Ab Initio Molecular Orbital Studies of Cl + C₂H₄ and H + C₂H₂Cl

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The following reactions have been examined: chlorine addition to ethylene to form 2-chloroethyl radical, and hydrogen addition to chloroethylene to form 1-chloroethyl radical and to form 2-chloroethyl radical. Equilibrium geometries and transition structures were fully optimized with 3-21G* and 6-31G* basis sets, and energies were computed with Hartree–Fock and Møller–Plesset methods. The 2-chloroethyl radical adopts an antiperiplanar conformation and has a rotation barrier of 4 kcal mol⁻¹. It is predicted not to have the low-frequency CH stretch mode considered characteristic of radicals with β-hydrogens. A barrier of less than 0.5 kcal mol⁻¹ is found for chlorine addition to ethylene. For hydrogen addition to the unsubstituted carbon of chloroethylene, the barrier is ca. 1 kcal mol⁻¹; for attack on the substituted carbon the barrier is 4–6 kcal mol⁻¹. The C–Cl dissociation energy of 2-chloroethyl radical is calculated to be 17 kcal mol⁻¹. Compared to ethyl radical, the C–H dissociation energy for 1-chloroethyl radical is 1.4 kcal mol⁻¹ higher while that of 2-chloroethyl radical is 2.5 lower.

Introduction

Atom-addition reactions are being investigated actively both experimentally and theoretically. For the C₂H₄Cl system, some of the possible reactions are outlined in Scheme I. There are two intermediates, 1-chloroethyl radical (I) and 2-chloroethyl radical (II). Hydrogen can add to chloroethylene at the unsubstituted carbon (transition state III) to yield 1-chloroethyl radical (I) or at the substituted carbon (transition state IV) to form II, which can decompose to chlorine plus ethylene via V. Alternatively, chlorine can add to ethylene via transition state V to form 2-chloroethyl radical (II).

Studies on photochlorination of unsaturated hydrocarbons in the gas phase indicate that the rate of addition of chlorine atom to olefins is affected little by the nature of the hydrocarbon. The activation energy is small (1.5 ± 0.5 kcal mol⁻¹) or zero for a wide variety of chlorinated and brominated olefins. Chemical results support this, in that the F + CH₂CHCl → CH₂CH₂CFCl → Cl + CH₂CH₂ system has no appreciable exit-channel barrier. The most favorable position for attack appears to be the least-substituted carbon. The kinetics of both chlorine addition and radical decomposition have been interpreted theoretically by using activated-complex theory based on model transition structures. Hydrogen addition to chloroethylene has not been examined directly, but experimental and theoretical results for H + CH₂CH₂ and FCH₂CH₂ → H + CH₂CH₂Cl suggest barriers of 2–6 kcal mol⁻¹.

The intermediate radicals have been studied by ESR techniques. In 2-chloroethyl radical (II) the α-carbon is essentially planar and the chlorine atom is syn- or anti-terminated to the half-filled orbital, as shown in Scheme I. Halogen bridging has been invoked to explain the stereochemistry of addition, elimination, and rearrangement reactions of β-halo radicals, but measurements of the rotation barrier have ruled this out for 2-chloroethyl radical. Several 2-haloethyl radicals have been studied by semiempirical and ab initio molecular orbital methods to determine the structure and conformation. No bridging was found and hyperconjugation with the halogen was used to explain the preference for the anti conformation in the chloro and bromo radicals. In contrast, fluoroethyl radical is gauche, as a result of more favorable interactions with the C–H bond than with C–F.

In previous work, we have examined hydrogen and fluorine atoms adding to ethylene, By combining the theoretical structure and vibrational frequencies of the transition state with the recent revision of the heat of formation and determination of the vibrational frequencies of ethyl radical, we were able to resolve a longstanding paradox concerning the forward and reverse rates of ethyl radical decomposition. For the F + C₂H₄ system, a small barrier was found for fluorine addition; the barrier for hydrogen addition to Cl of fluoroethylene was calculated to be 3–4 kcal mol⁻¹ larger than for ethylene. Heats of reaction, barrier heights, and dissociation energies were difficult to compute directly because of large basis set and correlation effects. However, through the use of isodesmic reactions and by careful calibration against experiment, useful estimates were obtained. In the present paper we apply the same techniques to the C₂H₂Cl system.

