

# Carbon–Oxygen Hydrogen Bonding in Dehydrohalogenation Reactions: PM3 Calculations on Polyhalogenated Phenylethane Derivatives

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Received November 18, 1996<sup>®</sup>

The dehydrohalogenation reactions of PhCH<sub>2</sub>-CH<sub>2</sub>Cl and PhCHCl-CX<sub>2</sub>LG (X = H, F; LG = F, Cl) with methoxide have been studied using PM3 quantum chemical calculations in vacuo and within a dielectric medium. For PhCH<sub>2</sub>-CH<sub>2</sub>Cl and PhCHCl-CH<sub>2</sub>Cl the loss of HCl is predicted to occur via an E2 mechanism, while for the other three compounds loss of hydrogen halide occurs via a two-step mechanism, with a hydrogen-bonded carbanion as an intermediate. The mechanistic implications of these calculations are discussed in comparison with experimental data.

## Introduction

Elimination of hydrogen halide from 1-phenyl-1-halo-2-haloalkanes by methoxide or ethoxide in the corresponding alcoholic solvent smoothly yields 1-phenyl-1-haloalkenes as the main product. The mechanism of this reaction has been proposed to occur via two types of carbanions: one is stabilized by a hydrogen bond, **HB**, while the other, free carbanion has no contact stabilization by either solvent molecules or a counterion, **FC**. The full mechanism which explains both the formation of elimination products and the occurrence and yield of isotopic exchange products resulting from internal return is displayed in Scheme 1.<sup>1</sup>

Scheme 1 can also account for the extreme element effect,  $k^{\text{HCl}}/k^{\text{HF}} = 1.5 \times 10^5$ , associated with the dehydrohalogenation from *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHClCF<sub>2</sub>Cl versus *p*-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>CHClCF<sub>3</sub>.<sup>2</sup> Loss of Cl<sup>-</sup> can occur from a hydrogen-bonded carbanion, {*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CClCF<sub>2</sub>Cl}<sup>-</sup>...HOME, while formation of another species, the free carbanion {*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CClCF<sub>3</sub>}<sup>-</sup>, is required before F<sup>-</sup> departs. This is supported by the fact that exchange of the benzylic hydrogen in *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHClCF<sub>3</sub> is 75 times faster than the loss of HF. In contrast, a normal element effect,  $k^{\text{HCl}}/k^{\text{HF}} = 53$ , is obtained from the reactions of *p*-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>CHClCH<sub>2</sub>Cl versus *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHClCH<sub>2</sub>F, which is consistent with the loss of both chloride and fluoride from one and the same type of species, a hydrogen-bonded carbanion. However, most of the experimental data for loss of halide from **HB** would be virtually the same as for a concerted E2 mechanism (stereochemistry in the resulting alkene, the observance of significant kinetic hydrogen isotope effects and element leaving group effects, and the absence of isotopic exchange). Therefore, the Arrhenius behavior of the primary kinetic hydrogen

isotope effects ( $k^{\text{H}}/k^{\text{D}}$ ,  $k^{\text{H}}/k^{\text{T}}$  and  $k^{\text{D}}/k^{\text{T}}$ ),<sup>3</sup> and chlorine isotope effects [ $k^{35}/k^{37}$ ] that have been shown to be different for the elimination of HCl versus DCl,<sup>4</sup> was used to distinguish between the two mechanisms, and both were only consistent with the stepwise mechanism of Scheme 1. The nature of the reacting species was further investigated via measurement of the kinetic solvent isotope effect,  $k^{\text{MeOD}}/k^{\text{MeOH}}$ , for loss of LX (L = H, D, T) from the following species: C<sub>6</sub>H<sub>5</sub>CHClCH<sub>2</sub>Br (2.51), *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHClCH<sub>2</sub>Cl (2.4), *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CClCH<sub>2</sub>Cl (2.55), C<sub>6</sub>H<sub>5</sub>CTClCF<sub>2</sub>Cl (2.51), and *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CTClCF<sub>3</sub> (2.60).<sup>5</sup> The magnitude of the solvent isotope effects is consistent with three solvating methanol molecules being released from methoxide ion prior to hydron transfer from carbon to oxygen,<sup>6</sup> *i.e.*, methoxide only acts as a base in a desolvated state, feeling only the dielectric effects of the solvent.

