Ab initio molecular orbital studies of atomic chlorine + ethylene and atomic hydrogen + chloroethylene

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Ab Initio Molecular Orbital Studies of Cl + C_2H_4 and H + C_2H_3Cl

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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.
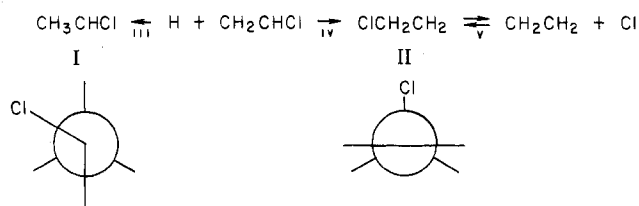
Introduction

Atom-addition reactions are being investigated actively both experimentally[1-6] and theoretically.[7-11] For the C_2H_4Cl 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 photochloroination 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.[1-3] The activation energy is small (1.5 ± 0.5 kcal mol⁻¹) or zero for a wide variety of chlorinated and brominated olefins.[1-3] Chemiluminescence results[4] support this, in that the F + CH_2CHCl → CH_2CHClF → Cl + CH_2CHF system has no appreciable exit-channel barrier. The most favorable position for attack appears to be the least-substituted carbon.[5,6] The kinetics of both chlorine addition and radical decomposition have been interpreted theoretically by using activated-complex theory based on model transition structures.[7] Hydrogen addition to chloroethylene has not been examined directly, but experimental and theoretical results[8-11] for H + CH_2CH_2 and FCH_2CH_2 → H + CH_2CHF suggest barriers of 2–6 kcal mol⁻¹.

The intermediate radicals have been studied by ESR techniques.[12,13] In 2-chloroethyl radical (II) the α-carbon is essentially planar and the chlorine atom is syn- or antiperiplanar 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,[12-14] but measurements of the rotation barrier have ruled this out for 2-chloroethyl radical.[13] Several 2-haloethyl radicals have been studied by semiempirical[15,16] and ab initio[9,11,17] molecular orbital methods to determine the structure and conformation. No bridging was found[9,11,15-17] and hyperconjugation with the halogen was used to explain the preference for the anti conformation in the chloro and bromo radicals.[15-17] In contrast, fluoroethyl radical is gauche,[9] 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.[9,10] By combining the theoretical structure and vibrational frequencies of the transition state[9] with the recent revision of the heat of formation[18] and determination of the vibrational frequencies[19] of ethyl radical, we were able to resolve a longstanding paradox concerning the forward and reverse rates of ethyl radical decomposition.[10] For the F + C_2H_4 system,[9] a small barrier was found for fluorine addition; the barrier for

Scheme I

$$CH_3CHCl \underset{III}{\rightleftharpoons} H + CH_2CHCl \underset{IV}{\rightleftharpoons} ClCH_2CH_2 \underset{V}{\rightleftharpoons} CH_2CH_2 + Cl$$

hydrogen addition to C_1 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 C_2H_4Cl system.

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TABLE I: Total Energies (in au) for the C_2H_4Cl System

			intermediate radicals		transition structures		
level	$CH_2CH_2 + Cl^a$	$CH_2CHCl + H^b$	CH_3CHCl^c	$ClCH_2CH_2^d$	$Cl-CH_2CH_2$	$H-CH_2CHCl^e$	$CH_2CHCl-H^f$
HF/3-21G	-534.877 54	-534.811 07	-534.880 62	-534.886 10		-534.807 09	-534.802 93
MP2/3-21G	-535.085 88	-535.035 78	-535.089 08	-535.092 18		-535.017 67	-535.011 89
MP3/3-21G	-535.107 18	-535.053 61	-535.111 23	-535.114 69		-535.037 30	-535.031 87
MP4/3-21G	-535.114 77	-535.061 58	-535.118 81	-535.122 54		-535.046 72	-535.041 31
HF/6-31G*	-537.479 68	-537.431 92	-537.503 37	-537.499 71	-537.481 28	-537.427 34	-537.422 06
MP2/6-31G*	-537.836 78	-537.813 97	-537.870 36	-537.863 92	-537.836 32	-537.795 01	-537.787 44
MP3/6-31G*	-537.872 46	-537.841 50					
MP4/6-31G*	-537.879 25	-537.846 87					

^{a} Reactants; energies for chlorine atom at HF, MP2, MP3, and MP4 are -457.276 55, -457.305 77, -457.310 18, and -457.311 17 au, respectively, with the 3-21G basis and -459.447 96, -459.552 43, -459.567 10, and -459.568 69 au with 6-31G*. ^{b} Products; energies for hydrogen are -0.492 60 au at HF/3-21G and -0.498 23 au at HF/6-31G*. ^{c} 1-Chloroethyl radical. ^{d} 2-Chloroethyl radical. ^{e} Addition to CH_2 group. ^{f} Addition to CHCl group.

