1,2-FCl Rearrangement as an Intermediate Step in the Unimolecular 1,3-HCl Elimination from Chlorofluoropropanes[†]

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Calculations at the B3PW91/6-311+G(2d,p) level of theory have been performed on a series of chlorofluoropropanes in order to account for the chemistry of the molecules $CF_2ClCF_2CH_3$ and $CF_2ClCF_2CD_3$, chemically activated in the gas phase, which form novel elimination products, $CF_3CF{=}CH_2$ or $CF_3CF{=}CD_2$, formally a 1,3-HCl or DCl elimination together with a 1,2-fluorine migration. The proposed mechanism involves an initial 1,2-FCl rearrangement, with an activation energy of 62.5 kcal/mol, giving $CF_3CFClCH_3$, which is 3.3 kcal/mol lower in energy than $CF_2ClCF_2CH_3$. Subsequently $CF_3CFClCH_3$ eliminates HCl with a barrier height of 55.4 kcal/mol. This mechanism accounts for both the unimolecular kinetics and the small kinetic isotope effect. A concerted transition geometry has been characterized for the 1,2-FCl rearrangement of each molecule of the type $CF_2ClCXFCY_3$, where X and Y are H, D, or F; in each case the rearrangement leads to a more thermodynamically stable rearrangement product $CF_3CXClCY_3$.

Introduction

The gas-phase chemistry of hydrochlorofluorocarbons (HCFCs) is important as these molecules are becoming present in increasing quantities in the atmosphere due to their being primary replacement compounds for chlorofluorocarbons (CFCs). In the atmosphere, these HCFCs are able to eliminate HCl and HF, but this channel is not possible for the CFCs they are replacing.

Recent experiments[1] have involved the preparation of the HCFC molecule $CF_2ClCF_2CH_3$ and $CF_2ClCF_2CD_3$ in the gas phase by a radical collision which results in a molecule having approximately 100 kcal/mol of (thermal) energy. The major decomposition products of $CF_2ClCF_2CH_3$ were $CF_2ClCF{=}CH_2$, the result of a 1,2-HF elimination, and $CF_3CF{=}CH_2$, formally a 1,3-HCl elimination accompanied by the migration of a fluorine atom. This latter product is intriguing for a number of reasons. First, the reaction kinetics are unimolecular, suggesting that the mechanism of the reaction is not a radical abstraction, followed by rearrangement and recombination. Further evidence for the absence of a radical pathway is provided by the lack of larger recombination or addition products. Second, there is a relatively small kinetic isotope effect between HCl and DCl elimination from $CF_2ClCF_2CH_3$ and $CF_2ClCF_2CD_3$, suggesting that the reaction indeed takes part as a multistep process with unimolecular kinetics, and that the rate-determining step does not involve the H or D atoms which are eliminated from the molecule. Third, at higher pressures, the ratio of the HCl elimination to HF elimination decreases significantly − if this is a multistep process, there could be some stable intermediate molecule which is stabilized by multiple collisions at the greater pressure.

This type of gas-phase system at low pressure is ideal for the application of ab initio and density functional theory (DFT) calculations, as both intermolecular interactions and condensed media effects can be safely ignored. Kinetic isotope effects are well-reproduced by even low-level calculations, since they are dependent on relative rather than absolute electronic energies.

In this paper, we propose a reaction mechanism for the 1,3-HCl elimination from $CF_2ClCF_2CH_3$ which involves an initial 1,2-FCl rearrangement, followed by a 2,3-HCl elimination, the rearrangement being the rate-determining step. This pathway is supported by ab initio and DFT calculations of the properties of the molecules and transition geometries, and RRKM[2] calculation of the kinetic rate constants for the rearrangement and elimination pathways. We extend this work to related molecules $CF_2ClCHFCH_3$, $CF_2ClCF_2CF_3$ and $CF_2ClCHFCF_3$ in order to determine whether any of those molecules would follow the same pathways, and to investigate the effects of fluorine substitution on the energetics and kinetics of these molecules.

