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A PRELIMINARY QUANTUM-CHEMICAL STUDY OF THE MECHANISMS FOR THE REACTIONS OF PERCHLOROFLUOROETHANES WITH NUCLEOPHILES INITIATED BY CHLOROPHILIC ATTACKS

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ABSTRACT

A preliminary theoretical study of the mechanisms for the reactions of the perchlorofluoroethanes CF_2ClCCl_3 (**1**), CF_2ClCCl_2F (**2**) and CF_3CCl_3 (**3**), with nucleophiles has been carried out by the MNDO method, following the experimentally suggested process shown in Scheme 1. The unlikely chlorophilic attack in the first step of Scheme 1 has been shown to be feasible for **1**, **2** and **3** by analysis of the MO interactions. The second step has been found to be affected by the anionic hyperconjugation which stabilizes the anions $CF_2ClCCl_2^-$ (**4**), $CF_2ClCClF^-$ (**5**) and $CF_3CCl_2^-$ (**6**) and would make reactions (2) (the second step) unfeasible in gas phase, but in solution reaction (2) may still easily occur for **4** and **5**.

INTRODUCTION

The carbon atoms of perhalofluoroalkanes are not vulnerable to direct S_N2 type attack by nucleophiles, thus the nucleophiles can only attack the exposed halogen atoms.

$$\mathrm{Nu^- + Hal{-}C{\leq} \rightarrow Nu{-}Hal + {}^-C{\leq}}$$

Recently, X.-Y. Li *et al.* reported the spontaneous reactions of sodium thiophenoxide,[1] aryloxides and alkoxides[2] with 1,1-difluorotetrachloroethane (**1**), 1,1,2-trichlorotrifluoroethane (**2**) and 1,1,1-trichlorotrifluoroethane (**3**) leading to the formation of $Nu{-}CF_2CYCl_2$ (Y = F, Cl) type of products. Experimental investigations have suggested that the reactions proceed via an anionic chain process with the direct attack of the sulphur and oxygen nucleophiles on the chlorine atoms as the initiation step. This process has recently been defined as 'Nucleophilic substitution initiated by halophilic attack'[3] (Scheme 1). The first step, i.e. the attack of the nucleophiles on the chlorine atoms, results in carbanions (**4**, **5** and **6**), which become perchlorofluoroethenes in the second step.

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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

$$\begin{array}{llr}
Nu^- + CF_2XCCl_2Y & \longrightarrow Nu\text{—}Cl + CF_2XCClY^- & (1) \\
CF_2XCClY^- & \longrightarrow CF_2{=}CClY + X^- & (2) \\
Nu^- + CF_2{=}CClY & \longrightarrow NuCF_2\text{—}CClY^- & (3) \\
NuCF_2\text{—}CClY^- + CF_2XCCl_2Y & \longrightarrow NuCF_2\text{—}CCl_2Y + CF_2XCClY^- & (4) \\
NuCF_2\text{—}CClY^- + Nu\text{—}Cl & \longrightarrow NuCF_2CCl_2Y + Nu^- & (5) \\
Nu^- + Nu\text{—}Cl & \longrightarrow Nu\text{-}Nu + Cl^- & (6)
\end{array}$$

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

Scheme 1

The chlorophilic attacks by sulphur or oxygen nucleophiles involve the cleavage of a C—Cl bond and the formation of a relatively weaker S—Cl or O—Cl bond. At first glance, it seems that this reaction will be energetically unfavourable. However, the experimental results showed that the reactions can occur spontaneously at room temperature or even below. Therefore a theoretical study on the energetics of this reaction would be interesting and may give some answers to this puzzling problem.

Thus we have been trying a quantum-chemical study for the mechanisms of these interesting reactions. In general, *ab initio* calculations (SCF, CI and MBPT...) with double-zeta basis sets augmented with polarization functions can give reliable theoretical descriptions for chemical reactions. However the big numbers of electrons in perchlorofluoroethanes have forced us to turn to the semi-empirical MNDO method.[4] The MNDO method usually predicts reliable equilibrium geometries and heats of formation for organic molecules containing C, O and H atoms.[5] However semi-empirical methods such as MNDO may not give reliable descriptions for the reaction paths and only a few MNDO studies for halogenides have ever been reported in the literature.[6] These would be the potential difficulties for our MNDO study.