Scheme I

CH₂CHCl $\rightarrow$ H + CH₂CHCl $\rightarrow$ CH₂CH₂Cl $\rightarrow$ CH₂CH₂ + Cl

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bond lengths increased systematically by small, predictable study. It was indicated that optimization at the MP2 level did not affect with gradient methods at the Hartree-Fock level; the C2H4F system of programs using extended' (3-21G) and polarizationz at the HF/6-31G* level; the results significantly (bond angles were almost unchanged and amounts). As in previous studies on the C2H4F system: the hydrogen-addition transition states were fully optimized Fock (UHF) method for open shells. All equilibrium geometries

| Method | Ab initio calculations were performed with the GAUSSIAN 80 system of programs using extended (3-21G) and polarization (6-31G*) basis sets. The restricted Hartree-Fock (RHF) method was used for closed-shell systems, and the unrestricted Hartree-Fock (UHF) method for open shells. All equilibrium geometries and the hydrogen-addition transition states were fully optimized with gradient methods at the Hartree-Fock level; the C2H4F study indicated that optimization at the MP2 level did not affect the results significantly (bond angles were almost unchanged and bond lengths increased systematically by small, predictable amounts). As in previous studies on the C2H4F system, the halogen-addition transition state was determined by optimizing several points along the reaction path at the HF/6-31G* level; i.e., the carbon–halogen distance was fixed and the energy minimized.

| TABLE II: Vibrational Frequencies of CH3CHCl, CH2ClCH2, and CH2ClCH2Cl. | 
| --- | --- | --- | --- | --- | --- |
| CH3CH2 | CH2ClCH2 | CH2ClCH2Cl | CH2ClCH2Cl | CH2ClCH2Cl | CH2ClCH2Cl |
| 944 (826) | 417 (395) | 183 | 309 a' | 361 a' | 845 s' |
| 1115 (949) | 664 (620) | 338 | 316 a' | 177 a' | 257 s' |
| 1157 (943) | 696 (724) | 494 | 415 a' | 354 a' | 408 a' |
| 1165 (1073) | 1097 (896) | 619 | 707 a' | 939 a' | 506 a' |
| 1378 (1420) | 1186 (940) | 1067 | 1057 a' | 696 a' | 616 a' |
| 1522 (1342) | 1156 (1030) | 1141 | 1124 a' | 1069 a' | 952 a' |
| 1640 (1444) | 1401 (1280) | 1182 | 1323 a' | 1341 a' | 1098 a' |
| 1842 (1630) | 1362 (1170) | 1362 | 1372 a' | 1375 a' | 1154 a' |
| 3228 (3026) | 3337 (3030) | 1579 | 1602 a' | 1628 a' | 1344 a' |
| 3371 (3103) | 3423 (3080) | 1660 | 1648 a' | 1694 a' | 1428 a' |
| 3404 (3105) | 3456 (3130) | 3181 | 3319 a' | 3300 a' | 1647 a' |
| 3244 | 3326 a' | 3317 a' | 3333 a' | 3425 a' | 3423 |
| 3275 | 3400 a' | 3378 a' | 3425 | 3423 |
| 3401 | 3433 a' | 3412 a' | 3449 | 3442 |

*In cm^{-1}; experimental values in parentheses. a Theoretical frequencies from ref 24, experimental from ref 40. c Experimental frequencies from ref 41.

**Figure 1.** Chloroethylene geometry: HF/3-21G optimized (no superscript), HF/6-31G* optimized (asterisk), and experimental26 (parentheses).
Results and Discussion

The optimized geometries of chloroethylene, 1- and 2-chloroethyl radical, and the transition structures are collected in Figures 1-3, respectively. Total energies, vibrational frequencies, and relative energies are given in Tables I-V. Since basis set and correlation effects on the relative energies are large, the heats of reaction, dissociation energies, and barrier heights will be examined separately, after the optimized geometries and vibrational frequencies are discussed.