There has been no previous work on a reaction scheme similar to the one presented in this paper, however calculations of 1,2-fluorine migrations have been performed on the radical FCH_2-CH_2,[3] and the carbene CF_3CH,[4] both open-shell systems. The barrier to migration was calculated to be 41 kcal/mol for FCH_2-CH_2 and 23.5 kcal/mol for CF_3CH. In a theoretical study of the $ClCH_2CH_2$ radical, a chlorine-bridged structure was determined to be a transition geometry which was 1.7 kcal/mol higher in energy than the classical nonbridged structure at the B3PW91/6-31G(d,p) level of theory.[5]

Theoretical Methods

Standard ab initio and DFT calculations have been performed using the GAUSSIAN 98[6] suite of programs. The ground-state molecules and transition geometries have been optimized using density functional theory involving Becke's three-parameter exchange functional[7] along with the correlation function of Perdew and Wang.[8] The basis set for the calculations is Pople's 6-311+G(2d,p);[9] this level of calculation is referred to as B3PW91/6-311+G(2d,p), and has previously been demonstrated to give accurate geometries and energies for HF and HCl

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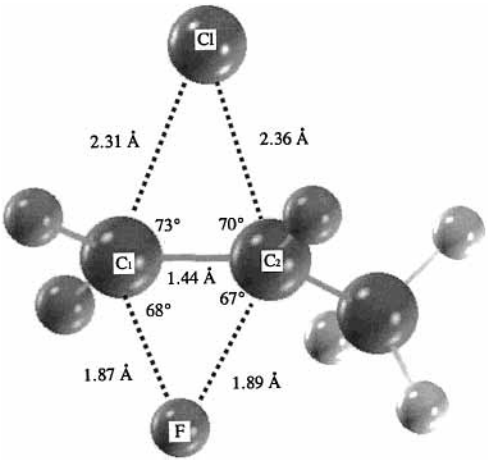


Figure 1. Calculated transition geometry at B3PW91/6-311+G(2d,p) for a 1,2-FCl rearrangement of $CF_2ClCF_2CH_3$ to $CF_3CFClCH_3$

TABLE 1: Important Internuclear Distances (Å) and Angles (Degrees) in the Rearrangement of $CF_2ClCF_2CH_3$ to $CF_3CFClCH_3$ Calculated at B3PW91/6-311+G(2d,p)

	$CF_2ClCF_2CH_3$	transition geometry	$CF_3CFClCH_3$
C−C	1.551	1.437	1.544
C_1−Cl	1.779	2.313	
C_2−Cl		2.357	1.791
C_1−F		1.865	1.341
C_2−F	1.362	1.886	
C−C−C	115.4	125.7	113.1
Cl−C_1−C_2	111.7	73.77	
Cl−C_2−C_1		70.41	108.2
F−C_2−C_1	105.6	66.72	
F−C_1−C_2		68.24	109.2

elimination from HCFCs.[10] All transition geometries have been characterized by calculations of the vibrational frequencies, and traced from the initial to the final geometry by the intrinsic reaction coordinate (IRC) method.[11] Animations along the IRC pathway have been generated using See The Molecule (STM)[12] and Advanced Visual Systems (AVS) and are available for viewing on the worldwide web.[13]

Vibrational frequencies and zero-point vibrational energies have been calculated at the B3PW91/6-311+G(2d,p) level of theory, with isotopic effects on the frequencies taken into account by adjusting the mass-weighted coordinates. All relative energies reported in this paper have been corrected for zero-point energy. Atomic charges and bond paths have been calculated using the theory of Atoms in Molecules,[14] with the electron densities generated from the B3PW91/6-311+G(2d,p) wave function. Additional calculations on the $CF_2ClCF_2CH_3$ rearrangement and elimination pathways have been carried out using the larger basis set B3PW91/cc-pvtz,[15] and also using second-order Moller Plesset perturbation theory MP2/6-311+G-(2d,p).

Results and Discussion

The transition geometry for the 1,2-FCl rearrangement of $CF_2ClCF_2CH_3$ is shown in Figure 1, and the important internuclear distances and angles and the changes they undergo during the rearrangement are displayed in Table 1. The exchanging fluorine and chlorine atoms are near planar with the two carbon atoms to which they are bonded, the torsional angle is 1.4°. The chlorine atom is at a distance of 2.31 Å from the carbon it is initially attached to and 2.36 Å from the carbon it is approaching, a very extended bond compared to the bond distance of 1.78 Å in the initial molecule. The fluorine atom is 1.89 Å from the initial carbon atom and 1.87 Å from the terminal carbon atom to which it is migrating, compared with 1.36 Å in the initial molecule. As might be expected with these very weak bonds, the remainder of the molecule resembles an alkene, with a C−C bond distance of 1.44 Å, shorter than the 1.55 Å bond in the initial molecule.

