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The anionic chain process mechanism for reactions of perchlorofluoroethanes with nucleophiles in solution: a theoretical study

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ABSTRACT: Anionic chain process mechanism (including reactions (1)–(4)) suggested by the experimental investigations for the reactions of nucleophile (CH_3O^-) with perchlorofluoroethanes CF_2ClCCl_3 (**1**), CF_2ClCCl_2F (**2**), and CF_3CCl_3 (**3**) in solution is examined by performing calculations using the B3LYP method and the SCIPCM (self-consistent isodensity polarizable continuum) model for simulating solution effects. The SCIPCM-B3LYP calculations indicate that anionic species have large solvation energies and solvation energy values for different kinds of anions are quite different, which effects changes in ΔH's for the reactions in solution. Competition between anionic hyperconjugation and solvation leads to negative ΔH values for reactions (2) from **1** and **2** in solution. Reactions (3) and (4) from **1**, **2**, and **3** in solution are predicted to be exothermic or highly exothermic. Since the ΔH values for reactions (1) and (2) from **1** and **2** in solution are negative or small positive values, the reactions of CH_3O^- with **1** and **2** in solution proceed via the anionic chain process. For **3** in solution, reactions (1) and (2) are endothermic while reactions (3) and (4) are exothermic or highly exothermic. The reactions of CH_3O^- with **3** in solution may proceed via the anionic chain process. All these conclusions are in agreement with the experimental indications for reactions of nucleophiles with **1**, **2**, and **3** in solution. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: perchlorofluoroethanes; nucleophiles; anionic chain process mechanism; chlorophilic attack; anionic hyperconjugation; solvent effects; DFT B3LYP; SCIPCM model

INTRODUCTION

The spontaneous reactions of sodium thiophenoxide, aryloxides, and alkoxides with 1,1-difluorotetrachloroethane (**1**), 1,1,2-trichlorotrifluoroethane (**2**), and 1,1,1-trichlorotrifluoroethane (**3**) were reported by Li *et al.*,[1–5] and the reactions lead to the formation of $NuCF_2—CCl_2Y$ (Y = F, Cl) type of products. The carbon atoms of the perchlorofluoroethanes are not vulnerable to direct S_N2 type attack by the nucleophiles. The experimental investigations[1–5] suggested that these spontaneous reactions proceed via an anionic chain process with the direct attack of the nucleophiles on the chlorine atoms as the initiation step. This process was defined as 'nucleophilic substitution initiated by chlorophilic attack'[4] (Scheme 1).

In reactions (1) of Scheme 1 the attack of the nucleophiles on the chlorine atoms of **1**, **2**, and **3** results in carbanions **4**, **5**, and **6**, and in reactions (2) the carbanions become perchlorofluoroethenes. In reactions (4) of Scheme 1 the $NuCF_2—CCl_2Y$ (Y = F, Cl) products are formed.

Theoretical explanations (examinations) for the experimentally suggested mechanisms for the reactions of perchlorofluorethanes with nucleophiles are interesting. Reactions (1) and (2) of Scheme 1 in the gas phase were previously studied based on semiempirical MNDO calculations,[6] and the CH_3O^- anion was chosen as a model nucleophile. In the previous MNDO study,[6] the authors concluded that the strong HOMO-LUMO interaction between CH_3O^- and the perchlorofluoroethanes incorporated the attack of CH_3O^- on one of the chlorine atoms of **1**, **2**, and **3**, leading to the breaking of the corresponding C—Cl bond. The MNDO energetic calculations[6] indicated that reactions (1) of CH_3O^- with **1**, **2**, and **3** were exothermic and the unlikely chlorophilic attacks were energetically feasible (in the gas phase). However, the MNDO calculations[6] indicated that anionic hyperconjugation stabilized the anions **4**, **5**, and **6** and made reactions (2) energetically unfeasible (in the gas phase). Experimentally these spontaneous reactions occur in solution. Solution effects were not considered in the

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CF_2XCCl_2Y **1**: X = Cl, Y = Cl; **2**: X = Cl, Y = F; **3**: X = F, Y = Cl

