carbanion center to a fluorine via transition structure **17**. This species is only 2.7 kcal above **16** and a full 16.8 kcal below the separated reactants. The only caveat with respect to **17** is that its formation requires a reorientation of the water molecule and a concomitant conformational change of the carbanion which may present dynamic problems.

Another process open to **16** is return to the ion−dipole complex **14**, which can occur via a barrier of only 1.0 kcal. Whether this process would lead to proton exchange depends on the ease with which the water molecule of **16** can reorient so as to exchange the positions of its two protons. Unfortunately, a transition structure for this interconversion could not be located. The potential surface resulting as the water molecule is moved with respect to the β-carbon is evidently not sufficiently curved for a saddle point to be found. It appears that a barrier of ca. 4 kcal is required, which means the elimination **16** → **18** should be easier than exchange via **16** → **14**.

Isotope effects at the various positions of **14**−**18** are listed in Table 3. Some changes from the reactant **3** are evident even in the ion−dipole complex **14**, but they are not large enough to indicate serious alterations in bond strengths. The proton-transfer transition structure **15**, however, shows substantial KIEs at all positions. The deuterium KIE for the transferred (primary) proton indicates that it is close to half transferred. The KIE for the anti fluorine is 57% of its value in the proton-transfer product **16**. Changes in the two carbon atoms and the β-secondary protons are also in the range 54−60% of their values in **16**. The fluorine KIE for **15** can be compared with the value of 1.0258 in the product ion−dipole complex **18**. The latter value is consistent with the maximum KIE of 1.032 estimated for the cleavage of a C−F bond.[26] The largest fluorine KIE found experimentally so far is below 1.03.[27] The fluorine KIE for **15** is thus only about 20% of that expected for complete loss of fluorine. The structure **15** can be characterized as E1cB-like because C−H cleavage has proceeded farther than C−F cleavage. The fact that there are substantial changes at all positions, however, clearly indicate that **15** resembles a *concerted E2* transition structure, albeit with carbanion-like character.

To see how **15** compares with the transition structure for a true E2 reaction, KIEs were calculated for the reaction of ethyl fluoride with hydroxide ion.[28] Results of optimizations at MP2/6-31+G* and MP2/6-311+G**

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Table 2. Changes in Fluorine Atoms on Ionization of Fluoroethanes to Carbanions

	quantity[a]					
carbanion	ΔR_{CF}(a)	ΔR_{CF}(g)	ΔQ_F(a)[b]	ΔQ_F(g)[b]	F EIE(a)[c]	EIE(g)[c]
7[d]	1.4120	0.0086	−0.5068	−0.0254	1.0246	1.0004
8	0.1492	0.0365	−0.1316	−0.0426	1.0147	1.0032
9	0.0726	0.0298	−0.0911	−0.0525	1.0112	1.0055
10	0.1536	0.0327	−0.1292	−0.0403	1.0152	1.0040
11	0.0443	0.0234	−0.0591	−0.0443	1.0056	1.0024
12	0.0823	0.0261[e]	−0.0840	−0.0397[e]	1.0093	1.0028[e]
13	0.0414	0.0199	−0.0579	−0.0403	1.0044	1.0020

[a] Value for the carbanion (lowest energy conformation with an F anti to unshared pair) − value for the conjugate acid (corresponding conformation). (a) refers to the anti and (g) to the gauche fluorine. [b] NPA (natural population analysis) charges: Glendenning, E. D.; Reed, A. E.; Carpenter, E.; Weinhold, F. NBO Version 3.1 in *Gaussian 94* (ref 10). [c] $^{18}F/^{19}F$ at 293 K. [d] Carbanion is unstable. Actual structure is an ion−dipole complex between F^- and $CH_2{=}CHF$. [e] Average of values for the two nonequivalent gauche fluorines.

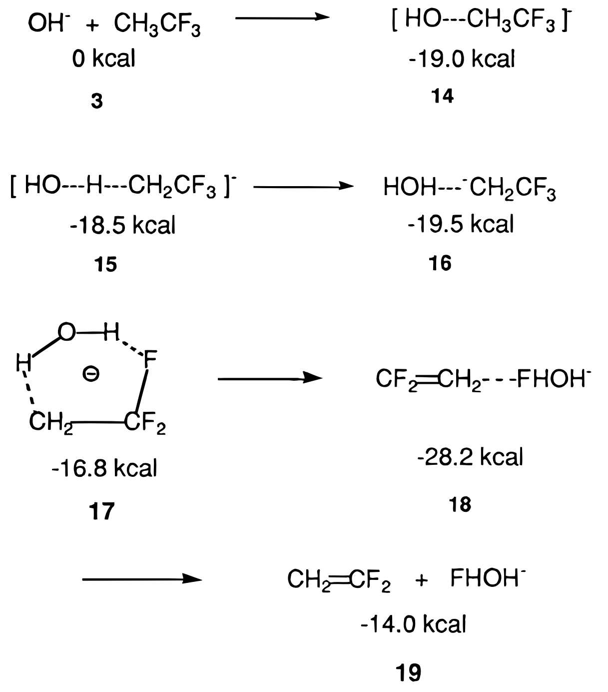

Figure 3. Stationary points in the elimination reaction of 1,1,1-trifluoroethane promoted by hydroxide ion with enthalpies in kcal/mol relative to the reactants corrected for ZPE values and for contributions of the translational, rotational, and vibrational partition functions (frequencies scaled to 0.95).