TABLE II: Vibrational Frequencies^a

$CH_2CH_2^b$	CH_2CHCl^c	CH_3CHCl	$ClCH_2CH_2$	$Cl-CH_2CH_2$	$H-CH_2CHCl$	$CH_2CHCl-H$
944 (826)	417 (395)	183	309 a'	36i a'	639i	845i
1115 (949)	664 (620)	338	316 a''	177 a'	270	393
1157 (943)	698 (724)	494	415 a'	354 a''	408	461
1165 (1073)	1097 (896)	659	707 a'	939 a''	430	506
1387 (1220)	1151 (943)	1067	860 a''	1024 a'	662	616
1522 (1342)	1156 (1030)	1141	1113 a'	1057 a''	705	659
1640 (1444)	1401 (1280)	1182	1124 a''	1069 a'	971	952
1842 (1630)	1569 (1370)	1362	1323 a'	1341 a'	1069	1032
3305 (3021)	1834 (1610)	1579	1372 a''	1375 a''	1145	1132
3238 (3026)	3337 (3030)	1642	1602 a'	1628 a'	1356	1344
3371 (3103)	3423 (3080)	1651	1648 a'	1694 a'	1444	1428
3404 (3105)	3456 (3130)	3181	3319 a'	3300 a'	1647	1639
		3244	3326 a'	3317 a'	3333	3328
		3275	3400 a''	3378 a''	3425	3423
		3401	3433 a'	3412 a'	3449	3442

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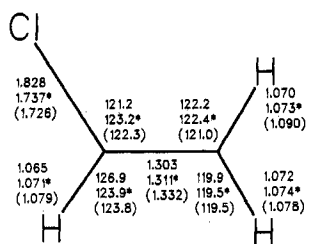

Figure 1. Chloroethylene geometry: HF/3-21G optimized (no superscript), HF/6-31G* optimized (asterisk), and experimental[26] (parentheses).

Method

Ab initio calculations were performed with the GAUSSIAN 80 system of programs[20] using extended[21] (3-21G) and polarization[22] (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[23] at the Hartree–Fock level; the C_2H_4F study[9] 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 C_2H_4F system,[9] 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 min-

TABLE III: Heats of Reaction (in kcal mol^{-1})

level	$Cl + C_2H_4 \rightarrow$ $H + C_2H_3Cl$	$Cl + CH_4 \rightarrow$ $H + CH_3Cl$	$CH_4 +$ $C_2H_3Cl \rightarrow$ $CH_3Cl +$ C_2H_4
HF/3-21G	41.71	42.50	0.79
MP2/3-21G	31.43	34.79	3.35
MP3/3-21G	33.61	36.43	2.81
MP4/3-21G	33.37	36.13	2.75
HF/6-31G*	29.96	32.47	2.50
MP2/6-31G*	14.31	23.11	8.80
MP3/6-31G*	19.43	27.21	7.78
MP4/6-31G*	20.32	28.13	7.81
ZPE	-5.80	-4.79	1.01
exptl $\Delta H°$(0 K)	19.2 ± 0.2^a 15.3 ± 1^b	21.4 ± 0.2	2.2 ± 0.4^a 6.1 ± 1.2^b

^{a} Based on $\Delta H_f°(298) = 8.6 \pm 0.2$ for C_2H_3Cl from ref 35. ^{b} Based on $\Delta H_f°(298) = 5.0 \pm 1$ for C_2H_3Cl from ref 36.