CF_2XCClY^- **4**: X = Cl, Y = Cl; **5**: X = Cl, Y = F; **6**: X = F, Y = Cl

$$Nu^- + CF_2XCCl_2Y \rightarrow NuCl + CF_2XCClY^- \quad (1)$$

$$CF_2XCClY^- \rightarrow CF_2{=}CClY + X^- \quad (2)$$

$$Nu^- + CF_2{=}CClY \rightarrow NuCF_2{-}CClY^- \quad (3)$$

$$NuCF_2{-}CClY^- + CF_2XCCl_2Y \rightarrow NuCF_2{-}CCl_2Y + CF_2XCClY^- \quad (4)$$

Where $Nu^- = RS^-, RO^-$

Scheme 1

previous MNDO study.[6] The previous MNDO study[6] is considered as a preliminary theoretical work.

In the present work we have studied the reactions of nucleophiles with perchlorofluoroethanes **1**, **2**, and **3** using the DFT B3LYP (the Becke's three-parameter hybrid function[7] with the nonlocal correlation of Lee–Yang–Parr[8]) calculation method and the SCIPCM (self-consistent isodensity polarizable continuum) model[9] of the SCRF (self-consistent reaction field) theory to simulate solution effects. We have chosen CH_3O^- as a model nucleophile. The main purpose of the present work is to explain (examine) the experimentally suggested anionic chain process mechanism (Scheme 1) for the reactions of nucleophiles with perchlorofluorethanes in solution on the basis of the SCIPCM-B3LYP calculations. We note that for the reaction of **3** with thiophenoxide, the experiments[3] also indicated another reaction pathway, which will also be examined.

COMPUTATIONAL METHODS

All the calculations were carried out using the Gaussian 03W suite of programs.[10] A 6-31+G(d) basis was used.

We considered two solvents: DiEthylEther and DiMethylSulfoxide, which are denoted as s-DEE and s-DMS and have dielectric constant values of 4.335 and 46.7, respectively. S-DMS is a polar solvent used in the experiments,[1,3] and s-DEE is a nonpolar solvent similar to diglyme used in the experiments.[1,3] In the SCIPCM model we used an isodensity value of 0.0004, which was recommended by Wiberg and Rablen.[11]

For all the reactants and products of reactions (1)–(4) of Scheme 1 ($Nu^-{=}CH_3O^-$) from perchlorofluoroethanes **1**, **2**, and **3**, we performed the gas-B3LYP (in the gas phase) and SCIPCM-B3LYP (in the two solvents) geometry optimization and frequency analysis calculations. For the species **2**, **4**, and **5** we determined their most stable conformers in the gas phase and in the two solvents. Our calculations indicate that for each of the three species the most stable conformations in the gas phase and in the s-DEE and s-DMS solvents are the same, and we report only the most stable conformers of **2**, **4**, and **5**. In the rest part (text, Tables, and Figure) of the present paper, '**2**' means 'the most stable conformer of **2**' (the same for **4** and **5**). Atom labelings used in **1**, **2**, **3**, **4**, **5**, and **6** are given in Fig. 1.

For checking if there exists any transition state (TS) or intermediate (IM) along the reaction paths, the gas-phase reaction paths were checked. For obtaining *ab initio* electronic structures of **1**, **2**, and **3**, the HF single-point calculations were performed at the gas-B3LYP optimized geometries.

RESULTS AND DISCUSSION

Reactant and product species in the solvents

In Table 1 given are the relative energies (solvation energies) of the reactant and product species in the s-DEE and s-DMS solvents to the species in the gas phase. In Fig. 1 given are the optimized structures of CF_2XCCl_2Y (**1**, **2**, and **3**) and CF_2XCClY^- (**4**, **5**, and **6**). In Table 2 given are the optimized geometries of **1**, **2**, and **3** in the gas phase and in the s-DEE and s-DMS solvents. In Table 3 given are the optimized geometries of **4**, **5**, and **6** in the gas phase and in the s-DEE and s-DMS solvents.