Table 3. Isotope Effects at the Various Positions of 14−18 Relative to Reactant 3

	IE at 20 °C				
atom	**14**	**15**	**16**	**17**	**18**
F(lg)[a]	1.0026	1.0058	1.0102	1.0235	1.0258
F(gauche)[a]	1.0007	1.0022	1.0029	1.0039	1.0025
H(β-sec)[b]	1.0597	1.1462	1.2685	1.3777	1.1789
H(trfd)[b]	1.1245	4.7076	1.1255	1.0117	1.0236
C(α)[c]	1.0073	1.0199	1.0334	1.0452	1.0253
C(β)[c]	1.0023	1.0158	1.0266	1.0353	1.0125

[a] $^{18}F/^{19}F$. [b] H/D. [c] $^{13}C/^{12}C$.

Table 4. Isotope Effects at Various Positions in the anti-E2 Reaction between Hydroxide Ion and Ethyl Fluoride

	IE at 20 °C	
atom	MP2/6-31+G*	MP2/6-311+G**
F[a]	1.0088	1.0072
H(α-sec)[b]	1.0512	1.0510
H(β-sec)[b]	1.1958	1.1821
H(prim)[b]	4.7114	4.5548
C(α)[c]	1.0184	1.0152
C(β)[c]	1.0188	1.0166

[a] $^{18}F/^{19}F$. [b] H/D. [c] $^{13}C/^{12}C$.

Table 5. Changes at Reacting Positions in the E1cB Reaction of CH_3CF_3 and the E2 Reaction of CH_3CH_2F with OH^- at MP2/6−31+G*//MP2/6−31+G*

	reactant	
quantity[a]	CH_3CF_3[b]	CH_3CH_2F[c]
ΔQ_F	−0.0274	−0.0987
$\Delta Q_{\alpha-C}$	−0.0152	−0.0182
$\Delta Q_{\beta-C}$	−0.1992	−0.2147
ΔQ_H	0.2342	0.2353
ΔQ_{OH}	0.2140	0.2371
ΔR_{CF}	0.0192	0.1027
ΔR_{CC}	−0.0459	−0.0492
ΔR_{CH}	0.2785	0.3553

[a] Charges are NPA (natural population analysis) charges (see footnote b, Table 2). [b] Proton-transfer TS−reactant. [c] E2 TS−reactant.

are given in Table 4. Comparison of these values with those for **15** (column 3 in Table 3) shows little difference. There is somewhat more C−F cleavage in the E2 than in the E1cB reaction, but it is still less than 30% of the value expected for complete cleavage. The extents of C−H cleavage are essentially the same in the E2 and E1cB processes. Other KIEs show only minor differences. By the isotope-effect criterion, the E2 reaction must be characterized as E1cB-like and not much different from the proton-transfer step of the E1cB reaction. The patterns of results at the two levels in Table 4 are essentially the same, strongly suggesting that MP2/6-31+G* is adequate to describe the features of both the E2 and E1cB reactions.

Table 5 compares the changes in charge densities and bond lengths from reactants to transition structure for the E1cB and E2 reactions. There is more negative charge on the leaving group in the E2 reaction, but it is still small. Charges on the other atoms differ little between the two mechanisms. The increase in C−F bond length reflects the increase in KIE and charge between E1cB and E2 reactions, but even in the E2 reaction, it is only 0.1 Å. The C−C bond is a little shorter, and the C−H bond is a little longer in the E2 transition structure. Again, we are forced to the conclusion that both transition structures have considerable E1cB character with concerted bonding changes that are only slightly more synchronous in the E2 than in the E1cB mechanism.

Although the two reactions differ in the sense of one being stepwise and the other concerted, there is only a modest difference between the transition structures. There must be a spectrum of transition structures in the proton-transfer steps of E1cB reactions analogous to the familiar E1-like to concerted to E1cB-like spectrum for E2 reactions. If a carbanion intermediate is well stabilized by inductive effects, resonance, or solvation, little or no weakening of the bond to the leaving group in the transition structure leading to it is expected. A relatively unstable carbanion, on the other hand, can be formed via a transition structure that looks very much like that for an E2 reaction. Along the spectrum for E1cB reactions, the transition structure can be expected to resemble that for an E2 reaction well before the reaction goes over to the E2 mechanism.

Changes from stepwise to concerted reactions must occur when the barrier to decomposition of the intermediate vanishes and it consequently becomes too unstable to exist for more than a single vibrational period (ca. 10^{-13} to 10^{-14} s).[29] The E1cB reaction of **3** with hydroxide, with a transition structure **15** for deprotonation only 0.5 kcal above the ion−dipole complex **14**, is close to this point. As predicted by Gandler and Jencks[30] from their experimental studies on elimination reactions of 2-arylethylquinuclidinium ions, the transformation from stepwise to concerted occurs with very little change in the transition structure.

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Supporting Information Available: Energies in hartrees and Z matrixes for species optimized at MP2/6-31+G* (10 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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