TABLE IV: Comparison of Dissociation Energies (in kcal mol^{-1}) for Ethyl, 1-Chloroethyl, and 2-Chloroethyl Radicals

|	$D_0(CH)$			
level	CH_3- CH_2	CH_3- $CHCl$	$ClCH_2-$ CH_2	$D_0(CCl)$, $ClCH_2CH_2$
HF/3-21G	41.70	43.64	47.08	5.37
MP2/3-21G	32.30	33.44	35.39	3.95
MP3/3-21G	34.87	36.15	38.32	4.71
MP4/3-21G	34.39	35.91	38.35	4.87
HF/6-31G*	42.17	44.83	42.53	12.56
MP2/6-31G*	33.13	35.38	31.34	17.03
ZPE	-5.10	-6.00	-5.80	-0.09
exptl	35.5^a	$(37.)^b$	34.5^b	$21.3,^c$ 19.3^b

^{a} References 18 and 38. ^{b} Present work, see text. ^{c} Reference 39.

(20) J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, R. L. Kahn, and J. A. Pople, *QCPE*, **13**, 406 (1980).
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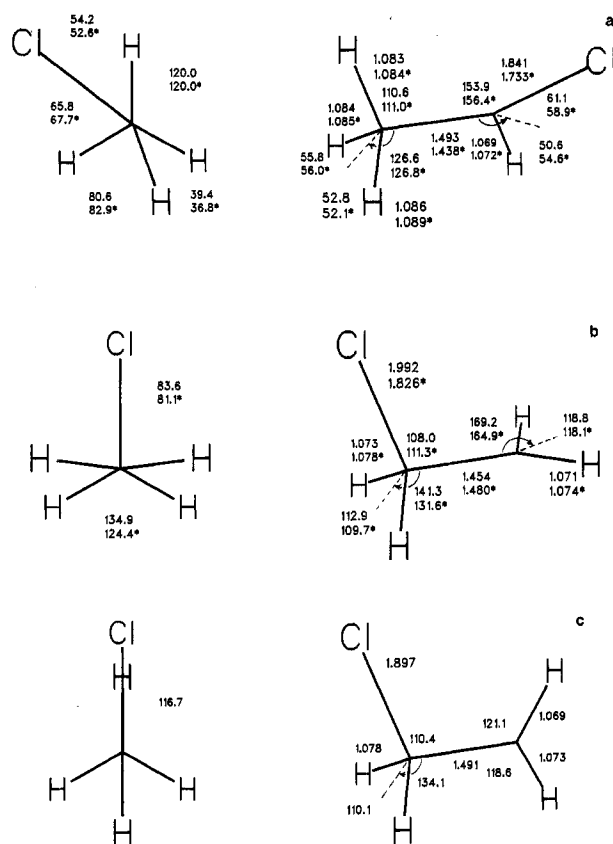
Figure 2. Optimized geometries of (a) 1-chloroethyl radical, (b) 2-chloroethyl radical minimum, and (c) 2-chloroethyl radical internal rotation transition structure, computed at the HF/3-21G level (no superscript) and the HF/6-31G* level (asterisk).

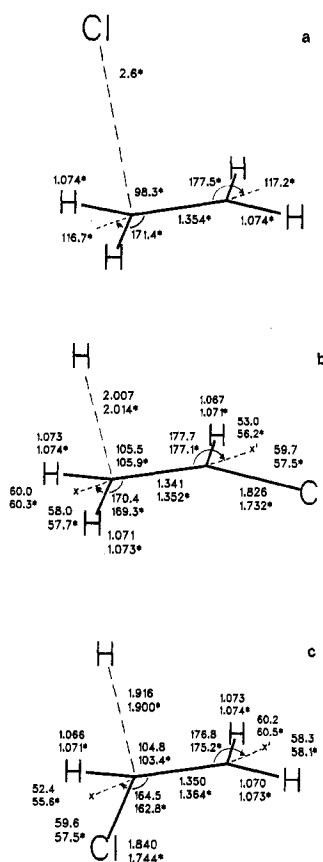TABLE V: Comparison of Barrier Heights (in kcal mol⁻¹) for Hydrogen Addition

level	H + CH₂CH₂ (attacking CH₂)	H + CH₂CHCl attacking CH₂	H + CH₂CHCl attacking CHCl	H + CH₂CHF (attacking CHF)
HF/3-21G	2.27	2.49	5.10	5.87
MP2/3-21G	10.88	11.36	14.99	15.26
MP3/3-21G	9.88	10.23	13.64	13.88
MP4/3-21G	9.09	9.32	12.71	12.99
HF/6-31G*	2.90	1.60	4.91	6.20
MP2/6-31G*	11.80	10.62	15.37	15.47
ZPE	0.18	0.16	0.30	0.25
exptl	2.04 ± 0.08[a]			

[a] Reference 10.

imized with respect to all other coordinates. Vibrational frequencies and zero-point energies were calculated by using analytical second derivatives[24] at the HF/3-21G level. The effect of electron correlation was estimated with Møller–Plesset perturbation theory up to fourth order, including all single, double, and quadruple excitations[25] (MP4SDQ, frozen core). With the larger basis set, open-shell systems could be accommodated only at the MP2/6-31G* level.