As shown in Table 2, the geometries of **1**, **2**, or **3** in the two solvents and in the gas phase are very similar. As shown in Table 3, the geometries of **4**, **5**, or **6** in the two solvents and in the gas phase are similar, except that the C10—C11 bond lengths and the C9C10Cl11 bond angles in **4** and **5** have somewhat different values in the solvents and in the gas phase. We will mention the geometries of **4**, **5**, and **6** again in the subsection 'Reactions (2)—anionic hyperconjugation in CF_2XCClY^-'.

As shown in Table 1, solvation energies of all the neutral species in the two solvents are negligibly small (0.5–2.4 kcal/mol), while all the anionic species have very

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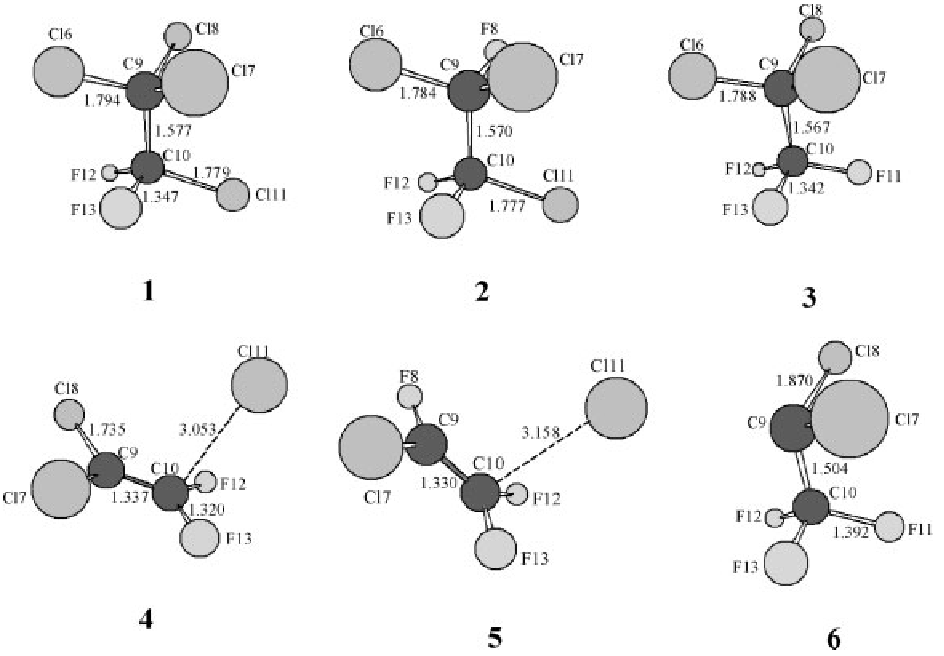

Figure 1. Optimized structures of CF_2XCCl_2Y (**1**, **2**, and **3**) and CF_2XCClY^- (**4**, **5**, and **6**) in the gas phase (optimized values for the important bond lengths are given in Å)

large solvation energies. Scheme 1 involves four kinds of anionic species: Nu^- (CH_3O^-), CF_2XCClY^-, X^-, and $NuCF_2$—$CClY^-$. In each of the four reaction equations in Scheme 1, two different kinds of anionic species appear in the two sides. It is noted in Table 1 that in each of the two solvents different kinds of anionic species may have quite different (large) solvation energy values, which will lead to the fact that the ΔH values (and the signs of the values) for the reactions in solution may be quite different from those in the gas phase.

Table 1. Relative energies (in kcal/mol) of the reactant and product species in the four reactions of Scheme 1 in the gas phase[a] and in the s-DEE and s-DMS solvents[b],[c]