Chloroethylene. The C-Cl bond length is overestimated by 0.1 Å with the 3-21G basis set, but this problem is largely overcome with the 6-31G* basis. A similar effect is found in CH3Cl (R(2)Cl) calculated, 1.892 at 3-21G, 1.785 at 6-31G*; observed, 1.778 Å) as well as other molecules containing electronegative second-row atoms. The remaining geometrical parameters are very similar to ethylene and fluoroethylene computed with corresponding basis sets. Vibrational frequencies are listed in Table II. On average, the calculated harmonic frequencies tend to be 10-15% too high compared to observed anharmonic frequencies, due to a combination of anharmonicity and correlation effects. The exceptions to this trend are two chlorine bonding frequencies that are lower than expected and an even more prominent reduction in the C-Cl stretch (694 cm⁻¹ calculated; 742 cm⁻¹ observed). This is due to the overestimation of C-Cl bond length by 0.1 Å at the HF/3-21G level. Similar problems can also be expected for vibrational modes involving the chlorine in other structures computed at HF/3-21G geometries.

1-Chloroethyl Radical. As shown in Figure 2a, the α-carbon is found to be significantly pyramidal, with an angle of 156° between the CHCl plane and the CC bond, compared to 165-170° for CH3CH2, FCH2CH2, and C2H2CH2. The effect of electronegative substituents on the equilibrium geometry and on inversion barrier heights is well established and has been at-

ttributed to conjugative and inductive effects.27-37 The CC bond length and the geometry of the methyl group are similar to those of CH₃CH₂. The CH bond antiperiplanar to the radical center is slightly elongated, as in ethyl and gauche-fluoroethyl radicals.9 Correspondingly, there is a low-frequency CH stretch in the vibrational spectrum (3181 cm⁻¹ calculated). By comparison with CH₃CH₂ and FCH₂CH₂, the barrier to CH rotation is estimated to be ca. 2850 cm⁻¹ for the experimental frequency. This CH mode is considered diagnostic of carbon radicals with β-hydrogens.18,32

2-Chloroethyl Radical. The optimized geometry corresponds to an anti conformation with a slightly pyramidal CH₃ group (Figure 2b). This structure is the only minimum of the internal rotation-inversion surface. Unlike earlier calculations,11 no gauche conformation could be found. The transition structure for rotation has C₂ symmetry and is shown in Figure 2c. At the HF/3-21G and MP4SDQ/3-21G levels, the barrier is 4.0 kcal mol⁻¹ in excellent agreement with experiment (4 kcal mol⁻¹). Thus, 2-chloroethyl radical does not undergo free internal rotation, in contrast to ethyl and fluoroethyl radicals (calculated barriers of 0.15° and 0.3 kcal mol⁻¹, respectively).

The most striking feature of the anti conformation of 2-chloroethyl radical is the long C-Cl bond. The elongation is exaggerated with the 3-21G basis set, because the energetics of CICH₂CH₂ → Cl + C₂H₄ are not well represented at the HF/3-21G level (see Table IV). However, with the more reliable 6-31G* basis, the C-Cl bond length (1.826 Å) is still 0.05 Å longer than CH₃Cl (1.785 Å). Similar changes in the C-Cl bond length were seen by Hopkinson, Lien, and Csizmadia.17 This lengthening is a manifestation of the hyper conjugation that stabilizes the anti conformation (donation from the radical p orbital to the C-Cl σ*, and C-Cl donation to the half-filled p). INDO calculations predict a sizeable distortion of the C-Cl angle (92°) suggestive of Cl bridging.15 In contrast, ab initio calculations indicate no significant deviation from tetrahedral at any basis set level (109.8 ± 1.8°, Figure 2 and ref 17).

