

Intramolecular Homolytic Translocation Chemistry: An ab Initio Study of 1,*n*-Halogen Atom Transfer Reactions in Some ω -Haloalkyl Radicals

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Ab initio calculations using all-electron (3-21G^(*), 6-311G^{**}) and pseudopotential (DZP) basis sets, with (MP2, QCISD) and without (UHF) the inclusion of electron correlation, predict that 1,*n*-halogen transfer reactions in the 5-halo-1-pentyl (**6**), 6-halo-1-hexyl (**7**), and 7-halo-1-heptyl radicals (**8**) proceed via *C_s*- and/or *C₂*-symmetric transition states (**9**–**11**), except for the 5-bromo-1-pentyl (**6**, X = Br) radical for which a *C_s*-symmetric transition state (**9**) was located only at the UHF/3-21G^(*) level of theory and the 5-iodo-1-pentyl radical (**6**, X = I) for which no transition state (**9**) could be located at any level of theory used in this study. Energy barriers for these translocation reactions of between 120.0 (1,7-iodine transfer) and 191.0 kJ mol⁻¹ (1,5-chlorine transfer) are predicted at the MP2/DZP level of theory; QCISD/DZP (single-point) calculations predict similar energy barriers. These high energy barriers are a consequence of unfavorable factors associated with ring size and long carbon–halogen separations in transition states (**9**–**11**) which lead to significant deviations from the collinear arrangement of attacking and leaving radicals preferred in transition states involved in homolytic substitution reactions at halogen. The dependence of transition state energy on attack angle at halogen has been explored for the attack of methyl radical at chloromethane. At the MP2/DZP level of theory, attack angles of between 80 and 90° are calculated to lead to increases in energy barrier of about 100 kJ mol⁻¹ when compared with the collinear (180°) arrangement of attacking and leaving groups. The mechanistic implications of these predictions are discussed.

Introduction

Homolytic *group* or *atom* transfer (translocation) reactions are important free-radical processes which often involve homolytic substitution by alkyl, aryl, and other radicals at heteroatoms such as silicon, germanium, tin, chalcogen, and halogen.¹ Curran has provided significant insight into the synthetic utility of intermolecular homolytic translocations involving halogen and provides an excellent account of many efficient bromine and iodine transfer reactions in his 1988 review.² Other commonly used intermolecular group transfer processes include the use of phenyl selenide which has been shown to proceed readily by Curran³ as well as Byers,⁴ while work reported by Crich,⁵ Barton,⁶ and Engman⁷ and experiments performed in our laboratories⁸ have utilized aryl telluride transfer as the key step in several synthetic strategies (Scheme 1). Stannyl groups appear also to undergo intermolecular translocation chemistry; Scaiano reported that *tert*-butoxyl radicals undergo intermolecular homolytic substitution at the tin atom in hexabutyliditin.⁹

In addition to several reports involving 1,2-silyl and germyl shifts,¹⁰ intramolecular homolytic group transfers involving silicon, germanium, and tin have been put to good use by Davies and co-workers¹¹ as well as by Kim and his associates (Scheme 2).¹² There also appear to be several early reports of 1,2 migrations of halogen,¹³ the Nesmeyanov rearrangement¹⁴ (1,2-migration of chlorine) typifying the chemistry in question. Despite the appearance of rearranged products in these transforma-

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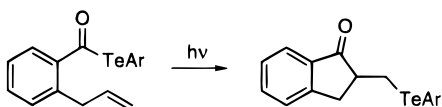
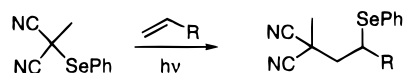
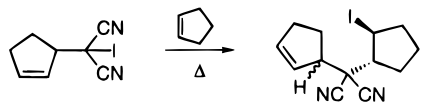
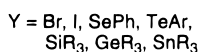
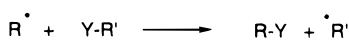
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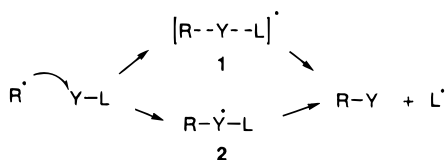
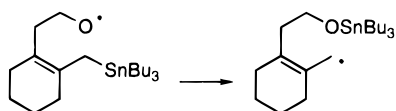
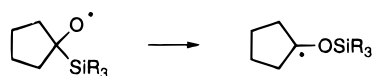
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Scheme 1



