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**Computational Study of the Threshold Energy for the 1,2-Interchange of X
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Groups) on CH₂XCH₂R.**

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12

13 **Abstract**

14 Transition state geometries and threshold energies, E_0 , were computed for an unusual
15 unimolecular isomerization reaction that exchanges two groups (X, R) on $\text{CH}_2\text{XCH}_2\text{R}$. An
16 objective is to determine which are the most energetically feasible interchanges in order to guide
17 experimental investigations. The interchanging species included halogens (F, Cl, Br), and
18 pseudohalogens and monovalent hydrocarbons (H, SH, CH_3 , NH_2 , OH, OCF_3 , OCH_3 , $\text{CH}=\text{CH}_2$,
19 CH_2CH_3 , CH_2OH , $\text{C}\equiv\text{CH}$, CH_2CF_3 , CCl_3 , CF_3) attached to a two carbon backbone. Ground state
20 and transition state geometries were optimized with the B3PW91 level of theory and 6-
21 311+G(2d,p) basis set. The Br-Br interchange had the lowest E_0 (141 kJ/mol), and CH_3 -H had
22 the highest (582 kJ/mol). In general, larger atoms/groups with lone pairs of electrons such as
23 halogens, SH, OH, OCH_3 , OCF_3 and NH_2 tend to lower the E_0 barrier for interchange, making
24 them the most likely to be experimentally observed.

25 **Keywords**

26 Transition state geometry, unimolecular rearrangement, interchange

1. INTRODUCTION

In previous studies we have demonstrated the existence of a series of unimolecular, gas-phase reactions involving the interchange of two halogen (F, Cl and Br) atoms on adjacent carbon atoms.¹⁻⁵ This interchange mechanism has been supported by experimental and computational evidence for $\text{CF}_2\text{ClCF}_2\text{CH}_3$,^{1,2} $\text{CF}_2\text{ClCF}_2\text{CD}_3$,^{1,2} $\text{CHF}_2\text{CH}_2\text{Cl}$,^{6,7} $\text{CF}_2\text{ClCHFCH}_3$,⁴ $\text{CF}_2\text{ClCHFCD}_3$,⁴ $\text{CF}_2\text{ClCHFC}_2\text{H}_5$,⁵ $\text{CF}_2\text{ClCHFC}_2\text{D}_5$,⁵ $\text{CF}_2\text{ClCFCICH}_2\text{F}$,⁸ $\text{CF}_2\text{BrCF}_2\text{CH}_3$,⁹ $\text{CF}_3\text{CHFCH}_2\text{Cl}$,⁸ $\text{CH}_3\text{CHFCH}_2\text{Cl}$,¹⁰ $\text{CH}_2\text{FCH}_2\text{Cl}$,¹¹ $\text{CH}_2\text{FCD}_2\text{Cl}$,¹¹ $\text{CH}_2\text{FCHCl}_2$,¹² $\text{CF}_3\text{CH}_2\text{Cl}$,¹³ and $\text{CF}_2\text{ClCH}_2\text{F}$ ¹³ and can be competitive with unimolecular 1,2-HX (X = F, Cl, or Br) eliminations. These halogen-interchange processes are also known as type-1 dyotropic¹⁴⁻¹⁹ rearrangement reactions and a number of computational studies have appeared for interchange of halogens.^{2, 12, 14-17} In conjunction with our experimental work for $\text{CF}_2\text{ClCF}_2\text{CH}_3$ and $\text{CF}_2\text{ClCF}_2\text{CD}_3$ ¹ we showed² that replacing the four hydrogen atoms of $\text{CF}_2\text{ClCHFCH}_3$ with fluorine caused the threshold energy computed using B3PW91/6-311+G(2d,p) to increase from 230 to 290 kJ/mol for the 1,2-FCl interchange reaction. It was also noted that the C-C moiety of the transition state resembled an alkene. Zuo and Yu¹⁴ used B3LYP/6-311++G(d,p) to compute activation energies for interchange of Cl and Br for a series of C2 to C8 hydrocarbons. For $\text{CH}_2\text{XCH}_2\text{Y}$ the computed E_0 s were 175 (X,Y = Cl), 156 (X,Y = Cl, Br) and 136 (X,Y = Br) kJ/mol. They¹⁴ suggested that conjugation and hyperconjugation effects on the ethylenic transition state facilitate interchange for linear systems and for cycloalkanes the variation in E_0 mirrors the ring strain. The B3LYP method was also used for interchange of two Br atoms¹⁵ in CHXBrCHXBr and X = electron-donating groups lowered the E_0 while electron-withdrawing substituents had the opposite effect. Two recent computational studies reported the interchange of F and Cl along a C—Si and Si—Si backbone¹⁶ and the interchange of two X species (X =