Although 2-chloroethyl radical has β-hydrogens, the low-frequency CH stretches that are diagnostic of such radicals are calculated to be absent. In the minimum-energy conformation, the β-CH bonds are both gauche and are not affected by hyper conjugation. Therefore, the CH bonds are not lengthened, the force constants are normal, and the CH stretching frequency are not lowered. The C-Cl is antiperiplanar to the half-filled orbital and should have a lower stretching frequency. However, the calculated shift is exaggerated because the C-Cl bond is too long (Figure 2b) and too weak (Table IV) at the 3-21G level.

An anomalously low β-hydrogen hyperfine coupling constant in 2-chloroethyl radical has been used to suggest large distortions of the CICH₂ group.12,13 Closing the C₂-C₂ angle and opening the angle between the C₂-C₂ and the β-CH₂ plane would move the hydrogens toward the nodal plane of the p orbital containing the unpaired electron, thus reducing the hyperfine coupling. INDO calculations suggest that a 25-30° distortion from tetrahedral would be needed to account for the shift,13a,13b At the HF/6-31G* level, the X-β-C angle is essentially the same as in CH₃CH₂ and gauche- and trans-FCH₂CH₂, and gauche- and trans-CH₂CHCl. The H₂CC angle is opened by ca. 3° relative to the same group of compounds, i.e., much too small to change the hyperfine coupling appreciably. The calculated Fermi contact integrals for ethyl, gauche-fluoroethyl, and 2-chloroethyl radicals (0.015, 0.019, and 0.006 au, respectively, at UHF/6-31G*) agree with the trends in the hyperfine coupling constants (26.9, 27.9, and 10.2, respectively). The anti conformation of fluoroethyl radical, which is a local maximum on the internal rotation surface, has a small Fermi contact integral as well (0.004 au), indicating that electronic factors, not geometric distortions, account for the low hyperfine coupling in CICH₂CH₂. The g value for CICH₂CH₂ is also unusually small and has been rationalized in terms of delocalization of the unpaired electron.11b Analysis of the UHF spin densities does suggest greater spin delocalization in chloroethyl radical than in ethyl or fluoroethyl radical but suggests that the involvement of chlorine d orbitals is quite small.

Chlorine-Addition Transition State. Experimental data indicate that there should be little or no barrier to addition.8-3 Since transition states for small barriers are difficult to find by direct optimization, we proceeded to locate the transition structure by optimizing several points along the reaction path. The 3-21G basis set severely underestimates the exothermicity of chlorine addition (Table IV) and this, in turn, affects the position of the transition state. Therefore, the optimization was carried out only at the HF/6-31G* level. The C-Cl distance was fixed at 2.4, 2.6, 2.8 Å, and the energy was minimized with respect to the remaining coordinates. As shown in Figure 4, a small maximum is found near 2.6 Å, at both the HF and MP2 levels using the HF/6-31G* optimized geometry. For R₄C₃ = 2.6 Å, the ethylene moiety is only weakly perturbed from its equilibrium geometry (Figure 3a). Comparison of the C-C bond and the CH₃ out-of-plane angle with the transition structure for F + C₂H₄ indicates that chlorine addition occurs somewhat earlier along the reaction path (R₀C₃ = 1.353 Å for Cl, 1.371 Å for F; ΔH₀CC = 171.5° for Cl, 164.8° for F). The XCC angle is 2° smaller for Cl addition. The HF/3-21G vibrational frequencies listed in Table II for this transition structure were computed at the HF/6-31G* geometry. The Cl bending modes occur at 177 and 354 cm⁻¹, considerably higher than assumed in previous models of the transition state.7 The remaining frequencies are near or slightly lower than the corresponding vibrations in CH₃CH₂. The smallness of the imaginary frequency is probably an artifact associated with the underestimated of the chlorine-addition exothermicity at HF/3-21G.