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

(24) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum. Chem., Quantum. Chem. Symp.*, **13**, 225 (1979).

(25) R. Krishnan and J. A. Pople, *Int. J. Quantum. Chem., Quantum. Chem. Symp.*, **14**, 91 (1980).

(26) D. Kivelson, E. B. Wilson, Jr., and D. R. Lide, *J. Chem. Phys.*, **32**, 205 (1960).

Figure 3. Optimized transition structure geometries at the HF/3-21G level (no superscript) and the HF/6-31G* level (asterisk): (a) chlorine addition to ethylene (Cₛ symmetry), (b) hydrogen addition to the unsubstituted carbon of chloroethylene (dihedral angles X'CCX = 179.9°, 180.1°* and H*CCX' = −0.6, −0.8°*, i.e., H* twisted toward Cl, and (c) hydrogen addition to the substituted carbon of chloroethylene (dihedral angles X'CCX = 180.5°, 181.3°* and H*CCX' = 5.7°, 7.3°*, i.e., H* twisted away from Cl.

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_{C-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.[22] The remaining geometrical parameters are very similar to ethylene and fluoroethylene computed with corresponding basis sets.[9] 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.[24] The exceptions to this trend are two chlorine bending 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 ClCH₂CH₂. The effect of electronegative substituents on the equilibrium geometry and on inversion barrier heights is well established[27,28] and has been at-

(27) J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, **23**, 209 (1972).

(28) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).

tributed to conjugative and inductive effects.[27-37] The CC bond length and the geometry of the methyl group are similar to those of CH_3CH_2. 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 CH_3CH_2[19] and FCH_2CH_2,[32] we predict ca. 2850 cm^{-1} for the experimental frequency. This CH mode is considered diagnostic of carbon radicals with β-hydrogens.[19,32]

   2-Chloroethyl Radical. The optimized geometry corresponds to an anti conformation with a slightly pyramidal CH_2 group (Figure 2b). This structure is the only minimum of the internal rotation–inversion surface. Unlike earlier calculations,[17] no gauche conformation could be found. The transition structure for rotation has C_s 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[13] (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[19] and 0.5[9] 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 $ClCH_2CH_2 \rightarrow Cl + C_2H_4$ 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 CH_3Cl (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 hyperconjugation that stabilizes the anti conformation (donation from the radical p orbital to the C–Cl σ^*, and C–Cl σ donation to the half-filled p). INDO calculations predict a sizeable distortion of the C–C–Cl angle (92°) suggestive of Cl bridging.[15] In contrast, ab initio computations 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 hyperconjugation. 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[12,13] has been used to suggest large distortions of the $ClCH_2$ group.[13,33] Closing the Cl–C–C angle and opening the angle between the C–C bond and the β-CH_2 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,33] At the HF/6-13G* level, the X–C–C angle is essentially the same as in CH_3CH_2, *gauche-* and *trans*-FCH_2CH_2, and *gauche-* and *trans*-CH_3CHCl. The H_2CC 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
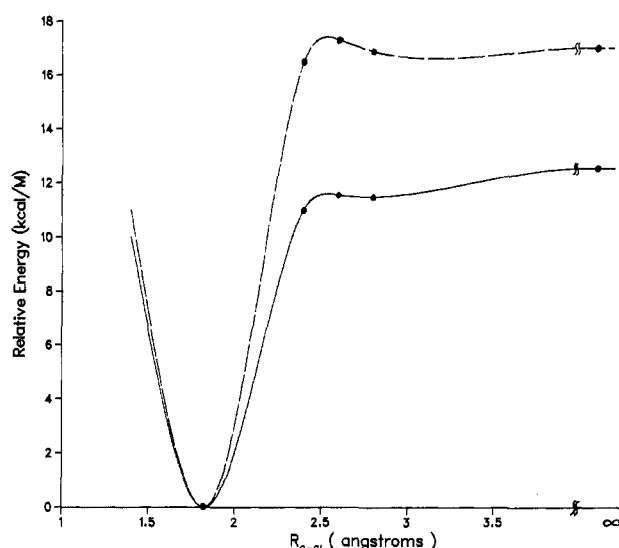