halogens, H, CH₃, and SiH₃) along a C—C and C—Si backbone.¹⁷

We experimentally and computationally investigated the interchange of Cl-CH₃ for chemically activated (CH₃)₃CCD₂Cl and concluded that interchange forming (CH₃)₂CClCD₂CH₃, followed by 1,2-HCl and 2,3-DCI elimination, was a better mechanism to explain the formation of CH₂=C(CH₃)CD₂CH₃ and (CH₃)₂C=CDCH₃ than a Wagner-Meerwein process. It was also shown that a Br-CH₃ interchange mechanism was more likely than the Wagner-Meerwein mechanism for (CH₃)₃CCH₂Br.²⁰ Finally, the interchange of Cl with CH₃ was suggested to explain the decomposition of 1,1-dichloroacetone.²¹ The experimental observation of the halogen-halogen and halogen-methyl interchange reactions leads to the question of whether or not pseudohalogens²² and monovalent hydrocarbons (H, OH, SH, NH₂, OCH₃, CH₃, OCF₃, OCH₃, CH=CH₂, CH₂CH₃, CH₃, CH₂OH, C≡CH, CH₂CF₃, CCl₃, CF₃) also undergo interchange with halogens, themselves, or each other. We are interested in computing the threshold energy, E₀, to predict whether or not the interchange reaction barrier might be low enough to be observed. This information will assist in the selection of other experimental systems to explore.

To examine these possibilities electronic structure calculations were performed using density functional theory on molecules of the form CH₂XCH₂R, where X and R represent a halogen or one of the groups listed above. A diagram of the conversion from CH₂XCH₂R to its interchange transition state to CH₂RCH₂X can be found in Scheme 1. The lowest energy conformation was used in all calculations; in each case this was the *anti* conformation, which is the conformation the molecule must be in to undergo the interchange reaction. The B3PW91 level of theory, and the 6-31G(d',p') and 6-311+G(2d,p) basis sets were used, which we have found to give energies close to those determined from experimental investigations for the

halogen interchange reaction.¹⁻¹³ The main focus of this paper is on the threshold energy barriers and geometries of the transition state and it is hoped that these predictions will serve as a guide to future experimental investigations.

Scheme 1. A general transition state for the interchange of substituents X and R, where $\text{CH}_2\text{XCH}_2\text{R}$ converts into $\text{CH}_2\text{RCH}_2\text{X}$ (e.g. $\text{CH}_2\text{FCH}_2\text{Br}$ converts to $\text{CH}_2\text{BrCH}_2\text{F}$).

2. Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian 09 suite of programs.²³ Ground state and transition state geometries were optimized and vibrational frequencies and unscaled zero-point energies were calculated using Becke's three-parameter exchange functional²⁴ with Perdew and Wang's correlation functional,²⁵ B3PW91. The 6-31G(d',p') basis set was used initially to find the optimized geometries. Upon successful optimizations, the 6-311+G(2d,p) basis set was employed to determine all threshold energy values and geometries reported here. Transition states were characterized by exactly one imaginary frequency and intrinsic reaction coordinate (IRC) calculations were performed to verify that the transition state connected reactants and products. Atomic charges were calculated using the QTAIM²⁶ analysis of electron densities obtained using the B3PW91/6-311+G(2d,p) level of theory.