The aim of this paper is to investigate the existence of hydrogen-bonded and free carbanion intermediates that might occur in the dehydrohalogenation of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-CH<sub>2</sub>Cl (**1**), PhCHCl-CH<sub>2</sub>Cl (**2**), PhCHCl-CF<sub>2</sub>Cl (**3**), PhCHCl-CH<sub>2</sub>F (**4**), and PhCHCl-CF<sub>3</sub> (**5**) in basic methanol by quantum chemical means, using semiempirical PM3 calculations.<sup>7</sup> The PM3 parametrization has been shown to be able to mimic hydrogen bonds effectively, both intra- and intermolecularly between neutral species<sup>8</sup> and specifically between negatively charged carbon atoms and alcohols [C(-)···H-O].<sup>9</sup> A recent study suggests that PM3 is the parametrization of choice for semiempirical studies of molecular systems in which hydrogen-bonding interac-

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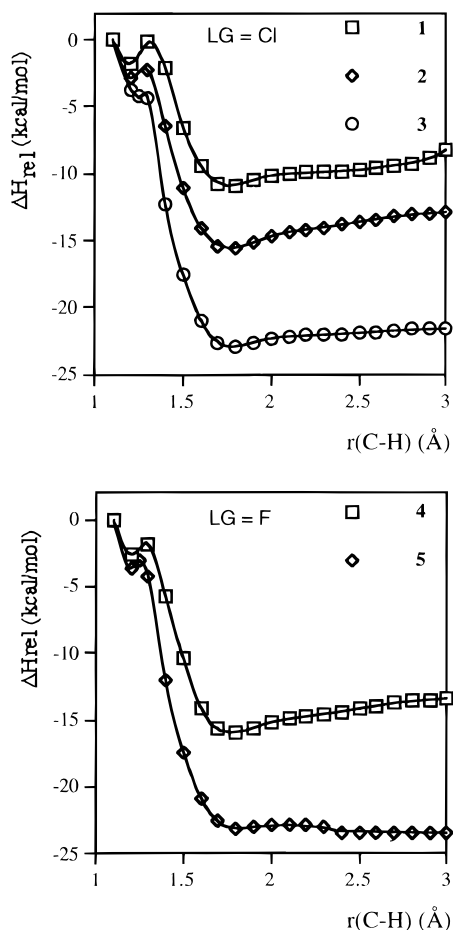
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® Abstract published in *Advance ACS Abstracts*, September 15, 1997.

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**Figure 2.** Relative heats of formation  $\Delta H_{rel}$  (wrt  $r(\text{C}-\text{H}) = 1.1 \text{ \AA}$ ) for methoxide complexes of **1**–**5** for lengthening of the  $\text{C}_\alpha\text{-H}$  bond at  $\theta = 180^\circ$ : (Top) complexes of **1**–**3** (LG = Cl); (bottom) complexes of **4** and **5** (LG = F).

barriers in these systems,<sup>16</sup> it prevents finding the local minima along a reaction path, when starting out with a geometry optimization without torsional restraints.<sup>18</sup> The calculations for compound **1** (Figure 2) are with the hydrogen gauche to the chloride leaving group to allow comparison to the other compounds.

**Encounter Complexes.** As the energy profiles for increasing  $r(\text{C}-\text{H})$  in vacuo at  $\theta = 180^\circ$  (Figure 2) show, lengthening of the  $\text{C}-\text{H}$  bond for the ion–molecule clusters of **1**, **2**, and **4** results in the formation of an energy minimum corresponding to an encounter complex around  $r(\text{C}-\text{H}) = 1.2 \text{ \AA}$ , while for the complexes of **3** and **5** such a minimum is either absent (**3**) or very shallow (**5**). Full optimization of the complexes starting at  $r(\text{C}-\text{H}) = 1.2 \text{ \AA}$  does indeed result in encounter complexes **1EC-1**, **1EC-2**, **2EC** and **4EC**, which are definite minima for **1**, **2**, and **4**, respectively (Figure 3). For **3** and **5** no such encounter complex was observed in

vacuo: the energy dips in their reaction profiles (Figure 2) are a direct result of the fixation of  $\theta$  at  $180^\circ$  and disappear at full optimization. This difference between complexes of **1**, **2**, and **4** versus clusters of **3** and **5** is caused by the electron-withdrawing effect of the  $\beta$ -fluorine atoms, which results in a diminished electron density at the  $\alpha$ -carbon atom. This, in turn, will favor the complete transfer of the proton to the alcohol due to the stabilization provided by this delocalization (*vide infra*),<sup>19</sup> but does not stabilize the hydrogen bond formed in the encounter complex. These conclusions are in line with recent measurements of the gas phase acidity of **5**, which is 29 kcal/mol more acidic than that of methanol.<sup>20</sup>

For **1** two encounter complexes were found. The more stable one (**1EC-2**) has an antiperiplanar orientation of the  $\text{C}_\beta\text{-Cl}$  bond with the lengthened  $\text{C}_\alpha\text{-H}$  bond (Figure 3) and is favored by 4 kcal/mol over the complex with  $\theta \approx 180^\circ$  (**1EC-1**, Figure 3). For **2** and **4** the antiperiplanar structure is disfavored due to repulsive halogen–halogen interactions which do not exist in complexes of **1** as that species lacks the  $\alpha$ -chloro atom.