TABLE 2: Atomic Charges for $CF_2ClCF_2CH_3$, $CF_3CFClCH_3$, and the Transition Geometry Connecting Them[a]

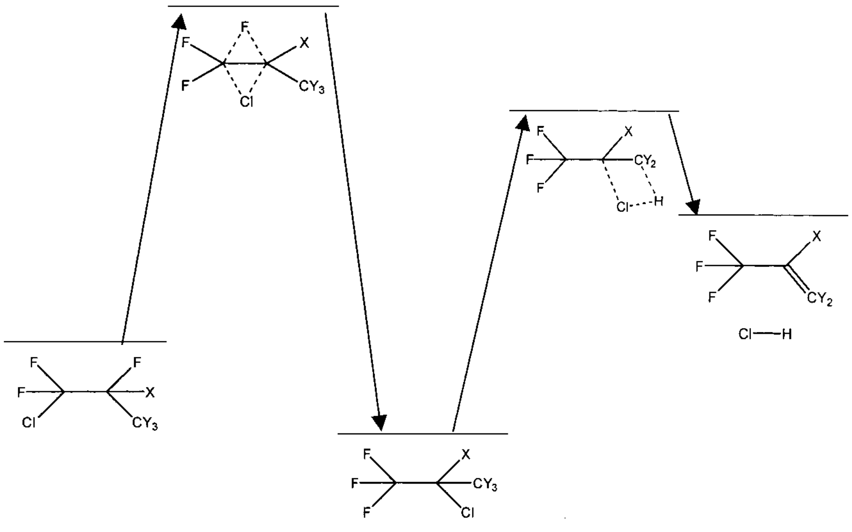
	$CF_2ClCF_2CH_3$	transition geometry	$CF_3CFClCH_3$
C_1	+1.29	+1.64	+1.80
C_2	+1.15	+0.93	+0.67
F (rearranging)	−0.62	−0.56	−0.62
Cl (rearranging)	−0.14	−0.44	−0.17
CH_3	+0.16	+0.30	+0.17
F (on C_1)	−0.62	−0.62	−0.63
F (on C_1)	−0.62	−0.63	−0.63
F (on C_2)	−0.63	−0.62	−0.62

[a] Densities are generated at the B3PW91/6-311+G(2d,p) level of theory.

The difference in energy between the initial molecule and the transition geometry, the barrier to rearrangement, is 62.5 kcal/mol. Considering that $CF_2ClCF_2CH_3$ when formed has approximately 100 kcal/mol of internal energy from the radical recombination reaction, it is expected that this barrier height would not prohibit the reaction. The energy barrier for the deuterated molecule $CF_2ClCF_2CD_3$ is also 62.5 kcal/mol, and so there is predicted to be only a small kinetic isotope effect due to the differences in vibrational frequencies. The frequency for rotation of the C−CH_3 bond is calculated to be 206.5 cm^{-1} for the initial molecule and 178.0 cm^{-1} for the transition geometry, whereas the frequency for rotation of the C−CD_3 bond is calculated to be 150.6 cm^{-1} for the initial geometry and 129.3 cm^{-1} in the transition geometry. There is also a difference in the CH_3−C−C bending motion, 225.4 cm^{-1} in the initial geometry and 240.0 cm^{-1} in the transition geometry, compared with 211.3 and 218.9 cm^{-1} for the CD_3−C−C bend. In addition, the rearranged molecule, $CF_3CFClCH_3$ is predicted to be 3.3 kcal/mol lower in energy than the initial molecule.

The calculated atomic charges for the initial geometry, transition geometry and rearranged molecule are presented in Table 2. In the transition geometry there is a large increase in electron density on the chlorine atom and a decrease in charge on the methyl group. The migrating fluorine atom also loses some charge. These charges will be helpful in interpreting the substituent effects later in this study.