	Gas	S-DEE	S-DMS
CH_3O^-	0.0 (−115.11153)[d]	−45.2[e]	−58.4[e]
$CF_2ClCCl_2^-$ (**4**)[f]	0.0 (−1656.53455)	−36.1	−47.6
$CF_2ClCClF^-$ (**5**)[f]	0.0 (−1296.17576)	−36.8	−48.5
$CF_3CCl_2^-$ (**6**)	0.0 (−1296.17136)	−32.0	−41.2
Cl^-	0.0 (−460.27473)	−43.2	−55.4
F^-	0.0 (−99.85970)	−55.2	−70.6
$CH_3OCF_2CCl_2^-$	0.0 (−1311.44408)	−33.7	−44.1
$CH_3OCF_2CClF^-$	0.0 (−951.08510)	−35.8	−46.8
CH_3OCl	0.0 (−575.26336)	−1.4	−2.1
CF_2ClCCl_3 (**1**)	0.0 (−2116.66299)	−0.5	−0.8
CF_2ClCCl_2F (**2**)[f]	0.0 (−1756.31999)	−0.5	−0.7
CF_3CCl_3 (**3**)	0.0 (−1756.32570)	−0.5	−0.7
$CF_2{=}CCl_2$	0.0 (−1196.25014)	−0.6	−0.9
$CF_2{=}CClF$	0.0 (−835.89195)	−0.7	−1.0
$CH_3OCF_2CCl_3$	0.0 (−1771.61362)	−1.6	−2.4
$CH_3OCF_2CCl_2F$	0.0 (−1411.27013)	−1.6	−2.4

[a] Gas-B3LYP calculations were performed for the species in the gas phase.
[b] SCIPCM-B3LYP calculations were performed for the species in the two solvents.
[c] s-DEE = DiEthylEther (ε = 4.335) and s-DMS = DiMethylSulfoxide (ε = 46.7).
[d] Values in parentheses are total energies in a.u.
[e] Relative energy values listed in the third and fourth columns are just the solvation energies in the two solvents.
[f] The most stable conformer.

In Table 4 given are the ΔH values for reactions (1)–(4) of Scheme 1 from **1**, **2**, and **3** in the gas phase and in the s-DEE and s-DMS solvents. It is noted that the calculated ΔH values for each of the reactions of Scheme 1 from **1**, **2**, or **3** in the nonpolar s-DEE solvent and in the polar s-DMS solvent are quite similar and have the same signs. The last row of Table 4 shows information obtained in the gas-phase reaction path calculations, and it tells that there are intermediates along the paths of reactions (1) from **1**, **2**, and **3** and the path of reaction (4) from **3** and that no transition states (no barriers) exist for all the reactions (reactions (1)–(4) from **1**, **2**, and **3**).

Reactions (1)—the chlorophilic attacks of CH_3O^-

The chlorophilic attack involved in reactions (1) was previously explained by the reasoning of the HOMO-LUMO interaction between CH_3O^- and perchlorofluoroethanes (**1**, **2**, and **3**) based on the MNDO electronic structures.[6] In *ab initio* HF (//gas-B3LYP) electronic structures of CH_3O^- and of **1**, **2**, and **3**, we have found: (i) the negative LUMO energy values of **1**, **2**, and **3** are close to the HOMO energy value of CH_3O^-; (ii) the HF charge values on all the chlorine atoms in **1**, **2**, and **3** are

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Table 2. Optimized geometries of CF_2XCCl_2Y (**1**, **2**, and **3**) in the gas phase[a] and in the s-DEE and s-DMS solvents[b,c] (bond lengths, bond angles, and dihedral angles are denoted as R, A, and D, and given in Å, degrees, and degrees, respectively; for notations, refer to Fig. 1)