Scheme 2

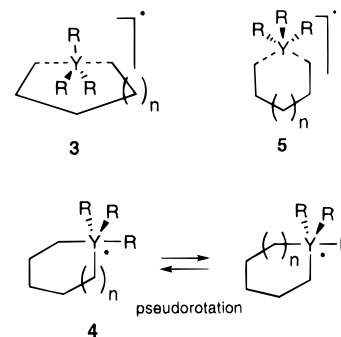


tions, there is still some considerable ambiguity concerning the reaction mechanism, namely, concerted migration versus a process involving dissociation followed by recombination.¹³

Apart from the 1,2-translocation chemistry mentioned above, we are aware of only one example involving intramolecular homolytic translocation of a sulfur-containing group¹⁵ and are unaware of any examples involving selenium, tellurium, or halogen.¹ The question of why so few intramolecular transfers involving halogen and chalcogen-containing groups have appeared is a topical one and is likely to be a consequence of the mechanism of homolytic substitution at these heteroatoms.¹⁶

It is generally agreed that homolytic substitution by a radical (R^{\cdot}) at a group (Y) proceeds via either a transition state (**1**) in which the attacking and leaving groups adopt a collinear (or nearly so) arrangement resulting in Walden inversion or with the involvement of a hypervalent intermediate (**2**) which may or may not undergo pseudorotation prior to dissociation.^{1,17} 1, n -Translocation processes typify the intramolecular version of this reaction which might be expected to proceed either via

transition state (**3**) or intermediate (**4**). If one considers carefully the pathways available for this intramolecular translocation reaction, it seems reasonable that in addition to mechanisms involving structures (**3**, **4**) a third *front-side* mechanism involving transition state (**5**) is also possible. Roberts recently suggested that a similar mechanism might be important in hydrogen atom transfers between heteroatoms which have available orbitals and are not coordinately saturated.¹⁸



Ab initio calculations performed in our laboratories (MP2/DZP, QCISD/DZP) suggest that intermolecular homolytic substitutions by alkyl radicals at the halogen atom in alkyl halides proceed via transition states in which the attacking and leaving radicals prefer to adopt a collinear arrangement.¹⁹ Indeed, similar geometric requirements are predicted for homolytic attack the chalcogens,²⁰ while some reactions at silicon, germanium, tin, phosphorus, and chalcogen are predicted to involve hypervalent intermediates.^{1,21-22} Recently, we reported the results of an extensive ab initio study of 1,2-translocations involving silicon, germanium, and tin-containing groups (front-side attack mechanism). These studies predict that homolytic 1,2-translocations involving group(IV) heteroatoms proceed via concerted mechanisms involving front-side homolytic substitution.²³

To provide further insight into the mechanistic details of intramolecular homolytic substitution chemistry, we began to explore 1, n -halogen transfer reactions in 5-halo-1-pentyl (**6**), 6-halo-1-hexyl (**7**), and 7-halo-1-heptyl radicals (**8**) (Scheme 3) through the use of ab initio molecular orbital calculations. We now report that consistent with the lack of literature precedent,¹ 1,5-, 1,6-, and 1,7-(intramolecular) homolytic translocations of halogen atoms between carbon centers in radicals **6**, **7**, and **8** are predicted not to be synthetically viable, with MP2/DZP calculated energy barriers ranging from 120 to 193 kJ mol⁻¹.

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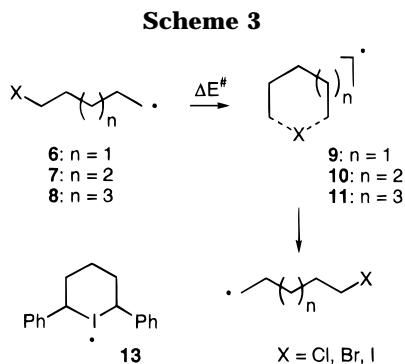
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Methods

Ab initio molecular orbital calculations were performed on a Sun SparcServer 10/512, DEC AlphaStation 400 4/233, Cray Y-MP4E/364, or Cray J916 computer using the Gaussian 92²⁴ or Gaussian 94²⁵ system of programs. Wherever possible, geometry optimizations were performed using standard gradient techniques at the UHF and MP2 levels of theory using the 3-21G^(*) and 6-311G^{**} (for calculations involving 1,6-translocations of chlorine) and a (valence) double- ζ pseudopotential basis set (DZP). Full details of the DZP basis have been published elsewhere.^{19,21–23} Except for reactants and transition structures involved in 1,7-halogen transfers, further single-point QCISD calculations were performed on all MP2 optimized structures. All ground-state structures (**6**, **7**, **8**) were verified by vibrational frequency analysis at the UHF level of theory, except for structures (**6**) which were also verified at the MP2 level. All transition states were verified by vibrational frequency analysis at the UHF and MP2 levels of theory.