**Hydrogen-Bonded Complexes.** Further lengthening of  $r(\text{C}-\text{H})$  yields for all five complexes an energy minimum at about 1.8  $\text{\AA}$  (Figure 2). These structures all have a near-linear orientation of the  $\text{C}(\text{-})\cdots\text{H}-\text{O}$  moiety, have a total  $\text{C}(\text{-})\cdots\text{H}-\text{O}$  bond length of 2.7–2.75  $\text{\AA}$ , and display a small  $\text{C}-\text{H}$  bond order ( $<0.1$ ). All these features clearly point to the presence of a complex-stabilizing hydrogen bond.<sup>21</sup> The presence of energy minima on the potential energy surfaces with the fixed value of  $\theta$  is in line with the postulate of  $\text{C}(\text{-})\cdots\text{H}-\text{O}$  hydrogen bonds for **2**–**5** on the basis of kinetic data.<sup>1,4</sup>

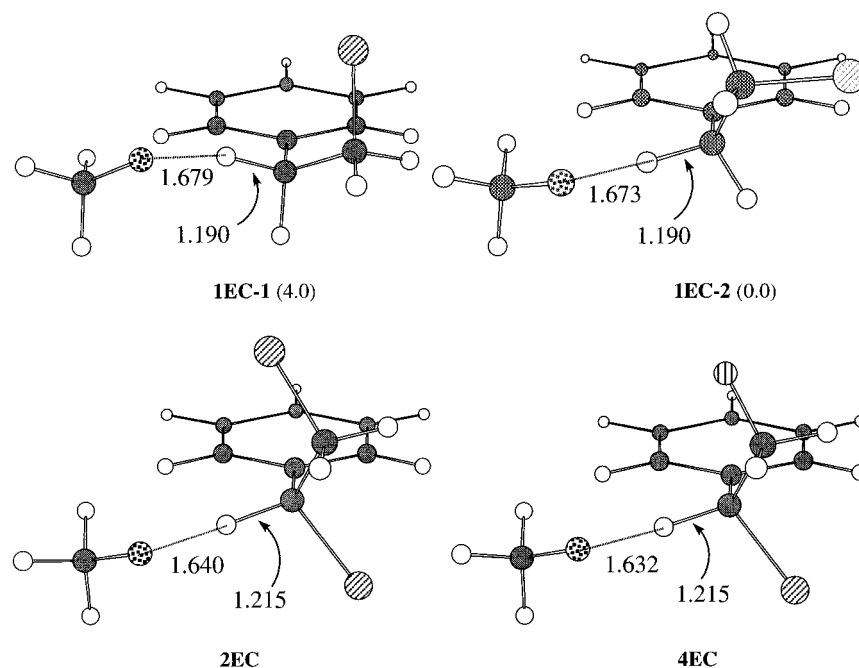
Full optimization of all five hydrogen-bonded complexes starting with  $r(\text{C}-\text{H}) = 1.8 \text{ \AA}$  for several conformers of the carbanion yielded stable hydrogen-bonded complexes for **3**–**5** (Figure 4). Although for **3** and **4** also other minima were observed (see below), the most stable minimum for all these three compounds has the  $-\text{CX}_2\text{LG}$  group effectively rotated  $90^\circ$  from the initial conformation to align the leaving group to the lone pair electrons for maximum overlap of the  $\text{C}-\text{LG} \sigma^*$  and the  $p_z$  orbital on the  $\alpha$ -carbon atom. Upon full optimization no minima were found for **1** and **2**, so the local minima observed in Figure 2 for **1** and **2** turn out to be a consequence of the fixation of  $\theta$  at  $180^\circ$  with this computational method. When  $\theta$  is let free to be optimized in these two clusters, it reduces to  $90^\circ$ , with concomitant loss of chloride. A more detailed study of the loss of chloride in **2** shows that during the rotation of the  $\text{CH}_2\text{Cl}$  group the  $\text{C}_\beta\text{-Cl}$  bond is lengthened gradually, thereby reducing the steric hindrance present for further rotation. The energy gain for this rotation and  $\text{C}_\beta\text{-Cl}$  bond lengthening comes from the alignment of the filled  $p_z$  orbital on  $\text{C}_\alpha$  and the  $\sigma^*$  orbital of  $\text{C}_\beta\text{-Cl}$ , ultimately resulting in the loss of chloride