	Parameter	Gas	S-DEE	S-DMS
1: CF_2ClCCl_3 (X = Cl, Y = Cl)	R(Cl6–C9)	1.794	1.794	1.794
	R(Cl7–C9)	1.787	1.787	1.786
	R(C9–C10)	1.577	1.576	1.576
	R(C10–Cl11)	1.779	1.777	1.777
	R(C10–F13)	1.347	1.349	1.349
	A(Cl6C9C10)	107.7	107.6	107.6
	A(Cl7C9C10)	109.5	109.5	109.5
	A(Cl11C10C9)	113.5	113.6	113.6
	A(F13C10C9)	109.0	109.0	109.0
	D(F13C10C9Cl6)	−58.7	−58.6	−58.6
	D(Cl7C9C10Cl11)	−60.7	−60.7	−60.7
2: CF_2ClCCl_2F[d] (X = Cl, Y = F)	R(Cl6–C9)	1.784	1.784	1.784
	R(Cl7–C9)	1.779	1.778	1.778
	R(F8–C9)	1.355	1.356	1.357
	R(C9–C10)	1.570	1.570	1.570
	R(C10–Cl11)	1.777	1.776	1.776
	R(C10–F12)	1.348	1.349	1.349
	R(C10–F13)	1.346	1.347	1.347
	A(Cl6C9C10)	109.4	109.4	109.4
	A(Cl7C9C10)	111.2	111.3	111.3
	A(F8C9C10)	107.6	107.5	107.4
	A(Cl11C10C9)	112.3	112.4	112.5
	A(F12C10C9)	108.5	108.4	108.4
	A(F13C10C9)	109.6	109.6	109.5
	D(F13C10C9Cl6)	−62.2	−61.8	−61.9
	D(Cl7C9C10Cl11)	−61.2	−60.9	−61.0
3: CF_3CCl_3 (X = F, Y = Cl)	R(Cl6–C9)	1.788	1.788	1.788
	R(C9–C10)	1.567	1.566	1.566
	R(C10–F11)	1.342	1.342	1.342
	A(Cl6C9C10)	108.6	108.5	108.5
	A(C9C10F11)	110.6	110.6	110.7
	D(Cl6C9C10F13)	−60.0	−60.0	−60.0

[a,b,c,d] Refer to footnotes a, b, c, and f of Table 1, respectively.

small negative values or positive values (the B3LYP charge values are all positive); and (iii) the LUMOs of **1**, **2**, and **3** have very small amplitudes on the fluorine atoms, but have important amplitudes on all (for **3**) or some (for **1** and **2**) chlorine atoms. These three points are just those found in the MNDO electronic structures,[6] and the present calculations support the previous explanations[6] for the chlorophilic attacks. As shown in Table 4, the present calculations predict negative ΔH values for reactions (1) of **1** and **2** in the gas phase and a small positive ΔH value (within the accuracy of calculation) for reaction (1) of **3** in the gas phase.

Now we see in Table 4 how solvation energy affects the ΔH value of reaction (1) in solution. For reaction (1) of **1**, the large negative ΔH value in the gas phase becomes small negative ΔH values in the solvents; for reaction (1) of **2**, the small negative ΔH value in the gas phase becomes small positive ΔH values in the solvents; and for reaction (1) of **3**, the small positive ΔH value in the gas phase becomes large positive ΔH values in the solvents. The reason for these changes is that the solvation energies of the CH_3O^- anion are significantly larger than those of the CF_2XCClY^- anions **4**, **5**, and **6**.

Reactions (2)—anionic hyperconjugation in CF_2XCClY^-

In our previous study,[6] the reactant anions CF_2XCClY^- (**4**, **5**, and **6**) of reactions (2) were considered as hyperconjugative anions,[12–14] analogous to CF_3—CF_2^-. The geometric and energetic features of anionic hyperconjugation in **4**, **5**, and **6** in the gas phase were discussed on the basis of the MNDO calculations, and the calculated positive ΔH values for reactions (2) were the predicted hyperconjugative stabilization energy values.

In the gas-B3LYP geometries of **4**, **5**, and **6**, we note: (i) the local geometries at the C9 center are nonplanar (see the XC9C10Cl11and XC9C10F11dihedral angle values in the gas phase in Table 3); (ii) the C—C bonds are (significantly) shorter than those in **1**, **2**, and **3**,

Table 3. Optimized geometries of CF$_2$XCClY$^-$ (**4**, **5**, and **6**) in the gas phase[a] and in the s-DEE and s-DMS solvents[b,c] (bond lengths, bond angles, and dihedral angles are denoted as R, A, and D, and given in Å, degrees, and degrees, respectively; for notations, refer to Fig. 1)