Results and Discussion

1,6-Translocations in 6-Halo-1-hexyl Radicals **7**.

We began our computational study by attempting to locate the anticipated C_2 symmetric transition structures involved in the 1,6-translocation of the halogen atom in the 6-chloro-1-hexyl, 6-bromo-1-hexyl, and 6-iodo-1-hexyl radicals (**7**). Indeed, as expected, structures of C_2 symmetry (**10**) were located on the $C_6H_{12}X$ ($X = \text{Cl, Br, I}$) potential energy surfaces at both UHF and MP2 levels with all basis sets used in this study. Structures (**10**) proved to correspond to transition states for 1,6-halogen transfers in the 6-halo-1-hexyl radicals (**7**). Structures (**10**, $X = \text{Cl}$) of C_s symmetry were also located at the UHF/3-21G^(*) and UHF/6-311G^{**} levels of theory; these proved to correspond to second-order saddle points (two imaginary frequencies) with one vibrational mode corresponding to the collapse to the corresponding C_2 transition state. Calculated transition state geometries are displayed in Figure 1, while calculated reaction energy barriers (ΔE^\ddagger , Scheme 3), asymmetric (imaginary) vibrational frequencies, and important geometric features of the transition states are listed in Table 1.

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Inspection of Table 1 reveals that the transition state (**10**, $X = \text{Cl}$) associated with 1,6-transfer of chlorine is calculated to lie some 184.9 kJ mol⁻¹ above the energy of the reactant (**7**, $X = \text{Cl}$) using UHF/3-21G^(*). The energy barrier (ΔE^\ddagger) is predicted to increase somewhat with the better basis sets to values of 217.5 (UHF/DZP) and 213.3 kJ mol⁻¹ (UHF/6-311G^{**}). Inclusion of electron correlation in these calculations serves to reduce the energy barrier to 170.9 and 156.4 kJ mol⁻¹ at the MP2/DZP and MP2/6-311G^{**} levels, respectively. Further single-point QCISD refinement is seen to have only a minor influence; QCISD/DZP//MP2/DZP calculations predict a barrier of 167.6 kJ mol⁻¹ for 1,6-chlorine transfer in (**7**, $X = \text{Cl}$). The similarities in the data generated using the 6-311G^{**} (triple- ζ) and DZP basis sets provide confidence in the use of the latter basis; we have previously noted that the DZP basis set behaves more like a triple- ζ all-electron basis than a similarly sized double- ζ set.²¹ The convergence in the MP2 and QCISD generated data is also pleasing, reinforcing the need for the inclusion of electron correlation in calculations of this type²¹ and providing confidence in the ability of the theoretical methods employed to model intramolecular halogen transfer processes.

Similar trends are predicted for transfers involving bromine and iodine. In the former case, transition state (**10**, $X = \text{Br}$) is calculated to lie 163.3 (UHF/3-21G^(*)), 191.8 (UHF/DZP), 149.2 (MP2/DZP), and 144.9 kJ mol⁻¹ (QCISD/DZP//MP2/DZP) above the energy of the reactant (**7**, $X = \text{Br}$). In the reaction involving 1,6 transfer of iodine, energy barriers (ΔE^\ddagger) of 163.4 (UHF/3-21G^(*)), 176.4 (UHF/DZP), 136.0 (MP2/DZP), and 131.3 kJ mol⁻¹ (QCISD/DZP//MP2/DZP) are predicted. The energy barriers calculated in this work, which range from 131.3 to 167.6 kJ mol⁻¹ at the highest level of theory, are substantially higher than those calculated previously for the analogous intermolecular transfer of halogen atom between methyl radicals which range from 51.5 to 115.9 kJ mol⁻¹ at the same level of theory.¹⁹

Inspection of Table 1 together with Figure 1 reveals some interesting geometrical features which may help in our understanding of the intrinsically high barriers associated with the intramolecular halogen transfer reactions in this study. The UHF/DZP carbon-halogen distances in the transition states (**10**) are calculated to be 2.200 (Cl), 2.376 (Br), and 2.691 Å (I), while at the MP2/DZP level of theory, these distances are predicted to be 2.047 (Cl), 2.175 (Br), and 2.325 Å (I). These large separations lead to substantial deviations from the ideal collinear arrangement of attacking and leaving groups.¹⁹ Indeed, the C-X-C angle becomes increasingly more severe as the C-X distance increases; MP2/DZP calculations predict angles of 144° (Cl), 138° (Br), and 131° (I). We believe these deviations to be responsible for the high energy barriers predicted to be associated with these reactions (vide infra).