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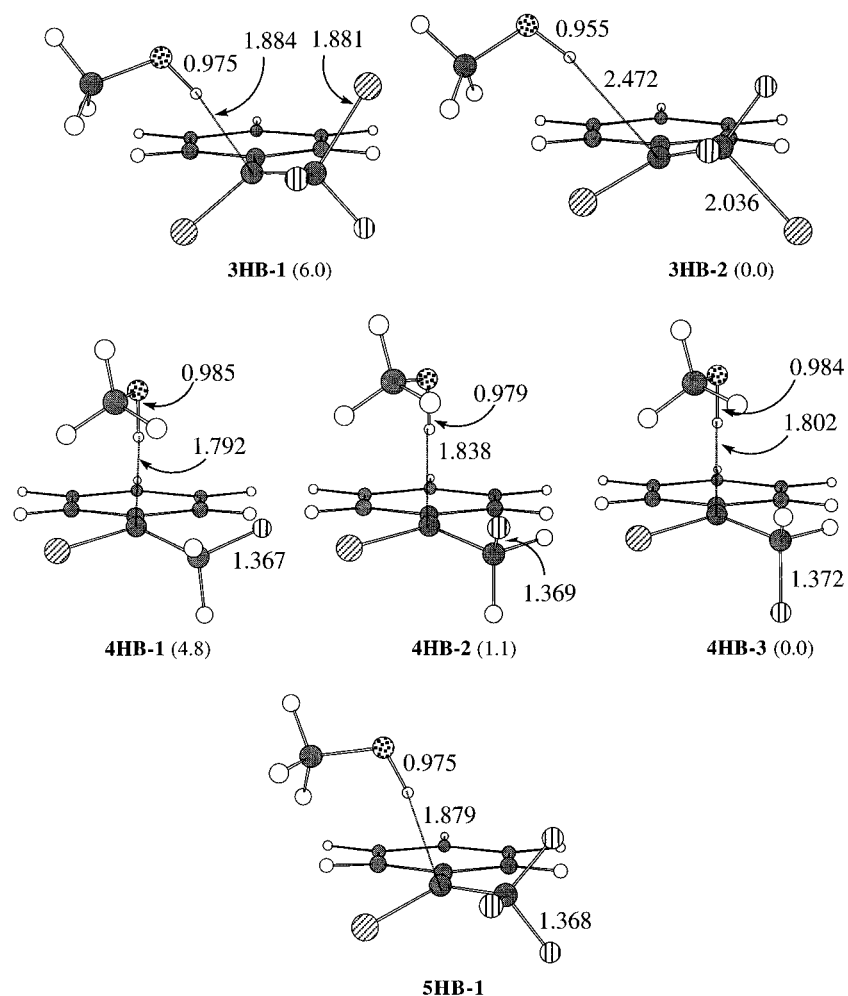
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(18) (a) It should be noted that with *ab initio* methods up to MP2 calculations with triple- $\zeta$  basis sets the barrier for rotation is significantly overestimated (up to a factor of 2), yielding deviations significantly larger than PM3; this would in effect prevent rotation of the  $\text{CX}_2\text{Cl}$  moiety. Such calculations would therefore not necessarily imply a quantitatively better agreement with experiment, although Dixon and co-workers have found that a qualitative improvement for the potential energy surface for rotation is to be expected.<sup>16</sup> For earlier studies on rotational barriers in 1,2-haloethanes, see: (b) Dixon, D. A.; Smart, B. E. *J. Phys. Chem.* **1988**, *92*, 2729–2733. (c) Miyajima, T.; Kurita, Y.; Hirano, T. *J. Phys. Chem.* **1987**, *91*, 3954–3959. (d) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616–3620. (e) Smits, G. F.; Krol, M. C.; Van Kampen, P. N.; Altona, C. *J. Mol. Struct. (THEOCHEM)* **1986**, *139*, 247–253.



**Figure 3.** Encounter complexes of **1** (top), **2** (bottom left), and **4** (bottom right) (distances in Å; relative energies—for complexes of **1**, in parentheses—in kcal/mol).



**Figure 4.** Hydrogen-bonded carbanion–methanol complexes of **3** (top), **4** (middle), and **5** (bottom) (distances in Å; relative energies—in parentheses—in kcal/mol).

anion. If  $\theta$  is decreased from  $180^\circ$  to  $90^\circ$  at intervals of  $30^\circ$ , no loss of  $\text{Cl}^-$  is observed for  $\theta = 180^\circ$  and  $150^\circ$ , but  $\text{Cl}^-$  is lost from geometries with  $\theta = 120^\circ$  and  $90^\circ$ . Loss