Hydrogen-Addition Transition States. Hydrogen can add either to the substituted carbon of chloroethylene to form 2-chloroethyl radical or to the unsubstituted carbon to form 1-chloroethyl radical. The transition structure for the latter (Figure 3b) is very similar to that found for addition to ethylene.8,9 Both have R₃C = 2.0 Å, ΔH₀CC = 106°, and a CC bond elongation of 0.04 Å relative to the reactant olefin. Vibrational frequencies for the attacking hydrogen should be similar to H + C₂H₄; however, the analysis is complicated by interaction with the


Figure 4. Potential energy curve for C-Cl dissociation in 2-chloroethyl radical at HF/6-31G* (solid) and MP2/6-31G* (dashed).
Studies of Cl + C2H4 and H + C2H3Cl

low-frequency C–Cl rocking mode. The vibrations can be described approximately as CH* bend in the CCH* plane (430 cm⁻¹), CCl rock (408 cm⁻¹), and CH* bend perpendicular to the CCH* plane, but there is considerable mixing among these modes.

The transition structure for hydrogen addition to the substituted carbon (Figure 3c) has a shorter CH* bond length (1.9 Å), and closely resembles a hydrogen addition to C1 of fluoroethylene.\(^{11}\) Compared to attack on the unsubstituted carbon, the transition state occurs somewhat later along the reaction path with slightly more C–C elongation and greater deformation of the olefin from planarity. The C–H* bending frequencies (461 and 506 cm⁻¹) are similar to H + CH2F (461 and 552 cm⁻¹).

Energetics. As was the case for the C2H4F system,\(^{2}\) accurate energy differences and barrier heights are difficult to compute directly because of large basis set and correlation effects. However, reliable estimates can be obtained by comparison with reactions where more experimental data are available. Calculations of (a) the heats of reaction, (b) dissociation energies, and (c) barrier heights are collected in Tables III–V, respectively, and are discussed individually.

(a) The reaction Cl + C2H4 → H + C2H3Cl is endothermic, \(\Delta H^\circ = 9.2\) or 15.3 kcal mol⁻¹, depending on whether 8.4 ± 0.49\(^{12}\) or 5 ± 1.8 kcal mol⁻¹ is used for \(\Delta H^\circ(298)\) of C2H4Cl. The HF/3-21G level overestimates the heat of reaction (Table III); addition of electron correlation (MP2, MP3, MP4) reduces the error by 10 kcal mol⁻¹. A similar size improvement is seen when d orbitals are added to the basis set (HF/6-31G* vs. HF/3-21G). Our best estimate of the heat of reaction is 14.5 kcal mol⁻¹ at MP4SDQ/6-31G* plus zero-point energy (MP4SDQ/6-31G* + ZPE). Since there is some uncertainty in the experimental value,\(^{3,5,6}\) we performed the same series of calculations on CH4 + Cl → H + CH2Cl, also involving breaking a C–H bond and making a C–Cl bond. The difference between the two reactions constitutes an isodesmic reaction

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\text{CH}_2\text{CHCl} + \text{H} \rightarrow \text{CH}_2\text{CH}_2 + \text{CH}_3\text{Cl}
\]

and hence is much less sensitive to basis set or correlation effects, as can be seen from Table III. The experimental heat of formation is 2.2 or 6.1 kcal mol⁻¹. Our best calculation, 8.8 kcal mol⁻¹ at MP4/6-31G* + ZPE, supports the larger value, corresponding to the choice of \(\Delta H^\circ(298) = 5 \pm 1\) kcal mol⁻¹ for C2H4Cl and \(\Delta H^\circ = 13.5 \pm 1\) kcal mol⁻¹ for Cl + C2H4 → H + C2H3Cl. Direct comparison with experiment for CH4 + Cl → H + CH2Cl (23.3 calculated, 21.4 experimental\(^{13}\)) implies that the MP4SDQ/6-31G* + ZPE level overestimates the heat of reaction for Cl + C2H4 by 1–2 kcal mol⁻¹ as well. This suggests that a better estimate of the heat of reaction may be 13.5 ± 2 kcal mol⁻¹.