1,5-Translocations in 5-halo-1-pentyl Radicals **6**.

Despite considerable searching of the $C_5H_{10}X$ ($X = \text{Cl, Br, I}$) potential energy surfaces at both UHF and MP2 levels of theory using the 3-21G^(*) and DZP basis sets,²⁶ transition states **9** could only be located for reactions

(26) Due to the close similarity in data generated by the DZP and 6-311G^{**} basis sets for reactions involving the 6-chloro-1-hexyl radical (**7**, $X = \text{Cl}$), calculations involving the latter basis set were not performed on reactions involving **6** or **8**.

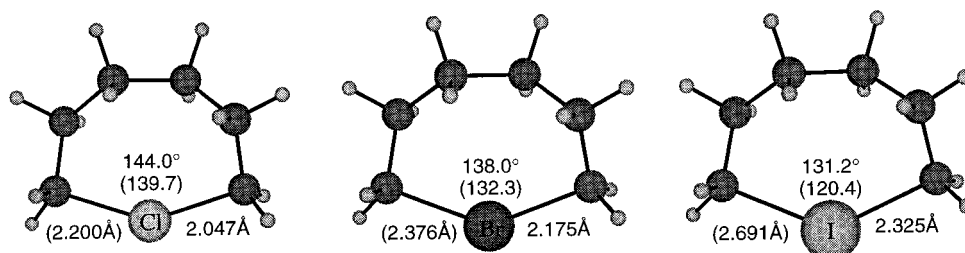


Figure 1. MP2/DZP calculated (C_2) transition structures (**10**) for 1,6-halogen transfer in 6-halo-1-hexyl radicals (**7**) (UHF/DZP data in parentheses).

Table 1. Calculated Energy Barriers^a(ΔE^\ddagger) for 1,6-Halogen Transfer Reactions in 6-Halo-1-hexyl Radicals **7** (Scheme 3) and the Corresponding Asymmetric Stretching Frequency^b (ν) and Important Geometric Parameters (r , θ)^c (Figure 1) of the Cyclic Transition States **10**

transition state 10		ΔE^\ddagger	$\Delta E^\ddagger + \Delta ZPE$	ν	r	θ
X = Cl	UHF/3-21G(*)	184.9	185.7	740i	2.201	141.4
	UHF/6-311G**	213.3		845i	2.198	139.5
	UHF/DZP	217.5	216.6	850i	2.200	139.7
	MP2/6-311G**	156.4			2.033	144.1
	MP2/DZP	170.9		912i	2.047	144.0
X = Br	QCISD/DZP//MP2/DZP	167.6				
	UHF/3-21G(*)	163.3	165.2	597i	2.278	137.4
	UHF/DZP	191.8	191.1	595i	2.376	132.3
	MP2/DZP	149.2		680i	2.175	138.0
X = I	QCISD/DZP//MP2/DZP	144.9				
	UHF/3-21G(*)	163.4	165.1	501i	2.503	127.2
	UHF/DZP	176.4	174.0	451i	2.691	120.4
	MP2/DZP	136.0		542i	2.325	131.2
	QCISD/DZP//MP2/DZP	131.3				

^a Energies in kJ mol^{-1} . ^b Frequencies in cm^{-1} . ^c Distances in angstroms, angles in degrees.

Table 2. Calculated Energy Barriers^a (ΔE^\ddagger) for 1,5-Halogen Transfer Reactions in 5-Halo-1-pentyl Radicals **6** (Scheme 3) and the Corresponding Asymmetric Stretching Frequency^b (ν) and Important Geometric Parameters (r , θ)^c (Figure 2) of the Cyclic Transition States **9**

transition state 9		ΔE^\ddagger	$\Delta E^\ddagger + \Delta ZPE$	ν	r	θ
X = Cl	UHF/3-21G(*)	207.6	204.9	989i	2.273	117.9
	UHF/DZP	235.9	231.7	1096i	2.295	116.4
	MP2/DZP	191.0	192.5	1228i	2.069	123.3
	QCISD/DZP//MP2/DZP	186.4				
X = Br	UHF/3-21G(*)	190.5	189.3	858i	2.331	115.3

^a Energies in kJ mol^{-1} . ^b Frequencies in cm^{-1} . ^c Distances in angstroms, angles in degrees.

involving transfer of chlorine at all levels of theory and for the transfer of bromine at the UHF/3-21G(*) level. These transition states proved to be of C_s symmetry. It is of some significance that no transition states could be located for the 1,5-translocation of iodine; this result is discussed in some detail below.