The rearranged molecule $CF_3CFClCH_3$ has the possibility of eliminating either HCl or HF via a 2,3 elimination pathway. A similar elimination pathway has been previously studied theoretically by Toto,[16] and our four-membered concerted transition geometry is similar in character to that previously found. The transition geometry for each of these eliminations has been characterized, and the energy barrier in going from the rearranged molecule to the transition geometry for loss of HCl is calculated to be 55.4 kcal/mol for HCl elimination, and 56.5 kcal/mol for DCl elimination. Both of the elimination transition geometries are lower in energy than the transition geometry for the FCl rearrangement, which would account for the unimolecular kinetics: the rearrangement is the rate-determining step, and the rearranged molecule will eliminate HCl/DCl unless it loses energy via collisions. This could explain the reason for the very low amount of HCl/DCl elimination product detected at higher pressures, the rearranged molecule may become stabilized and be unable to eliminate HCl/DCl. The transition geometry for the loss of HF is 5.1 kcal/mol higher in energy



X	Y	Relative energies (in kcal/mol)				
H	H	0.0	+55.0	-9.5	+47.8	+4.2
H	D	0.0	+54.9	-9.6	+48.8	+5.0
F	H	0.0	+62.5	-3.3	+52.1	+11.3
F	D	0.0	+62.5	-3.4	+53.1	+12.2
H	F	0.0	+61.6	-10.9		
F	F	0.0	+70.4	-3.4		

Figure 2. Energy profile for rearrangement and HCl/DCl elimination from $CF_2ClCXFCY_3$ calculated at B3PW91/6-311+G(2d,p). All energies are in kcal/mol.

(5.5 kcal/mol for DF) than the transition geometry for the loss of HCl, and so the preferred elimination pathway for the rearranged molecule is the loss of HCl/DCl to produce the observed molecules, $CF_3CF{=}CH_2$ and $CF_3CF{=}CD_2$.

To determine the effects of substitution, and investigate other molecules with the potential for this rearrangement mechanism, the following molecules have also been studied: $CF_2ClCHFCH_3$, $CF_2ClCHFCD_3$, $CF_2ClCHFCF_3$ and $CF_2ClCF_2CF_3$. The last of these, a CFC, could feasibly undergo rearrangement without subsequent elimination, and there could be the possibility of detecting the rearranged molecule $CF_3CFClCF_3$. For each of the molecules in this study, a transition geometry corresponding to the FCl rearrangement has been characterized, and the reaction energetics for rearrangement, followed by HCl/DCl loss where appropriate, are summarized in Figure 2. For all the molecules which can eliminate HCl/DCl after rearrangement, the transition geometry for the FCl rearrangement is higher in energy than the transition geometry for HCl/DCl elimination from the rearranged molecule and so the kinetics for 1,3-HCl/DCl elimination from all the systems would be expected to be unimolecular. The rearranged molecules are all lower in energy than the initial molecules. Both $CF_2ClCHFCF_3$ and $CF_2ClCF_2CF_3$ have a considerably higher barrier to rearrangement when compared with the corresponding molecules with a methyl group on the terminal carbon. The presence of a hydrogen atom on the central carbon lowers the barrier for rearrangement, and a lowering in the energy of the rearranged molecule, presumably an effect of the lower steric hindrance provided by the hydrogen atom in comparison with a fluorine. It was seen for $CF_2ClCF_2CH_3$ that the methyl group donated charge to the chlorine in the transition geometry, this would favor reaction with a CH_3 group rather than a CF_3 group. The molecule $CF_2ClCF_2CF_3$ has the highest barrier to rearrangement, 70.4 kcal/mol. As the combination reaction creates $CF_2ClCF_2CF_3$ with approximately 100 kcal/mol of internal energy, the 1,2-FCl rearrangement reaction with this energy barrier may be too slow to allow appreciable detection of the rearranged molecule.

TABLE 3: Energies (kcal/mol) for the Transition Geometries of Competing Rearrangement and Elimination Pathways for $CF_2ClCFXCY_3$ Molecules, along with the Difference in Energy between the Start and Rearranged Molecule[a]

molecule	pathway	E_0	$E_0(CD_3)$
$CF_2ClCHFCH_3$	rearrangement	55.0	54.9
	1,2-HCl loss	57.6	57.5
	2,3-HF loss	59.6	60.5
	1,2-HF loss	66.7	66.7
	ΔE(rearr)	−9.5	−9.6
$CF_2ClCF_2CH_3$	rearrangement	62.5	62.5
	2,3-HF loss	63.8	64.8
	ΔE(rearr)	−3.3	−3.4
$CF_2ClCHFCF_3$	rearrangement	61.6	
	1,2-HCl loss	58.0	
	1,2-HF loss	64.4	
	2,3-HF loss	67.6	
	ΔE(rearr)	−10.9	
$CF_2ClCF_2CF_3$	rearrangement	70.4	
	ΔE(rearr)	−3.4	

[a] All energies are calculated at B3PW91/6-311+G(2d,p).