	Parameter	Gas	S-DEE	S-DMS
4: CF$_2$ClCCl$_2^{-d}$ (X = Cl, Y = Cl)	R(Cl7–C9)	1.735	1.733	1.732
	R(C9–C10)	1.337	1.333	1.332
	R(C10–F13)	1.320	1.320	1.322
	R(C10–Cl11)	3.053	3.360	3.459
	A(Cl7C9C10)	121.3	121.2	121.2
	A(C9C10F13)	123.3	123.9	124.1
	A(C9C10Cl11)	103.8	104.1	101.0
	D(Cl7C9C10Cl11)	−87.0	−89.1	−89.2
	D(Cl8C9C10Cl11)	87.0	89.1	89.2
5: CF$_2$ClCClF^{-d} (X = Cl, Y = F)	R(Cl7–C9)	1.722	1.716	1.715
	R(F8–C9)	1.349	1.347	1.347
	R(C9–C10)	1.330	1.328	1.327
	R(C10–Cl11)	3.158	3.325	3.439
	R(C10–F12)	1.322	1.323	1.324
	R(C10–F13)	1.321	1.322	1.324
	A(Cl7C9C10)	124.7	125.0	125.1
	A(F8C9C10)	120.6	120.0	119.9
	A(C9C10Cl11)	102.8	97.5	95.0
	A(F12C10C9)	122.7	123.1	123.4
	A(F13C10C9)	123.4	124.0	124.0
	D(Cl7C9C10Cl11)	−87.1	−89.5	−90.9
	D(F8C9C10Cl11)	87.8	87.8	86.9
6: CF$_3$CCl$_2^-$ (X = F, Y = Cl)	R(Cl7–C9)	1.870	1.866	1.866
	R(C9–C10)	1.504	1.502	1.501
	R(C10–F11)	1.392	1.392	1.391
	R(C10–F12)	1.370	1.369	1.369
	A(Cl7C9C10)	105.4	105.3	105.3
	A(C9C10F11)	120.6	120.4	120.3
	A(C9C10F12)	110.6	110.6	110.6
	D(Cl7C9C10F11)	−56.2	−56.2	−56.1
	D(Cl8C9C10F11)	56.2	56.2	56.1

[a,b,c,d]Refer to footnotes a, b, c, and f of Table 1, respectively.

respectively (Fig. 1); and (iii) the C10—Cl11 and C10—F11 bonds are (significantly) longer than the respective bonds in **1**, **2**, and **3** (Fig. 1). These are just the geometric features[12–14] of anionic hyperconjugation in **4**, **5**, and **6** in the gas phase presented in the previous paper.[6] The positive ΔH values for reactions (2) in the gas phase, given in Table 4, are just the B3LYP stabilizing energies for **4**, **5**, and **6** in the gas phase (with respect to CF$_2$═

Table 4. Calculated ΔH values (in kcal/mol) for reactions (1), (2), (3), and (4) of Scheme1 from **1**, **2**, and **3** in the gas phase[a] and in the s-DEE, and s-DMS solvents[b,c]

Reactant	Solvent	Reaction (1)	Reaction (2)	Reaction (3)	Reaction (4)
1: CF$_2$ClCCl$_3$ (X = Cl, Y = Cl)	Gas	−14.7	6.1	−51.7	−25.8
	s-DEE	−6.4	−1.7	−39.6	−29.3
	s-DMS	−5.1	−2.7	−36.5	−30.8
2: CF$_2$ClCCl$_2$F (X = Cl, Y = F)	Gas	−4.8	5.7	−51.2	−25.6
	s-DEE	2.6	−1.4	−41.1	−27.8
	s-DMS	3.8	−2.3	−38.6	−28.9
3: CF$_3$CCl$_3$ (X = F, Y = Cl)	Gas	1.6	38.6	−51.7	−9.5
	s-DEE	13.8	14.8	−39.6	−9.0
	s-DMS	17.4	8.3	−36.5	−8.3
Along reaction path[d]		No TS, one IM	No TS, no IM	No TS, no IM	For **1** and **2**: no TS, no IM; for **3**: no TS, one IM

[a,b,c]Refer to footnotes a, b, and c of Table 1, respectively.

[d]Based on the gas-B3LYP reaction path calculations; TS and IM denote transition state and intermediate, respectively.

$CClY + X^-$), representing the energetic feature[12–14] of the hyperconjugative anions. So, the B3LYP calculations give proper descriptions for anionic hyperconjugation in **4**, **5**, and **6** in the gas phase.