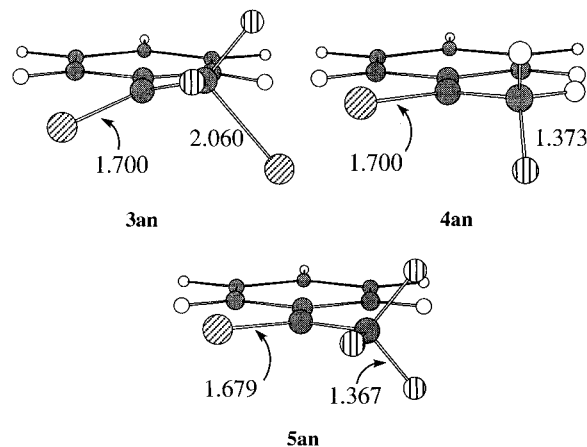
of LG anion is easiest from these orientations, due to the aforementioned orbital alignment. For both **1** and **2** chloride anion leaves without additional barrier. Length-

ening of the hydrogen bond is required for further lengthening of the  $C_{\beta}$ -Cl bond. If  $r(C-H)$  is fixed, e.g., at 1.5 or 2.0 Å, the C-Cl bond length increases up to a certain value and stays there. Upon placing the methanol further and further away from the carbanion, one breaks the hydrogen bond and obtains the free carbanions, **FC**, **1an-5an**. For **1** and **2** the loss of driving force for localizing some of the electron density on the  $\alpha$ -carbon atom causes the chloride anion to leave without further barrier for  $r(C-H) > 3.5$  Å. In line with this, the free anions **1an** and **2an** are not stable at this level of theory. The loss of the proton and the chloride are therefore really coupled in vacuo for **1** and **2**, in line with an E2 mechanism.

With **3-5** this is not the case, as several minima on the potential energy surface were observed (see Figure 4). Full optimization of the complex of  $\{C_6H_5CCl-CF_2Cl\}^-$  with methanol yields two minima, **3HB-1** and **3HB-2**, with a relative energy of 6.0 kcal/mol (**3HB-2** being more stable). In **3HB-1** the geometry of the carbanion part strongly resembles that of the precursor dichloroethane. The relative orientation of the chloro atoms at the  $\alpha$ - and  $\beta$ -carbon atoms is still anti, and the  $C_{\beta}$ -Cl bond length is still close to that in the neutral precursor: 1.881 versus 1.827 Å. Clearly, a near-linear hydrogen bond is formed between the highly negatively charged  $C_{\alpha}$  and the alcohol group of the methanol, with  $r(C-H) = 1.881$  Å and the hydrogen firmly bound to the oxygen:  $r(O-H) = 0.975$  Å. Rotation over  $120^\circ$  of the  $CF_2Cl$  group yields the other, more stable minimum, in which the  $\beta$ -chlorine atom is aligned anti-parallel to the  $C(-)\cdots H-O$  moiety. This orientation lowers the energy and is optimal for loss of  $Cl^-$ , as is reflected already in the significant increase of the  $C_{\beta}$ -Cl bond length to 2.036 Å; minimum **3HB-1** therefore seems to exist due to the barrier for rotation of the  $CF_2Cl$  group. The total  $C(-)\cdots H-O$  length in **3HB-2** is over 3.4 Å, substantially longer than what is normally found for hydrogen bonds between second row elements:  $< 2.95$  Å.<sup>21</sup> It therefore seems that this complex is kept together in vacuo by general charge-dipole attraction rather than by specific hydrogen bonding (*vide infra*).

Despite the significant lengthening of the C-Cl bond in **3HB-2**, the mechanism for loss of HCl from this system cannot be E2, since even in the free anion **3an** (no MeOH around), the  $\beta$ -chlorine atom stays bonded (*vide infra*). Along the reaction path for deprotonation the C-Cl bond order is reduced from 0.86 (at  $r(C-H) = 1.1$  Å) to 0.55 (at  $r(C-H) = 3.0$  Å), and although the bond length still increases slightly, this value of the bond order is only marginally lower than that of 0.57 already obtained at  $r(C-H) = 1.8$  Å and close to the 0.52 obtained for the isolated, free ion. Correspondingly, the C-Cl bond length is only increased with 0.004 Å (to 2.040 Å) with an increase of  $r(C-H)$  from 2.472 (in **3HB-2**) to 3.000 Å, and at  $r(C-H) = 10.0$  Å,  $r(C-Cl)$  is still only 2.056 Å.

Similar results are obtained for **4**. Three minima are found on the potential energy surface of the complex of 1-phenyl-1-chloro-2-fluoroethanide with methanol (Figure 4, complexes **4HB-1**, **4HB-2**, and **4HB-3**). All three correspond to a methanol-carbanion cluster held together by a near-linear  $C(-)\cdots H-O$  hydrogen bond and differ only in the relative orientation of the  $CH_2F$  group.



**Figure 5.** Optimized structures for the isolated carbanions **3an** (top left), **4an** (top right), and **5an** (bottom), together with selected geometrical features (distances in Å).