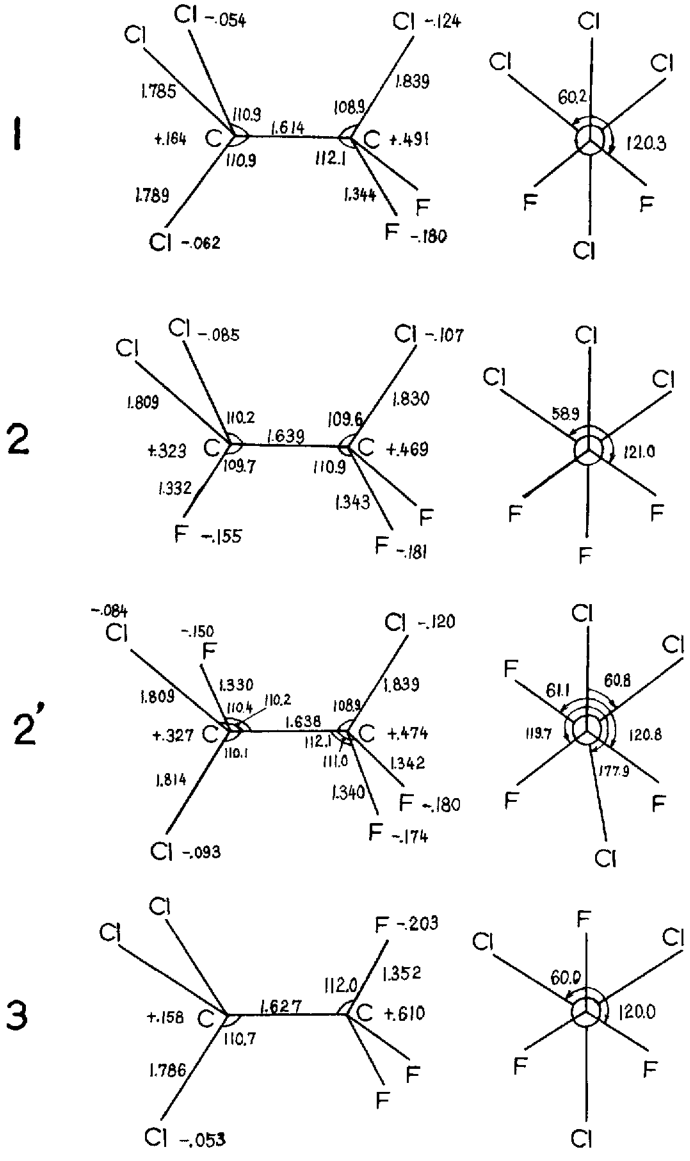
We have performed the MNDO geometry optimization calculations for all the reactants and products in reaction steps (1) and (2) for **1**, **2** and **3**, respectively. To save computing time, we have chosen CH_3O^- as a model nucleophile. For the species presenting two or more stable conformers in our MNDO calculations, we always consider the most stable one. However, for 1,1,2-trichlorotrifluoroethane we have obtained two almost equally stable conformers **2** and **2′** (see Figure 1).

The calculated results are given in Figure 1 (the MNDO optimized geometries, charge distributions, and the LUMO energies for **1**, **2**, **2′** and **3**), Figure 2 (the MNDO optimized geometries and charge distributions for **4**, **5** and **6**), and Table 1 (the calculated heats of formation). Based on these results, we will discuss reactions (1) and (2) and present our preliminary explanations for the experimentally suggested mechanisms for the reactions of perchlorofluorethanes with nucleophiles, especially for the 'chlorophilic attacks'.

RESULTS AND DISCUSSION

1. Chlorophilic attacks of nucleophiles

The reactions (1) shown in Scheme 1 involve the attack of Nu^- (CH_3O^-) on the chlorine atoms of perchlorofluoroethanes. We will explain why it is feasible.