In the (SCIPCM-B3LYP) geometries of **6** in the two solvents, we can find the three geometric features of anionic hyperconjugation. In the (SCIPCM-B3LYP) geometries of **4** and **5** in the two solvents, we can find the geometric features (ii) and (iii) of anionic hyperconjugation, but the local geometries at the C9 center are almost planar (probably because the C10—Cl11 bonds are too long). We should still say that the **4**, **5**, and **6** anions in solution have the geometric features of anionic hyperconjugation.

In the gas phase the energetic feature of anionic hyperconjugation is related to the positive ΔH value of reaction (2), which is just the hyperconjugative stabilization energy value. However, in solution the ΔH values of reactions (2) are not always positive (Table 4) and they are not directly related to the stabilization energies (see the following analyses).

For reactions (2) of **4** and **5** the positive ΔH values in the gas phase become small negative ΔH values in the solvents, and for reactions (2) of **6** the large positive ΔH value in the gas phase becomes a small positive ΔH value in the solvents. As shown in Table 1, the solvation energies of the Cl^- and F^- anions (as the products of reactions (2)) are significantly larger than those of **4**, **5**, and **6** (as the reactants of reactions (2)). It is realized that there are two factors affecting the ΔH value of reaction (2) in solution: (i) the hyperconjugative stabilization in the reactant anion, which makes the ΔH value (algebraic value) increase and (ii) the superiority of the solvation energy of the product anion over the reactant anion, which makes the ΔH value (algebraic value) decrease. The positive ΔH value for reaction (2) of **6** in solution indicates that factor (i) prevails over factor (ii). The negative ΔH values for reactions (2) of **4** and **5** in solution indicate that factor (ii) prevails over factor (i). The negative SCIPCM-B3LYP ΔH values for reactions (2) of **4** and **5** in solution support our previous supposition[6] that in solution reactions (2) of **4** and **5** might still easily occur.

Anionic chain process mechanism in solution

As shown in Table 4, the ΔH values for reactions (3) and (4) from **1**, **2**, and **3** in the two solvents are all negative (most of them being large negative values), which indicates that reactions (3) and (4) from **1**, **2**, and **3** in solution are always feasible. Therefore we could focus on reactions (1) and (2) in examining the anionic chain process mechanism for the reactions of nucleophiles with perchlorofluorethanes **1**, **2**, and **3** in solution.

For 1,1-difluorotetrachloroethane (**1**) in the s-DEE and s-DMS solvents, reactions (1) and (2) are predicted to be all exothermic (see the negative ΔH values in Table 4). Therefore we conclude that the reaction of nucleophile (CH_3O^-) with 1,1-difluorotetrachloroethane (**1**) in solution proceeds via the anionic chain process (Scheme 1). For 1,1,2-trichlorotrifluoroethane (**2**) in the s-DEE and s-DMS solvents, reactions (1) are predicted to be slightly endothermic (by 2.6 and 3.8 kcal/mol, respectively) and reactions (2) to be slightly exothermic (by 1.4 and 2.3 kcal/mol, respectively). The sums of the ΔH values of reactions (1) and (2) in the two solvents are evaluated to be only 1.2 and 1.5 kcal/mol, respectively, which are within the accuracy of calculation, and the two reaction steps (reactions (1) and (2)) are followed by the strongly exothermic reaction steps (3) and (4) (the ΔH values for reactions (3) and (4) in the solvents being around −40 and −28 kcal/mol, respectively). Therefore we conclude that the reaction of nucleophile (CH_3O^-) with 1,1,2-trichlorotrifluoroethane (**2**) in solution proceeds via the anionic chain process (Scheme 1).

For 1,1,1-trichlorotrifluoroethane (**3**) in the s-DEE and s-DMS solvents, reactions (1) are predicted to be endothermic (by 13.8 and 17.4 kcal/mol, respectively) and reactions (2) are predicted to be also endothermic (by 14.8 and 8.3 kcal/mol, respectively). However, reactions (3) from **3** in the s-DEE and s-DMS solvents are highly exothermic (by 39.6 and 36.5 kcal/mol, respectively) and reactions (4) from **3** in the two solvents are exothermic (by 9.0 and 8.3 kcal/mol, respectively). The sums of the ΔH values of reactions (1)–(4) in the two solvents are evaluated to be both around −20 kcal/mol. Therefore, the reaction of nucleophile (CH_3O^-) with 1,1,1-trichlorotrifluoroethane (**3**) in solution may proceed via the anionic chain process (Scheme 1).