Energy barriers (ΔE^\ddagger) able to be determined for the reactions in question are listed in Table 2 together with the important geometric features and the asymmetric (imaginary) vibrational frequencies of transition states **9**. The calculated transition structures **9** are displayed in Figure 2. Inspection of Table 2 reveals that the transition state (**9**, X = Cl) lies some 186–236 kJ mol^{-1} above the reactant (**6**, X = Cl), depending on the level of theory. At the highest level (QCISD/DZP//MP2/DZP) this barrier (186.4 kJ mol^{-1}) is calculated to be some 18.8 kJ mol^{-1} higher than the analogous 1,6-translocation in **7** (X = Cl); this difference is predicted to be 22.7 kJ mol^{-1} using UHF/3-21G(*). This increase in energy barrier in going from the 6-chloro-1-hexyl (**10**, X = Cl) to the

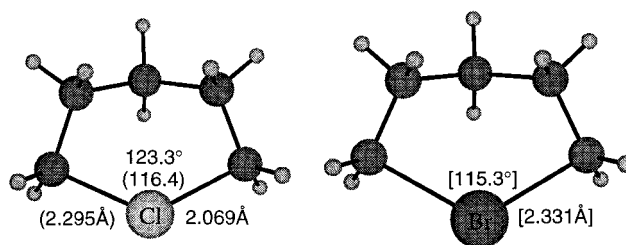


Figure 2. MP2/DZP calculated (C_s) transition structure (**9**, X = Cl) for 1,5-chlorine transfer and UHF/3-21G(*) calculated transition structure (**9**, X = Br) for 1,5-bromine transfer for 5-halo-1-pentyl radicals (**6**, X = Cl, Br) (UHF/DZP data in parentheses) [UHF/3-21G(*) data in brackets where no other data are available, see text].

5-chloro-1-pentyl system (**9**, X = Cl) is almost certainly the result of the even greater deviation from the collinear arrangement of attacking and leaving groups at chlorine in structure **9** (X = Cl) when compared to **10** (X = Cl). The C–Cl–C angle in the six-membered transition state **9** is calculated to be 123.3° (MP2/DZP), significantly smaller than the value of 144.0° in the analogous seven-membered structure at the same level of theory. It is interesting to note that the calculated C–Cl distances in **9** (X = Cl) are only marginally longer than those calculated for **10** (X = Cl) at the same level of theory, at 2.273 Å (UHF/3-21G(*)), 2.295 Å (UHF/DZP), and 2.069 Å (MP2/DZP).

The UHF/3-21G(*) generated transition structure **9**, (X = Br) involved in the 1,5 migration of bromine atom in the 5-bromo-1-pentyl radical is predicted to require an even smaller angle of attack, with the C–Br–C angle calculated to be 115.3°. Not unexpectedly, a significantly higher energy barrier (190.5 kJ mol^{-1}) is calculated for this translocation than for the analogous 1,6-transloca-