3. Transition State Geometry

The ground state and transition state geometries of Cl interchanging with each of the halogens, pseudohalogens, and hydrocarbon groups are shown in Figure 1. All geometries in Figure 1 have labeled bond lengths (Å) and angles (°). The two interchanging atoms/groups are located halfway between the two carbons, and these four atoms/groups are nearly planar in the transition state structure. The CH₂ moieties at the end of the C-C backbone are a trigonal planar, *sp*²-like geometry, and are perpendicular to the plane defined by the interchanging groups attached to the carbons. The C-C bond distance becomes shorter in the transition state compared to the ground state by about 0.10 Å.

The C-C bond lengths in the transition states geometries, see Figure 1 and the figures in Supporting Information, are approximately the same for interchange of F (1.36-1.40 Å), Cl (1.37-1.41 Å), and Br (1.37-1.42 Å). However, the C-Br bonds (2.51-2.95 Å) are about 0.2 Å longer than the C-Cl bonds (2.24-2.79 Å), and the C-Cl bonds are about 0.4 - 0.6 Å longer than the C-F bonds (1.82-2.19 Å). The longer carbon-halogen bond lengths support a correlation between longer bond lengths, hence weaker bonds, and lower *E*₀'s for interchange involving a halogen.

The C-Cl bond distances in the transition state geometry also vary depending on the nature of the other group, R, undergoing interchange, see Figure 1 and Supporting Information. With R = F, Cl and Br the C-Cl bond length is 2.26 ± 0.02 Å while the C-R bond length in the transition state geometry increases from 1.88 to 2.41 Å, respectively. The C-Cl bond lengths are 10% longer but relatively constant at 2.47 ± 0.03 Å for R = SH, OH OCF₃ and OCH₃. The C-Cl bond length increases about an additional 10% to 2.70 ± 0.1 Å when R is a H or an alkyl group (CH₃, CH₂CH₃, CH₂CF₃, CH₂OH, CH=CH₂, CCH). The longest C-Cl bond distance is 2.79 Å for

R = NH₂ for which the C-R bond length is the shortest at 1.56 Å and the shortest C-Cl bond distance is 2.15 Å for R = OCF₃ for which the C-R bond length is 2.06 Å. Not surprisingly the shortest C-R bond distance is 1.38 Å for R = H. These changes in C-Cl bond distances do not correlate with changes in the threshold energies.

Increasing the electron withdrawing ability of R shortens the C-Cl bond distance. For example, the C-Cl bond distance of 2.62 Å when R = CH₃ is reduced when the H atoms are replaced by halogens CCl₃ (r = 2.36 Å) or CF₃ (r = 2.41 Å); and the C-Cl bond length decreases from 2.64 to 2.50 Å when R changes from CH₂CH₃ to CH₂CF₃ and from 2.48 to 2.15 Å when R = OCH₃ becomes OCF₃.

If the interchanging group has an appendage (SH, OH, OCH₃, OCF₃, NH₂, CH=CH₂, CH₂CH₃, CH₂OH, CCH, CH₂CF₃) then that attachment is nearly perpendicular to the plane defined by the two bicyclic rings of the transition state geometry, see Figure 1. If each of the two interchanging species have an attachment then one attachment is in front and the other behind the plane defined by the bicyclic rings; see for example the interchange of two OCH₃, or two OH, or two SH groups in Figure S3 in Supporting Information.

4. Results and Discussion

The calculated threshold energies for the interchange reaction for the substituted ethanes in Tables 1 and 2 range from 141 to 582 kJ/mol for Br-Br and for CH₃-H. All reported values were calculated using the B3PW91 level of theory and 6-311+G(2d,p) basis set. Similar activation energies, 136¹⁴ and 134¹⁷ kJ/mol, have been calculated for Br-Br interchange using different DFT methods and basis sets. Our value for E₀(CH₃-CH₃) = 564 kJ/mol is consistent with the earlier report of 548 kJ/mol.¹⁷