For the reaction of **3** with thiophenoxide a competitive reaction pathway (Scheme 2) other than the anionic chain process was indicated by the experiments.[3] The first step (reaction (1)) of Scheme 2 involves the chlorophilic attack of PhS^- (similar to reaction (1) of Scheme 1) and the second step (reaction (5)) of Scheme 2 leads to the $NuCCl_2CF_3$ final product.

Our SCIPCM-B3LYP calculations in the s-DEE and s-DMS solvents predict that reactions (1) of Scheme 2 in the two solvents are endothermic by 12.0 and 12.2 kcal/mol, respectively. We performed SCIPCM-B3LYP calculations in the s-DEE and s-DMS solvents for the $CH_3O^- + {}^-CCl_2CF_3 \rightarrow CH_3OCCl_2CF_3 + Cl^-$ reaction and the predicted ΔH values are −83.2 and −86.1 kcal/mol, respectively. Since this reaction is similar to reaction (5) of Scheme 2, we believe that

$$Nu^- + CF_3CCl_3 \rightarrow NuCl + CF_3CCl_2^- \quad (1)$$

$$NuCl + {}^-CCl_2CF_3 \rightarrow NuCCl_2CF_3 + Cl^- \quad (5)$$

Where $Nu^- = PhS^-$

Scheme 2 (for **3**)

reactions (5) of Scheme 2 in the s-DEE and s-DMS solvents are also highly exothermic. Therefore we reach a conclusion that the reactions of PhS^- with **3** in solution can also follow the reaction pathway shown in Scheme 2.

Our conclusions presented in the second, third, and fifth paragraphs of the present subsection all support the experimental investigations.[1–5]

CONCLUSIONS

The main purpose of the present work is to examine the anionic chain process mechanism (Scheme 1) for the spontaneous reactions of nucleophiles with perchlorofluoroethanes, suggested by the experimental investigations.[1–5] In our previous MNDO work, only reactions (1) and (2) of Scheme 1 were studied and reactions (2) were predicted to be unfeasible because solution effects were not considered. In the present work, all the four reactions of Scheme 1 in the solution condition have been studied based on the SCIPCM-B3LYP calculations.

The gas-HF/B3LYP electronic structure calculations support the previous explanation for the chlorophilic attacks of nucleophiles in reactions (1) based on the MNDO electronic structure calculations and the gas-B3LYP geometric and energetic results for **4**, **5**, and **6** support the previous MNDO descriptions of anionic hyperconjugation in the three anions in the gas phase.

Our calculations indicate that the solvation energies of all the four kinds of anionic species, as the reactants and/or products in the four reactions of Scheme 1, are very large in the two solvents and the different kinds of anionic species have quite different (large) solvation energy values. Since the anionic species appear in both sides of each reaction equation of Scheme 1, different solvation energy values for the different kinds of anionic species result in the fact that the ΔH values for the reaction in solution are significantly different from the ΔH value in the gas phase (the ΔH values for each of the reactions in the nonpolar s-DEE and polar s-DMS solvents being similar). For reactions (2) there is another factor affecting the ΔH values: the hyperconjugative stabilization in the reactant anions, and the competition between the two factors (anionic hyperconjugation and solvation) leads to the negative ΔH values for reactions (2) of **4** and **5** (from **1** and **2**, respectively) in the two solvents.

Based on our SCIPCM-B3LYP calculations in the nonpolar s-DEE and polar s-DMS solvents, we have the following conclusions on the mechanisms for the reactions of nucleophiles with perchlorofluoroethanes **1**, **2**, and **3** in solution: the reactions of nucleophile (CH_3O^-) with **1** and **2** in solution proceed via the anionic chain process (Scheme 1); the reaction of nucleophile (CH_3O^-) with **3** in solution may proceed via the anionic chain process (Scheme 1); and the reaction of nucleophile (PhS^-) with **3** in solution may also follow the reaction pathway shown in Scheme 2. All these conclusions are in agreement with the experimental indications.[1–5]

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