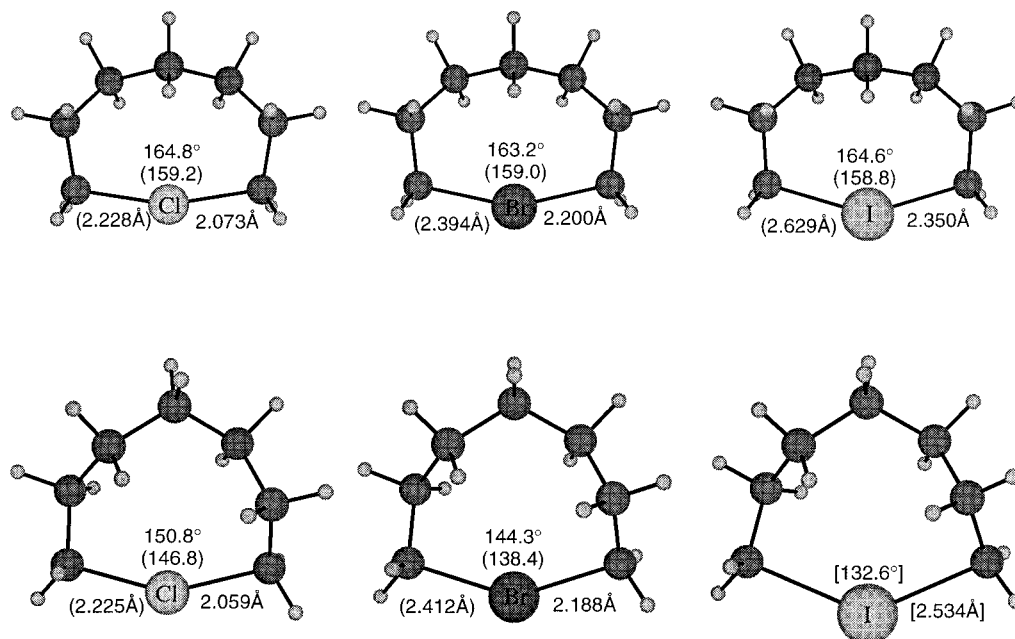


Figure 3. MP2/DZP calculated (C_s , upper; C_2 , lower) transition structures (**11**) for 1,7-halogen transfer in 7-halo-1-heptyl radicals (**8**) [UHF/DZP data in parentheses] [UHF/3-21G^(*) data in brackets where no other data are available, see text].

Table 3. Calculated Energy Barriers^a (ΔE^\ddagger) for 1,7-Halogen Transfer Reactions in 7-Halo-1-heptyl Radicals **8** (Scheme 3) and the Corresponding Asymmetric Stretching Frequency^b (ν) and Important Geometric Parameters (r , θ)^c (Figure 3) of the Cyclic Transition States **11**

transition state 11		ΔE^\ddagger	$\Delta E^\ddagger + \Delta ZPE$	ν	r	θ
X = Cl (C_s)	UHF/3-21G ^(*)	172.5	175.1	624i	2.220	161.4
	UHF/DZP	208.3		711i	2.228	159.2
	MP2/DZP	163.5		832i	2.073	164.8
X = Cl (C_2)	UHF/3-21G ^(*)	216.0	217.3	681i	2.222	147.4
	UHF/DZP	243.9		771i	2.225	146.8
	MP2/DZP	198.4		886i	2.059	150.8
X = Br (C_s)	UHF/3-21G ^(*)	147.6	151.2	490i	2.302	164.0
	UHF/DZP	178.5		476i	2.394	159.0
	MP2/DZP	137.9		601i	2.200	163.2
X = Br (C_2)	UHF/3-21G ^(*)	193.0	195.5	550i	2.299	143.6
	UHF/DZP	215.5		529i	2.412	138.4
	MP2/DZP	175.6		660i	2.188	144.3
X = I (C_s)	UHF/3-21G ^(*)	143.9	147.5	382i	2.505	163.7
	UHF/DZP	160.2		352i	2.629	158.8
	MP2/DZP	120.0		451i	2.350	164.6
X = I (C_2)	UHF/3-21G ^(*)	190.2	192.2	442i	2.534	132.6

^a Energies in kJ mol^{-1} . ^b Frequencies in cm^{-1} . ^c Distances in angstroms, angles in degrees.

tion of bromine atom at the same level of theory, as discussed previously.

The failure to locate any transition structures for the translocation of iodine atom in the 5-iodo-1-pentyl radical strongly suggests that transition states which require severe deviation from collinearity, as would be anticipated in this case, with an expected C–I–C angle of less than about 110° are simply not viable (vide infra).

1,7-Translocations in 7-Halo-1-heptyl Radicals **8.** Examination of the $\text{C}_7\text{H}_{14}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) potential energy surfaces at meaningful levels of theory proved to be very time-consuming tasks. At the 3-21G^(*) level of theory, between 110 and 130 basis functions were required, while DZP calculations generated 188 basis functions for each calculation. This, coupled with the necessity of performing DZP frequency analyses numerically, restricted our ability to acquire any QCISD/DZP data.

Calculated transition structures **11** are displayed in Figure 3. Except for the reaction involving iodine at the

UHF/DZP and MP2/DZP levels of theory, two transition states **11**, one of C_2 and the other of C_s symmetry, were located for each 1,7-translocation at all levels of theory. In each case, the transition state **11** of C_s symmetry is calculated to be lower in energy by some $37\text{--}46 \text{ kJ mol}^{-1}$ than the corresponding C_2 structure. Inspection of Table 3 provides some insight into why this is the case. In each C_2 -symmetric transition structure **11**, the C–X–C (attack) angle is calculated to be $15\text{--}30^\circ$ smaller than in the corresponding C_s structure; this additional deviation from collinearity is undoubtedly responsible for the higher energy barriers (ΔE^\ddagger).