Our primary interest is predicting whether any of these potential interchange reactions might be experimentally observed and to accomplish this we must consider unimolecular reactions that might have similar or lower E_0 s. Potential competing unimolecular pathways include C-X bond rupture or 1,2-HX elimination (X = any of the groups studied here). The weakest carbon-halogen bond²⁷ is C-Br at 293 ± 4 kJ/mol and sulfur appears to have the weakest single bond to carbon at 308 ± 2 kJ/mol among the other members. Elimination of hydrogen bromide from bromoethane will likely have the lowest threshold energy²⁸ with $E_0(\text{HBr}) = 225$ kJ/mol. The calculated E_0 s in Tables 1 and 2 suggest that when Cl, Br or SH are attached to carbon atoms the dominant unimolecular reaction will be interchange with themselves or each other and this has been verified for Cl-Br interchange in $\text{CH}_2\text{BrCD}_2\text{Cl}$.¹¹ Our experience is that when the $E_0(\text{interchange}) \leq 290$ kJ/mol the interchange reaction will be competitive with other decomposition processes for our chemical activation method that forms reactants with 350-420 kJ/mol of internal energy.^{1-5,7-11} Scanning Tables 1 and 2 suggests that the interchange of Cl or Br might be observed with all of the groups in Table 1 and OCF_3 , $\text{CH}=\text{CH}_2$, CH_2CH_3 , CH_2OH , and CCH groups in Table 2. Atomic fluorine might interchange with SH, OCH_3 , OH, NH_2 , and OCF_3 . The addition of substituents can lower the barrier for interchange. For example, the calculated E_0 for Cl- CH_3 interchange of $\text{ClCH}_2\text{CH}_2\text{CH}_3$ is 303 kJ/mol whereas experimental results confirm $E_0(\text{Cl-CH}_3) = 259$ kJ/mol for the CH_3 -Cl interchange reaction for 2,2-dimethyl-1-chloropropane; i.e., two methyl groups replace two hydrogen atoms on C-2 of 1-chloropropane.²⁰ In addition, reactions with $E_0(\text{interchange}) > 290$ kJ/mol might be observed for photochemical and thermal activation methods that prepare reactants with energy greater than 400 kJ/mol.

Next trends in the E_0 s will be analyzed. Among the halogens, see Tables 1 and 2, the migration of a Br has threshold energy barriers lower by 20-25 kJ/mol compared to migration of

163 Cl, while Cl interchange has E_0 's lower by 54-67 kJ/mol compared to F interchange. This
164 variation may be explained by the C-X bond dissociation energies (BDE) that are 473 ± 8 , $352 \pm$
165 3 and 293 ± 4 kJ/mol for $\text{CH}_3\text{CH}_2\text{X}$ with $\text{X} = \text{F}$, Cl and Br , respectively.²⁵ The interchange of a
166 specific halogen with H , CH_3 , CH_2CH_3 , and CH_2OH all have the same threshold energy within $\pm$
167 4 kJ/mol despite the 50 kJ/mol stronger BDE for a C-H bond compared to C-C bonds.
168 Replacement of the three H atoms of the CH_3 group undergoing interchange with Cl raises the
169 $E_0(\text{interchange})$ by approximately 30 kJ/mol for interchange with a halogen and by an additional
170 23-33 kJ/mol when F replaces the three Cl atoms on a trichloromethyl group, see Table 2. This
171 trend must be an inductive, rather than a steric effect as the electronegative Cl and F are reducing
172 the availability of electron density of the CX_3 group as the transition state forms; although the
173 group charge does not vary significantly, being -0.08 for CH_3 , -0.22 for CCl_3 and -0.17 for CF_3 ,
174 the partial charge on the carbon atom in the transition state geometry does show strong variation,
175 being -0.19 for CH_3 , +0.18 for CCl_3 and +1.72 for CF_3 .