	1	2	2'	3
ε_{LUMO} (eV)	-1.661	-1.594	-1.868	-1.372

Figure 1. The MNDO optimized geometries and the LUMO energies (ε_{LUMO}) of CF_2XCCl_2Y **1**, **2**, **2'** and **3**. Bond lengths in Å, angles in degrees, and charges given by the figures with the signs

For the ordinary S_N2 displacement reactions, Salem[7] considered the reaction of chloromethane with nucleophilic reagents (anions) as his model reaction and successfully predicted the choices of the directions of the nucleophilic attacks on the carbon atom. His theory is based on the interactions between the HOMO (lone pair) of nucleophiles and the LUMO of chloromethane. This LUMO is essentially the empty σ* antibonding orbital of the

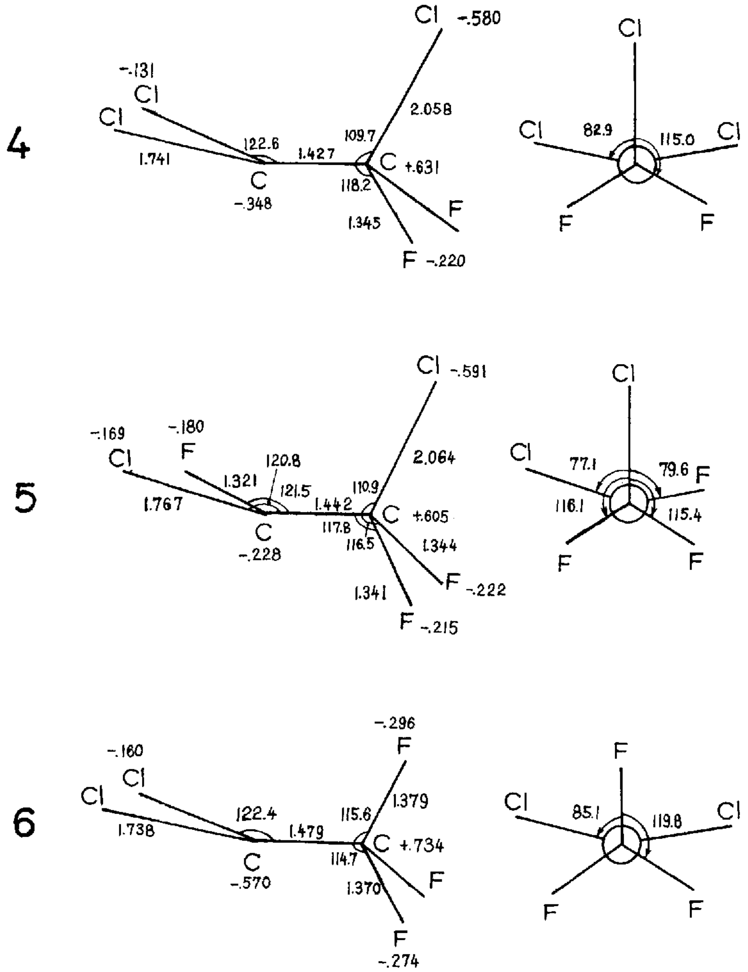


Figure 2. The MNDO optimized geometries of CF_2XCClY^- **4**, **5** and **6**. Bond lengths in Å, angles in degrees, and charges given by the figures with the signs

Table 1. The calculated heats of formation (kcal/mol) and the ΔH (kcal/mol) for the reaction step (1) of CH_3O^- with **1**, **2** and **3**

	CF_2XCCl_2Y	CH_3O^-	CF_2XCClY^-	CH_3OCl	$CF_2{=}CClY$	F^-	Cl^-	ΔH
X = Cl	−109·7	−39·8	−154·4	−11·3	−91·3		−54·9	−16·2
Y = Cl	(**1**)		(**4**)					
	−151·0							−14·3
X = Cl	(**2**)							
Y = F	−150·2	−39·8	−193·8	−11·3	−131·1		−54·9	
	(**2′**)		(**5**)					
X = F	−158·6	−39·8	−189·7	−11·3	−91·3	−59·9[a]		−2·6
Y = Cl	(**3**)		(**6**)					

[a] The experimental value (A.A. Woof. *Adv. Inorg. Chem. Radiochem.*, **24**, 1, 1981).

C—Cl bond, and it will be broken under the attack of the nucleophiles, leading to the departure of the chlorine atom. The attack on the chlorine atom was not considered, since the amplitude on it in this LUMO is smaller than that on the carbon atom. Another reason for this is probably that it carries relatively big negative charge, repulsing the attacking anion. However, it should be emphasized that electrostatic effects alone cannot account for the phenomena in this kind of reaction.[8]

We have performed the MNDO calculations for CH_3Cl and CH_3O^-. The LUMO energy of CH_3Cl and the HOMO energy of CH_3O^- are +0·996 and −2·415 eV, respectively, and the charge on the Cl atom is −0·215 e.