At the highest level of theory (MP2/DZP), energy barriers (ΔE^\ddagger) of 163.5 (Cl), 137.9 (Br), and 120.0 (I) kJ mol^{-1} are predicted for reactions involving the C_s -symmetric transition states **11**, while the C_2 pathway is predicted to require 198.4 and 175.6 kJ mol^{-1} for the chlorine and bromine transfers, respectively. These calculated energy barriers are to be compared with the results obtained for the 1,6-halogen transfers in the

6-halo-1-hexyl series (**7**) at the same level of theory. Differences of 7.4 (Cl), 11.3 (Br), and 16.0 kJ mol⁻¹ (I) favoring **11** (*C_s*) over **10** are predicted at the MP2/DZP level of theory and are consistent with the smaller C–X–C angles associated with transition structures **10**. The C–X separations in **11** are predicted to be only marginally shorter than the analogous distances in **10**, at 2.073 Å (Cl, *C_s*), 2.059 Å (Cl, *C₂*), 2.200 Å (Br, *C_s*), 2.188 Å (Br, *C₂*), and 2.350 Å (I, *C_s*) at the MP2/DZP level of theory.

Strain in Transition Structures 9–11. Contrary to expectation, the calculations presented in this paper predict homolytic 1,7-halogen transfer between carbon atoms to be more facile than the analogous 1,6-translocation, which in turn is more facile than the corresponding 1,5-migration. In other words, the eight-membered ring transition states **11** are predicted to be of lower relative energy than the seven-membered series **10**, which are (relatively) more stable than the six-membered structures **9**. At first glance, this result may seem counterintuitive, after all it is well established that cyclohexane is more stable than cycloheptane and even more stable than cyclooctane. Reactions that proceed via six-membered transition states are favored in many instances over those that require transition states of larger or smaller ring size. Why then is a different trend predicted for intramolecular homolytic translocation reactions involving halogen? The answer to this question depends on the mechanistic manifold available for free-radical attack at halogen, whether homolytic substitution at halogen involves a back-side (**3**) or front-side (**5**) mechanism or indeed whether both pathways are available to the attacking radical. It seems unlikely that intermediates **4** are involved, as neither this nor our previous study¹⁹ located any hypervalent structures resembling **2** or **4**.

In each transition state located in this study, the total energy is comprised of several components, of which contributions from C–C–C and C–X–C deformations imposed by the size of the ring and the nature of the heteroatom are likely to be major components. This work, as well as our previous study,¹⁹ predict that attack at halogen by an alkyl radical requires a transition state C–X distance of approximately 2.06 Å (Cl), 2.19 Å (Br), and 2.35 Å (I) at the MP2/DZP level of theory. When constrained in a ring by either a five, six, or seven carbon chain, necessarily severe C–X–C angles are required. Deviations from the ideal 180° arrangement for the back-side transition state **3** would be expected to contribute to the C–X–C deformation energy and therefore to the overall strain energy of the transition state; angles of between 115° and 165° predicted in this study, together with C–C–C angle strain expected due to the geometry imposed by the halogen, would certainly be expected to impart considerable strain on the transition states **9–11**.

On the other hand, as the C–X–C angle is further reduced, one might expect to realize the transition state geometry **5** for front-side homolytic substitution at halogen. Recent ab initio studies predict that C–Si–C angles of approximately 80° are required for homolytic substitution by the front-side mechanism at silicon.²⁷ 1,5-Iodine transfer, for example, with the C–I–C (transition state) angle expected to be less than 110° would be a good candidate for the front-side mechanism. Despite this,

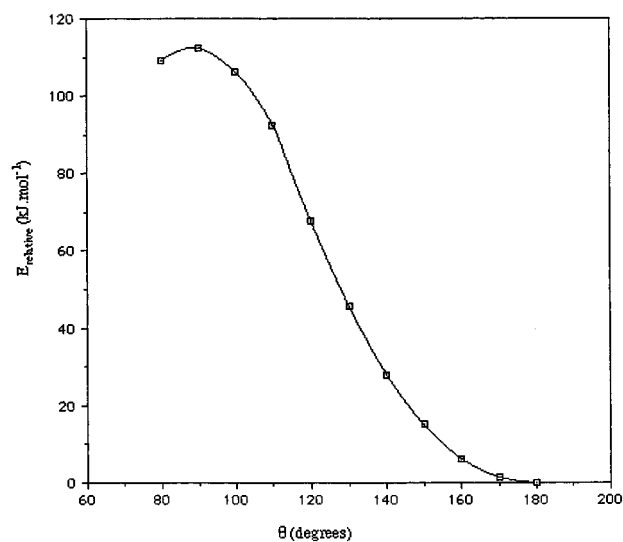
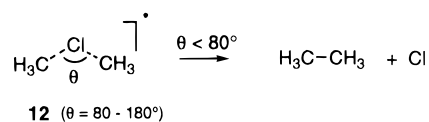


Figure 4. MP2/DZP calculated dependence of the energy of transition state (**12**) on angle of attack (θ) in the reaction of methyl radical at the chlorine atom in chloromethane with expulsion of methyl radical (Scheme 4).