The competition between rearrangement and elimination pathways for all the molecules in this study is presented in Table 3. The rearrangement pathway is predicted to have the lowest barrier height for $CF_2ClCHFCH_3$, $CF_2ClCHFCD_3$, $CF_2ClCF_2CH_3$ and $CF_2ClCF_2CD_3$. While the barrier for rearrangement is only 61.6 kcal/mol for $CF_2ClCHFCF_3$, the pathway for 1,2-HCl elimination is still lower in energy, and the rearrangement may not be observed for that molecule. In both of the molecules with methyl groups, there is little difference in the barrier to rearrangement between HCl and DCl, and the small kinetic isotope effect will result from the differences in the vibrational frequencies.

To examine the effect of a higher level of theory, the pathways for rearrangement, HF/DF elimination and HCl/DCl

TABLE 4: Calculations on $CF_2ClCF_2CH_3$ and $CF_2ClCF_2CD_3$ at Higher Levels of Theory[a]

	B3PW91/cc-pvtz			MP2/ 6-311+G(2d,p)
	E	E_0	E_0(CD$_3$)	E
$CF_2ClCF_2CH_3$	0	0	0	0
1,2-FCl rearrangement	64.7	63.0	63.0	71.0
2,3-HCl loss from $CF_3CFClCH_3$	55.3	51.1	48.3	64.5
2,3-HF loss from $CF_3CFClCH_3$	62.3	57.9	58.8	64.2
2,3-HF loss from $CF_2ClCF_2CH_3$	69.2	64.6	65.6	72.3
ΔE for 1,2-FCl rearrangement	−3.8	−3.9	−3.9	−4.7

[a] All energies are in kcal/mol. E refers to the equilibrium molecular energies without zero-point correction.

elimination from $CF_2ClCF_2CH_3$ have been optimizied at B3PW91/cc-pvtz and MP2/6-311+G(2d,p), results of which are summarized in Table 4. There is little difference in the reaction barriers when one goes to a larger basis set, the rearrangement is slightly higher in energy, as is the competing loss of HF/DF. The ab initio MP2 relative energies reported are molecular energies not corrected for zero-point vibrational enrgies, however they show that the transition geometry for rearrangement is not an artifact of the level of theory employed.

Conclusions

The calculations we have performed support our proposition that the unimolecular 1,3 elimination of HCl/DCl from $CF_2ClCF_2CH_3$/$CF_2ClCF_2CD_3$ proceeds initially via a 1,2-FCl rearrangement with an activation barrier of 62.5 kcal/mol. This rearranged molecule, $CF_3CFClCH_3$/$CF_3CFClCD_3$ has sufficient energy to pass smoothly over the transition state for HCl/DCl elimination, which has an energy barrier of 55.4 kcal/mol for HCl and 56.5 kcal/mol for DCl. There can be found a transition geometry for this reaction mechanism for all of the molecules of the type $CF_2ClCFXCY_3$, where X and Y are H, D, and F, with the energy barrier increasing significantly if either X or Y are fluorine atoms. This mechanism supports the observation of small kinetic isotope effects, unimolecular kinetics, and the absence of the 1,3-HCl elimination product at higher pressures, where the rearranged molecule may be stabilized by collisions.

The rearrangement leads to a molecule with a lower energy, which may be isolated if there are either sufficient collisions to prevent the elimination of HCl, or if there is no HCl elimination possible. However, calculations on a molecule where there is no possible elimination indicate that the barrier to rearrangement may be too high for this process to occur.

During the rearrangement there is a large transfer of charge on to the Cl atom, and the barrier to reaction is smaller when there are electron-donating groups attached to the central carbon: CH_3 and H substituents lead to smaller activation barriers than CF_3 and F. In future work, the effect of a second methyl group on this central carbon, as well as longer carbon chains will be investigated.

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