As we have mentioned, the carbon atoms of **1**, **2** and **3** are not vulnerable to the attacks of nucleophiles (CH_3O^-), since they are surrounded by six halogen atoms, the sizes of which are much bigger than protons. Based on our MNDO results, we have found that the electronic structures of **1**, **2** (**2′**) and **3** have two striking features, compared with that of CH_3Cl. First, the LUMOs of **1**, **2** (**2′**) and **3** have negative energies (see Figure1) and they are much lower in energy than the LUMO (+0·996 eV) of CH_3Cl. This is apparently because of the substitution of the electronegative halogen atoms for all the hydrogens in the molecules. Since the LUMOs of **1**, **2** (**2′**) and **3** are very close in energy to the HOMO ($\varepsilon = -2{\cdot}415$ eV) of CH_3O^-, the orbital interactions must be strong. Therefore reaction (1) can occur easily (even spontaneously). Secondly, the negative charges on the chlorine atoms in **1**, **2** (**2′**) and **3** are small (see Figure 1), which favours the attack of the negative ion CH_3O^- on a chlorine atom.

An effective HOMO–LUMO interaction also needs the best possible overlap. Our calculations indicate that the LUMOs of **1**, **2** (**2′**) and **3** have very small amplitudes on the fluorine atoms, but have important amplitudes on the two carbon atoms and all (for **3** and **2′**) or some (for **1** and **2**) chlorine atoms. Actually these LUMOs can be considered to consist of the σ^* antibonding orbitals of the C—Cl bonds. In conclusion, the strong HOMO–LUMO interaction between CH_3O^- and the perchlorofluoroethane eventually incorporates the attack of CH_3O^- on one of the chlorine atoms, leading to the breaking of the corresponding C—Cl bond, and then the products of the reactions (1) (CH_3OCl and CF_2XCClY^-) are obtained. This is our preliminary explanation for the chlorophilic attack in reactions (1).

It is difficult to predict on which chlorine atom in **1** and **2** (**2′**) the anion CH_3O^- attacks by only checking the amplitudes in the LUMOs and the small values of the charges. Since our calculated MNDO heats of formation for $CF_2ClCClY^-$ are slightly lower than the ones for $^-CF_2CCl_2Y$, we infer that the attack of CH_3O^- will presumably be on one of the chlorine atoms connecting with the carbon which has more chlorine atoms.

The above analyses, based on our MNDO results, are in agreement with the experimental indications.[1,2]

$$CH_3O^- + Cl{-}CClYCF_2X \rightarrow CH_3OCl + {}^-CClYCF_2X + \Delta H$$

Using the heats of formation shown in Table 1, the reactions (1) of CH_3O^- with the perchlorofluoroethanes are indicated to be exothermic by 16·2, 14·3 and 2·6 kcal/mol for **1**, **2** and **3** respectively. The largest value 16·2 kcal/mol presumably indicates that **1** has the largest reactivity, which is in agreement with the experimental results.[1,2] However, these thermodynamic parameters (ΔH) are not always parallel to the activation parameters and our calculated ΔH values serve only as a rough indicator of the reactivity. We also performed *ab initio* SCF (STO-3G) calculations for the energies of **1**, **4**, CH_3O^- and CH_3OCl at their MNDO optimized geometries, and the results indicate that the reaction (1) of **1** with CH_3O^- is exothermic by 80 kcal/mol (apparently this value is too large).

2. The CF_2XCClY^- ions and anionic hyperconjugation

The potential anionic hyperconjugation in CF_2XCClY^- (**4**, **5** and **6**) should stabilize the anions and therefore favours the chlorophilic attacks (the first step). However, it may cause a different effect on the second step in Scheme 1, namely, the β-elimination of the chloride or fluoride ions.

Detailed investigations on the hyperconjugation in anions CF_3—CH_2^- and CF_3—CF_2^- have recently been reported.[9,10,11] In terms of MO theory this effect is based on the stabilizing interaction of the lone pair (*n*) electrons on C^- by the C—F σ* orbital on the β-carbon. This interaction is strong becuase substitution of the electronegative fluorine atoms for the hydrogens on the β-carbon lowers the energy of the σ* orbital. Dixon *et al*[10] have shown, based on their *ab initio* calculations, that the energy of CF_3—CF_2^- is much lower than the sum of the energies of $CF_2{=}CF_2$ and F^-.