Scheme 4



transition state **9** (X = I) was unable to be located at any level of theory used in this study. This result brings into question the very existence of the front-side homolytic substitution pathway for reactions involving halogen.

To further investigate the mechanistic requirements for homolytic substitution at halogen, we examined the effect of variation in the C–Cl–C angle (θ) on the relative energy of transition state **12** involved in the intermolecular homolytic substitution reaction of methyl radical at the chlorine atom in chloromethane with expulsion of methyl radical at the MP2/DZP level of theory, with QCISD/MP2 (fully optimized) calculations performed at selected angles (90°, 180°). The MP2/DZP angular energy dependence is displayed in Figure 4 and illustrates clearly a continual increase in energy as the angle (θ) is reduced from the ideal collinear arrangement (180°) to a value of 90°, at which point the energy of the transition state has suffered an increase of some 112 kJ mol⁻¹. A slight decline in energy is observed in progressing to 80°; however, at even smaller angles, the system was found to spontaneously collapse to ethane with expulsion of chlorine atom (Scheme 4). Whether or not the 3.4 kJ mol⁻¹ decrease in energy at 80° relative to the 90° “transition state” **12** is due to the existence of a second saddle point on the potential energy surface and hence a second (front-side) transition state is questionable. Importantly, however, if a saddle point does exist in this region of the potential energy surface, it would add approximately 100 kJ mol⁻¹ to the energy barrier for homolytic substitution at chlorine; the front-side mechanism would simply be uncompetitive with the back-side mechanism.

These conclusions are supported by QCISD/DZP (full optimization) calculations on the 180° and 90° transition states structures **12**. These calculations not only predict that the collinear arrangement of attacking and leaving

(27) Schiesser, C. H.; Wild, L. M., unpublished.

radicals (180°) is preferred by $104.0 \text{ kJ mol}^{-1}$ over the 90° structure but they also confirm that **12** (180°) is a true transition state, with an asymmetric stretching frequency of $724i$.²⁸

Conclusions

Ab initio calculations predict that 1,5-, 1,6-, and 1,7-halogen transfer reactions in ω -halo-1-alkyl radicals **6–8** proceed via transition states **9–11** of C_2 or C_s symmetry at correlated (MP2) and uncorrelated (UHF) levels of theory using the 3-21G^(*), 6-311G^{**}, and DZP basis sets; importantly, no [9-X-2] intermediates were located for any reaction in this study. It is interesting to note a recent report by Scaiano in which the existence of cyclic hypervalent iodine radical intermediates **13** during laser flash and laser-drop experiments is postulated.²⁹

Energy barriers in excess of 120 kJ mol^{-1} are predicted at the MP2/DZP level for all intramolecular translocation reactions in this study. These high barriers are most likely due to significant deviations from the ideal colinear arrangement of attacking and leaving radicals at the halogen atom in transition states **9–11** together with significant C–C–C deformations due to ringsize and long carbon–halogen separations.

(28) The QCISD/DZP (fully optimized) geometries of **12** are predicted to have C–Cl separations of 2.117 \AA (180°) and 2.181 \AA (90°).

(29) Banks, J. T.; Garcia, H.; Miranda, M. A.; Perez-Prieto, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 5049.

These high barriers preclude reactions of this type from being synthetically useful and are consistent with the lack of reports of intramolecular homolytic translocations involving halogen.

Finally, MP2/DZP and QCISD/DZP investigations into the relationship between C–Cl–C angle and transition state energy in the reaction of methyl radical with chloromethane predict that homolytic substitution at chlorine exclusively proceeds via a back-side attack mechanism; any front-side mechanism is calculated to require at least 100 kJ mol^{-1} more energy.

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Supporting Information Available: UHF/3-21G^(*), UHF/DZP, and MP2/DZP optimized Cartesian coordinates for structures **6–11**; UHF/6-311G^{**} and MP2/6-311G^{**} optimized Cartesian coordinates for structures **7** (X = Cl) and **10** (X = Cl); QCISD/DZP optimized Cartesian coordinates for transition state **12** ($\theta = 180^\circ$); a table of absolute energies of all structures (**6–12**) in this study (32 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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