(b) The C–H bond dissociation energy of C2H5, \(D_0 = 35.5 \pm 1.0\) kcal mol⁻¹ is well established\(^{14,15}\) and can serve as a reference value for related C–H dissociations. The data in Table IV indicate that the C–H dissociation energy is 1.4 ± 0.5 kcal mol⁻¹ greater than C2H5 for 1-chloroethyl radical, and 2.5 ± 0.5 kcal mol⁻¹ less than C2H5 for 2-chloroethyl radical. The C–Cl dissociation energy in 2-chloroethyl radical is much more sensitive to electron correlation and basis set changes. At the MP2/6-31G* + ZPE level the calculated \(D_0(\text{C–Cl})\) is 16.9 kcal mol⁻¹, but this may still change by a few kcal mol⁻¹ because of residual basis set and correlation effects. A more accurate value can be obtained indirectly. If the above estimate for the C–H dissociation energy (33 kcal mol⁻¹) and the heat of reaction (13.5 kcal mol⁻¹) are considered reliable, our best theoretical value for the C–Cl dissociation energy is 19.5 ± 2 kcal mol⁻¹.

The experimental C–Cl dissociation energy has been reported\(^{16}\) as 21.3 kcal mol⁻¹. This value was based on an approximate heat of formation for CH2Cl2H, obtained by assuming \(D_0(\text{C–H})\) in a CH3 group is the same in C2H4 and C2H5Cl. However, the \(\Delta H^\circ\) of C2H4\(^{17}\) and C2H5Cl\(^{18}\) have both been revised by 2–4 kcal mol⁻¹. With these new data, the approximations of ref 39 lead to \(\Delta H^\circ(298) = 21.4, \Delta H^\circ(0) = 23.8, D_0(\text{C–Cl}) = 19.3 ± 1,\) and \(D_0(\text{C–H}) = 34.5 ± 1\) kcal mol⁻¹. Similarly, a revised value can be obtained for 1-chloroethyl radical (\(\Delta H^\circ(298) = 19\) kcal mol⁻¹) by interpolating \(D_0(\text{C–H})\) for a CH2Cl group in C2H5Cl from data for HCH3 and CHCl3.

(c) Hydrogen-addition barriers are reasonable at the unrestricted Hartree–Fock level (Table V and ref 9) but are seriously overestimated with Möller–Plesset perturbation theory. For a proper description of H-addition transition structure energies, single excitations appear to be important\(^{19}\) but are not treated adequately by perturbation theory. Therefore, direct computation of these barrier heights is not possible with Möller–Plesset theory. Nevertheless, reliable changes in barrier heights can be obtained by careful comprison with ethyl radical. With the 6-31G* basis, the barrier for addition of hydrogen to the unsubstituted carbon of chloroethylene is 1.2 kcal mol⁻¹ lower than addition to C2H4. Since the barrier for ethylene\(^{20}\) is 2.04 ± 0.08 kcal mol⁻¹, we estimate a barrier of 1.0 ± 0.4 kcal mol⁻¹ for chloroethylene. The transition state for addition to the substituted carbon is 3–5 kcal mol⁻¹ higher, leading to an estimated barrier of 4–6 kcal mol⁻¹ to the formation of 2-chloroethyl radical. This is in agreement with the experimental observation that addition to the unsubstituted carbon is preferred.\(^{5,6}\)

The potential energy curve for chlorine addition to ethylene is shown in Figure 4. At both HF/6-31G* and MP2/6-31G* there is a small maximum near 2.6 Å. At larger distances the energy is slightly lower than the dissociation limit because of long-range attractive forces. Correction for basis set superposition error lowers the dissociation limit by 0.8 kcal mol⁻¹ at HF/6-31G*. The total of the barrier is 1.0 kcal mol⁻¹ below the dissociation energy at the Hartree–Fock level, while it is 0.5 kcal mol⁻¹ above at the MP2 level. Thus, the calculations predict a barrier of 0.5 kcal mol⁻¹ or less for chlorine addition, in agreement with experiment.\(^{4}\)

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(38) Also see footnote 22 of ref 10.