Since the chlorine atom is also electronegative, we realize that the anions **4**, **5** and **6** are presumably analogous to CF_3—CF_2^- and hyperconjugation stabilization must be considered in the study of the reactions (2). The MNDO optimized geometries of **4**, **5** and **6** are shown in Figure 2. These geometries represent the most stable conformers of the anions, respectively, in our MNDO calculations.

Compared with the geometries of their parent neutral molecules **1**, **2** (**2′**) and **3** (see Figure 1), the C—C bonds of **4**, **5** and **6** are all shortened and the C—X bonds *anti* to the lone pair lengthened. These are actually the two geometric features of the hyperconjugative anions.[9,10] Using the heats of formation shown in Table 1, the reactions (2) are indicated to be endothermic by 8·2, 7·8 and 38·5 kcal/mol for **4**, **5** and **6**, respectively. (For the evaluation of the third value, the experimental heat of formation for F^- has been used, and it would have been even bigger if the calculated one was used.) Based on the above discussions, we claim that **4**, **5** and **6** are hyperconjugatively stabilized anions.

It is worthy of note that in the most stable conformer of **4** or **5**, predicted by the MNDO method, the lone pair on the C^- atom is *anti* to a C—Cl bond on the β-carbon rather than to a C—F bond (see Figure 2), and that the stabilizing energy of anionic hyperconjugation in **6** is much bigger than in **4** and **5**.

3. The reaction mechanisms of nucleophiles with 1, 2 and 3

The experimental investigations[1b] have suggested that the reactions of nucleophiles with **1** and **2** have an anionic chain process shown in Scheme 1, but for the reactions with **3**, there may exist some other mechanistic pathway. We will try to give a preliminary explanation for the experimental indications by investigating only the first two steps of Scheme 1, reactions (1) and (2), based on our discussion in the above two subsections. The analyses presented in subsection 1 have indicated that the reactions (1) are energetically feasible for all of the perchlorofluoroethanes **1**, **2**, and **3**, therefore we will consider the reactions (2).

Due to the hyperconjugation stabilization, the energies of the reactants **4**, **5** and **6** are lower than the ones of the products, respectively, in the reactions (2), which presumably implies that the reactions (2) would be less favourable than their reverse reactions.

$$XCF_2\text{—}CClY^- \rightleftarrows X^- + CF_2{=}CClY$$

However, the experimental results showed that there was no difficulty for the β-elimination of chloride from the carbanions **4** and **5**. The attempt of trapping **4** and **5** failed.[1b] Apparently the differences between the solvation energies of the carbanions **4** and **5** and the much smaller chloride ion (X^-) overwhelm the slight differences between the intrinsic energies of the reactants and the products. The situation for carbanion **6** is different since in this case the stabilizing energy of anionic hyperconjugation (38·5 kcal/mol) may be too large to be overridden. In fact, the trapping of **6** by forming CF_3CCl_2H has been achieved and a competitive reaction pathway other than the anionic chain process was indicated in the reaction of **3** with thiophenoxide.[1b]

$$\mathrm{PhS^- + CF_3CCl_3 \rightarrow PhS\overset{\curvearrowleft}{Cl + {}^-}CCl_2CF_3 \rightarrow PhSCCl_2CF_3 + Cl^-}$$

The optimized geometries and charge distributions of **4**, **5** and **6** (see Figure 2) also give hints supporting the experimental indications. In the geometries of **4** and **5**, the C—X (C—Cl) bond *anti* to the lone pair (the bond to be broken) is much longer than a normal C—Cl bond and the negative charge on the leaving X(Cl) atom is already big (−0·580 and −0·591 e for **4** and **5**), which make the X(Cl) atom easily leave with one unit of negative charge in the solutions. However, relatively small negative charges on the three F atoms and the three approximately equal C—F bond lengths in **6** make the departure of a single F atom with one unit of negative charge more difficult.

Based on the above discussions on the feasibility of the reactions (2) of the corresponding negative carbanions **4**, **5** and **6** in the solutions, we conclude that the mechanistic pathway for the reactions of the perchlorofluoroethanes with nucleophiles, shown in Scheme 1, is likely for **1** and **2**, but not always likely for **3**. This is in agreement with the experimental indications.

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