Since the charge capacity of fluorine is not as large as that of chlorine,<sup>22</sup> no substantial changes in the C-F bond length are observed for the three different complexes (differences  $< 0.006$  Å). This does, however, not imply that its preference for an anti-parallel orientation with the  $C(-)\cdots H-O$  moiety is not as large. The relative energies of **4HB-1**, **4HB-2**, and **4HB-3** are 4.8, 1.1, and 0 kcal/mol, which suggest that the preference for an anti-parallel orientation is almost 5 kcal/mol. Again, complete removal of the methanol molecule with the fluorine in the optimum anti-parallel orientation does not result in a loss of  $F^-$ :  $r(C-F)$  only lengthens marginally from 1.372 Å in complex **4HB-3** to 1.373 Å at  $r(C-H) = 10.0$  Å, therefore excluding an E2 mechanism for loss of HF in vacuo for this ion-molecule cluster.<sup>23</sup>

This is analogous to what is observed for the hydrogen-bonded complex of **5**. One minimum is found, with an anti-parallel orientation of the  $C(-)\cdots H-O$  moiety and one of the C-F bonds. Again, the cluster is held together by a near-linear hydrogen bond with  $r(C-H) = 1.880$  Å, and removal of the methanol to  $r(C-H) = 10.0$  Å does not change the C-F bond lengths substantially.

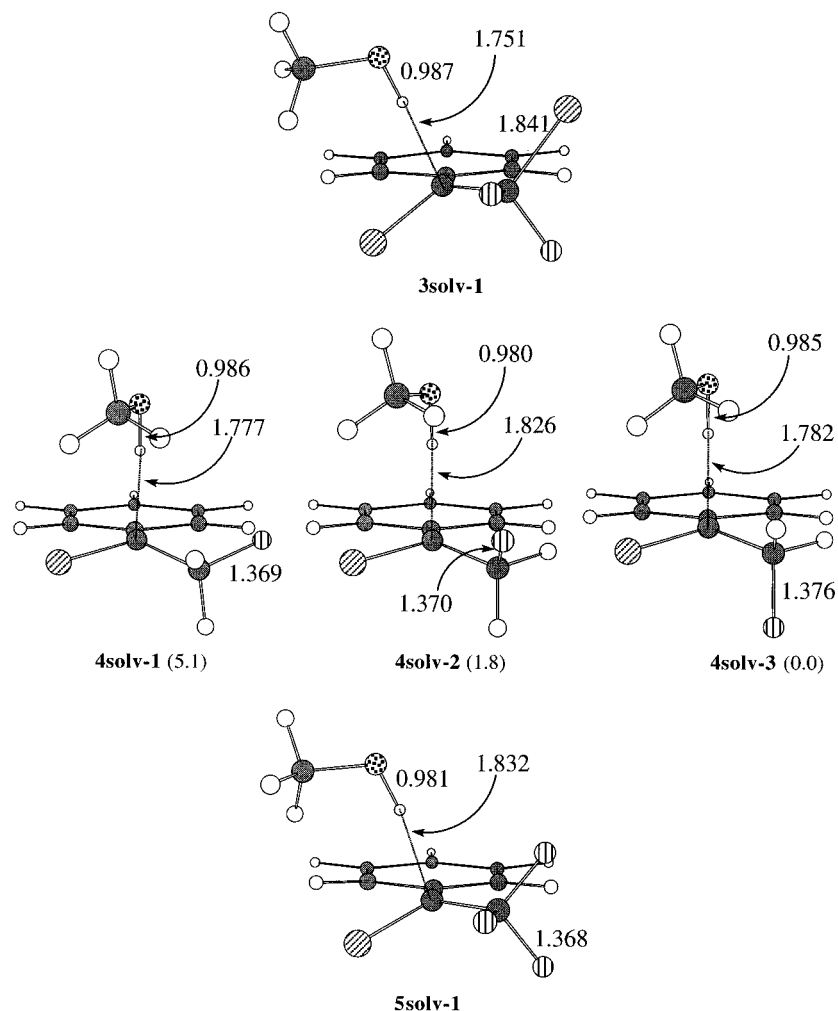
**Free carbanions.** A final common characteristic is that in the free carbanions **3an**, **4an**, and **5an**—originating from removal of the methanol molecules in the complexes as depicted in Figure 4—the hybridization around  $C_{\alpha}$  is changed from  $sp^3$  in the neutral precursors to  $sp^2$  in the free anions.<sup>24</sup> In this regard the structure of the carbanions under study therefore differs from that of simple alkyl or alkyl halide anions, which have been shown to be  $sp^3$  hybridized.<sup>25</sup> For **5an** the rehybridization results in a carbanion with  $C_s$  symmetry. The optimized structures of **3an-5an** are depicted in Figure 5, together with selected geometrical features.