176 The interchange of OH or OCH_3 with any other group have similar $E_0(\text{interchange})$ and
177 these are 63-84 kJ/mol lower than the interchange of a CH_3 with that same group. Migration of
178 SH has an even lower $E_0(\text{interchange})$ by 50-54 kJ/mol compared to OH or OCH_3 with the same
179 migrating partner. In fact, groups with a lone pair of electrons seem to have the lowest E_0
180 barriers, such as the halogens, SH, OCH_3 , OCF_3 , OH, and NH_2 . The mechanism for migration of
181 groups with lone pairs of electrons appears to be the donation of electron density associated with
182 the lone pair from the group undergoing interchange to the adjacent carbon. In many cases the
183 adjacent carbon atom has a partial positive charge if the other migrating species is more
184 electronegative than carbon. Consider for example the interchange of Cl and OH; in the ground
185 state geometry, there is a partial positive charge on carbon atoms attached to the Cl (+0.08) and

O (+0.48). The lone pair electron density on O and on the Cl is donated to the adjacent carbon with the partial positive charge as the bicyclic ring begins to form, leading to partial charges of +0.18 on each carbon atom and as the group completes the migration the electron density in the original C-Cl and C-O bonds becomes a lone pair on the Cl and O once migration is accomplished.

The mechanism for migration of groups lacking a lone pair of electrons must be subtly different. The electron density in the sigma bond must shift to the adjacent carbon as the original bond breaks – in the migration of Cl with CH₃ the partial charge on the carbon atoms in the bicyclic ring is slightly less positive, +0.05, reminiscent of the migration of H or CH₃ in the rearrangement to a more stable carbocation.

Reactions involving the interchange of a CN group were also investigated, but the C-CN bond lengths were deemed too long to be considered reasonable transition states structures and were omitted from this report.

5. Conclusions

The optimized ground state and transition state for several interchange reactions involving halogens, pseudohalogens, and other groups on a C-C backbone were found computationally. Zero-point energies were used to calculate the threshold energy barrier for interchange. In general, larger atoms/groups with lone pairs such as Br, Cl, SH, OH, NH₂, OCF₃ and OCH₃ tend to have the lowest energy barrier for interchange. The interchange of Cl, Br or SH with themselves or with each other have a very low E₀ and will likely be the dominant unimolecular decomposition reaction. A large number of potential interchanges have E₀s that are near or below 290 kJ/mol that would be in competition with bond rupture or HX elimination

reactions making them good candidates for experimental study in the gas phase. The systems studied here were done with four hydrogens on a two-carbon backbone. Future work could replace the hydrogens with various electron donating and withdrawing groups to determine their effect on the E_0 for interchange.

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Supporting Information

Figures S1-S3 are pictures of the ground state and interchange transition state geometries, with labeled bond lengths and angles, for the systems that are not shown in Figure 1. Table S1 contains selected QTAIM atomic charges.

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Table 1. Threshold energy barriers for interchange reactions (kJ/mol) calculated at the B3PW91/6-311+G(2d,p) level of theory and basis set.

	Br	Cl	F	SH	OCH ₃	OH	NH ₂	CH ₃	H
Br	141	162	216	166	220	225	184	282	280
Cl		183	236	186	244	245	204	303	300
F			289	242	293	299	273	361	356
SH				225	279	282	284	362	358
OCH ₃					328	332	336	411	400
OH						337	345	447	406
NH ₂							413	471	455
CH ₃								564	582

Table 2. Threshold energy barriers for halogen (F, Cl, Br) interchanges (kJ/mol) with various groups calculated at the B3PW91/6-311+G(2d,p) level of theory and basis set. E_0 is arranged in ascending order based on F systems.

R =	X = F	X = Cl	X = Br
OCF ₃	283	227	206
CH=CH ₂	346	277	254
CH ₂ CH ₃	357	297	276
CH ₂ OH	364	305	284
C≡CH	368	303	279
CH ₂ CF ₃	374	321	301
CCl ₃	393	336	312
CF ₃	421	368	347

292 **Figure Caption**

293 **Figure 1.** Computed structures of the ground state and transition state using B3PW91 with 6-
294 311+G(2d,p) for various Cl interchanges. The C-C, C-Cl, and C-R bond lengths (Å), and Cl-C-
295 C and R-C-C bond angles (°) are labeled.

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Figure 1