(23) The minimal lengthening of the C-F bonds in these systems is somewhat surprising and probably erroneous, given the significant lengthening that has often been calculated in simpler anions. It is currently unclear whether this can be fully accounted for by the possibilities for delocalization of the negative charge by the phenyl and  $\alpha$ -chloro substituents, but we suspect that limitations of the computational method used in this study also play a part.

(24) The planarity of the free carbanions does not arise from the minimal basis sets used in semiempirical computations. Recent B3LYP/6-31+G(d) computations on **4an** compute the dihedral angle  $C-C(-)-Cl-F$  to be  $173^\circ$  (Zuillhof, H.; Lodder, G.; Koch, H. F. Unpublished results), in very good agreement with the present PM3 data.

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**Figure 6.** Hydrogen-bonded carbanion–methanol complexes of **3** (top), **4** (middle), and **5** (bottom) as optimized in a dielectric medium mimicking methanol (distances in Å; relative energies—in parentheses—in kcal/mol).

The observance of stable free carbanions and hydrogen-bonded ion–molecule complexes has important mechanistic implications, since the stability of the anions in the global energy minimum precludes any E2-type elimination in the gas phase. Therefore loss of hydrogen halide from **3–5** is predicted to occur via a two-step mechanism, in which the proton is lost first followed by a loss of the leaving halide which requires crossing of another energy barrier. This behavior contrasts with that predicted for **1** and **2**: no hydrogen-bonded carbanion–methanol clusters are found, and the isolated carbanions are calculated to be unstable due to barrierless loss of chloride anion.

**Medium Effects.** To probe the influence of the solvent, the hydrogen-bonded carbanionic intermediates of **3–5** as calculated in vacuo were reoptimized in a dielectric medium simulating methanol using the COSMO technique (Figure 6).<sup>15</sup> No intermediate similar to gas-phase cluster **3HB-2** could be found: reoptimization of this complex in the dielectric medium resulted in loss of Cl<sup>−</sup> and further lengthening of  $r(\text{C–H})$ . This supports the idea that this complex is in vacuo kept together by nonspecific ion–dipole interactions—which are of course strongly diminished in solution—rather than by a real hydrogen bond. For the hydrogen-bonded complexes of **4** and **5**, the effect of the dielectric medium was rather small, both structurally—as can be seen from the structures in Figure 6—and energetically. The structures

of **4solv-1**, **4solv-2** and **4solv-3** differ only marginally from those of their gas-phase analogues, with solvent-induced bond length changes up to 0.020 Å. In **5solv-1** the hydrogen bond is somewhat shortened in comparison with gas-phase structure **5HB-1** ( $r(\text{C–H})$  decreases from 1.880 to 1.832 Å). This does, however, hardly affect the C–F bond lengths—all changes < 0.005 Å—or corresponding electronic properties. This suggests that despite the significant overall stabilization of these negatively charged complexes (in the range of 50–75 kcal/mol, as estimated from computations using COSMO) no significant specific solvent-induced structural changes are observed.

The situation is slightly different for **3solv-1**. Although the structures for **3HB-1** in Figures 4 and 6 resemble each other, apart from the somewhat shorter hydrogen bond length in the dielectric medium, the similarity is less than surmised at first sight. Both structures are definite minima on their respective potential energy surfaces, but where the gas-phase structure is rather robust—if the geometry is changed slightly and the system is allowed to reoptimize, the same structure is obtained—the structure in the dielectricum is not. If only minor changes in the hydrogen bond length, the C<sub>β</sub>–Cl bond length, or  $\theta$  are applied, the reoptimized structure in most cases loses Cl<sup>−</sup>. The minimum corresponding to **3solv-1** is therefore very shallow. Therefore the outcome of this specific calcula-

tion might yield different results with different computational methods, and we can only cautiously notice that with PM3/COSMO a minimum corresponding to a methanol-carbanion cluster is observed, in which the C(-)⋯H-O hydrogen bond is still intact.

The influence of the solvent shows up most clearly in the isolated anions **1an**–**5an**. For **1** and **2** a remarkable difference with the gas-phase data is to be noticed. In vacuo the increase in the C<sub>β</sub>–Cl bond length is gradual with a gradual increase in *r*(C–H), but loss of Cl<sup>–</sup> is only observed at *r*(C–H) > 3.5 Å. In the dielectric medium, however, there is a threshold value for *r*(C–H) between 1.4 and 1.5 Å: if *r*(C–H) passes that value, the charge-localizing effect of the C(-)⋯H-O hydrogen bond becomes too small and Cl<sup>–</sup> leaves. Where in the gas phase the isolated anion **3an** is stable, albeit with a significantly lengthened C<sub>β</sub>–Cl bond, in the dielectric medium Cl<sup>–</sup> is lost at *r*(C–H) > 1.4 Å. The loss of chloride anion is therefore solvent-induced. The leaving group F in **4an** and **5an** still does not leave without an additional barrier crossing, when the anion is reoptimized in the dielectric medium, yielding minima with structures that bear a close resemblance to those depicted in Figure 5.

The results obtained by optimizations of the methanol-carbanion cluster in a dielectric medium mimicking methanol therefore suggest that **1** and **2** would undergo base-catalyzed dehydrohalogenation via an E2 mechanism, while **4** and **5** will follow the stepwise mechanism depicted for this process. The case of **3** seems to be borderline, although we tentatively state that a stepwise mechanism is feasible. The presence and strength of a potential C(-)⋯H-O hydrogen bond in the complex of methanol and the carbanion seem to be crucial for the precise reaction path followed in the dehydrochlorination reaction.

**Comparison with Experimental Data.** The calculations on the complexes of **1**–**5** with methoxide in the dielectric medium allow for comparison with the experimentally observed phenomena in the dehydrohalogenation of **1**–**5** in basic methanol.<sup>4,5</sup> Compound **1** dehydrochlorinates under those conditions via an E2 mechanism, while **2**–**5** experimentally follow the pattern of a two-step elimination featuring some degree of internal return of the proton from the methanol back to the carbanion. The calculations on the complexes of **3**–**5** are in line with an E<sub>1CB</sub> mechanism, and the calculations of real intermediate energy minima both in vacuo and in the dielectric medium support the stepwise loss of HCl or HF, respectively, though for **3** the assignment in the dielectric medium is tentative. For **1** and **2** the calculated mechanism is basically of an E2 type, in which the loss of the proton and the chloride anion is concerted, though not necessarily synchronous. This is in line with the interpretation of the experimental results for **1**, but not for **2**. In other words: in the calculations the chloride anion is lost too easily, since the experimental data for **2** (and **3**) are not compatible with an E2 mechanism. This might be a consequence of the theoretical limitations of the PM3 method. The incorrect prediction might result from an

underestimation of the rotational barrier, as calculated for 1,2-dichloroethane by Dixon *et al.* to be about 1 kcal/mol, but this would unfortunately not improve by changing to *ab initio* calculations, since these overestimate the barrier by about 2–6 kcal/mol up to MP2/(triple- $\zeta$  plus diffuse and polarization functions) levels of theory.<sup>16,18b</sup> Alternatively, the stability of Cl<sup>–</sup> in the dielectric medium might be overestimated using PM3, which—following the Hammond postulate—reduces  $\Delta G^\ddagger$  and therefore increases the ease of loss of Cl<sup>–</sup>. This is probably partially compensated for by the limitation of the model to account for any hydrogen bond formation between the solvent and the leaving group. Therefore, the relative success of PM3/COSMO might be due to a cancellation of errors. To study the loss of chloride in more detail, further quantum chemical calculations are in progress.<sup>26</sup>

Finally, it is noteworthy that hydrogen bonds to carbanions have recently been observed in other systems as well. Ahlberg and co-workers have shown that substantial intramolecular C(-)⋯H-O hydrogen bonding occurs in indenide- and fluorenyl-substituted alcohols, in both polar and apolar media,<sup>27</sup> a finding that was confirmed later by PM3 computations.<sup>9</sup> Boche and co-workers have observed C(-)⋯H-N hydrogen bonds in crystal structures of fluorenyllithium·2-ethylenediamine and of ammonium 1,2,4-tricyanocyclopentadienide.<sup>28</sup> Since the negative charge on the carbon atom from which the proton is abstracted is delocalized to a very large extent in these systems, the involvement of C(-)⋯H-O hydrogen bonds of carbanions with more localized negative charge<sup>1–5</sup> is expected to be even more likely.

## Conclusions

The dehydrohalogenations of PhCHCl-CX<sub>2</sub>LG in basic methanol proceed, according to quantum chemical PM3 calculations, in a two-step mechanism via a hydrogen-bonded carbanionic intermediate for PhCHCl-CF<sub>2</sub>Cl, PhCHCl-CH<sub>2</sub>F, and PhCHCl-CF<sub>3</sub>, in line with experimental evidence<sup>1–5</sup> for a two-step mechanism involving internal return. For PhCH<sub>2</sub>-CH<sub>2</sub>Cl and PhCHCl-CH<sub>2</sub>Cl the calculations predict the occurrence of an E2 mechanism. This is in line with the experimental data for PhCH<sub>2</sub>-CH<sub>2</sub>Cl but in contrast with the interpretation of the experimental results for PhCHCl-CH<sub>2</sub>Cl, which suggest that also for this compound a two-step mechanism is operative.

JO962154W

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