Figure 4. Potential energy curve for C–Cl dissociation in 2-chloroethyl radical at HF/6-31G* (solid) and MP2/6-31G* (dashed).

that electronic factors, not geometric distortions, account for the low hyperfine coupling in $ClCH_2CH_2$. The g value for $ClCH_2CH_2$ is also unusully small and has been rationalized in tems of delocalization of the unpaired electron.[13b] Analysis of the UHF spin densities does support 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.[1-3] 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 R_{C-Cl} = 2.6 Å, the ethylene moiety is only weakly perturbed from its equilibrium geometry (Figure 3a). Comparison of the C–C bond and the CH_2 out-of-plane angle with the transition structure for F + C_2H_4 indicates that chlorine addition occurs somewhat earlier along the reaction path (R_{CC} = 1.353 Å for Cl, 1.371 Å for F; $\angle H_2CC$ = 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[34] 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 CH_2CH_2. The smallness of the imaginary frequency is probably an artifact associated with the underestimation 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 R_{CH} = 2.0 Å, $\angle HCC$ = 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 + C_2H_4; however, the analysis is complicated by interaction with the

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   (34) Since the 6-31G* basis set predicts C–Cl bond lengths correctly (see discussion of C_2H_3Cl and ref 22), the accuracy of these HF/3-21G Cl bending frequencies computed at the HF/6-31G* geometry should be comparable to modes not involving chlorine, i.e., at most 10–20° too high.

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 hydrogen addition to C_1 of fluoroethylene.[9,11] 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 + C_2H_3F (461 and 552 cm^{-1}).

Energetics. As was the case for the C_2H_4F system,[9] 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 + C_2H_4 → H + C_2H_3Cl is endothermic, ΔH° (0 K) = 19.2 or 15.3 kcal mol^{-1}, depending on whether 8.4 ± 0.4[35] or 5 ± 1[36] kcal mol^{-1} is used for ΔH_f°(298) of C_2H_3Cl. 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,[35,36] we performed the same series of calculations on CH_4 + Cl → H + CH_3Cl, also involving breaking a C–H bond and making a C–Cl bond. The difference between the two reactions constitutes an isodesmic reaction

$$CH_2CHCl + CH_4 \rightarrow CH_2CH_2 + CH_3Cl$$

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 ΔH_f°(298) = 5 ± 1 kcal mol^{-1} for C_2H_3Cl and ΔH° = 15.3 ± 1 kcal mol^{-1} for Cl + C_2H_4 → H + C_2H_3Cl. Direct comparison with experiment for CH_4 + Cl → H + CH_3Cl (23.3 calculated, 21.4 experimental[37]) implies that the MP4SDQ/6-31G* + ZPE level overestimates the heat of reaction for Cl + C_2H_4 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 C_2H_5, D_0 = 35.5 ± 1.0 kcal mol^{-1} is well established[18,38] 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 C_2H_5 for 1-chloroethyl radical, and 2.5 ± 0.5 kcal mol^{-1} less than C_2H_5 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(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[39] as 21.3 kcal mol^{-1}. This value was based on an approximate heat of formation for $ClCH_2CH_2$, obtained by assuming D_0(C–H) in a CH_3 group is the same in C_2H_6 and C_2H_5Cl. However, the ΔH_f° of C_2H_5[18] and C_2H_5Cl[36] have both been revised by 2–4 kcal mol^{-1}. With these new data, the approximations of ref 39 lead to ΔH_f°(298) = 21.4, ΔH_f°(0) = 23.8, D_0(C–Cl) = 19.3 ± 1, and D_0(C–H_β) = 34.5 ± 1 kcal mol^{-1}. Similarly, a revised value can be obtained for 1-chloroethyl radical (ΔH_f°(298) = 19 kcal mol^{-1}) by interpolating D_0(C–H_β) for a CH_2Cl group in C_2H_5Cl from data for HCH_3 and $CHCl_2$.[39]

(c) Hydrogen-addition barriers are reasonable at the unrestricted Hartree–Fock level (Table V and ref 9) but are seriously overestimated with Møller–Plesset perturbation theory. For a proper description of H-addition transition structure energies, single excitations appear to be important[9] but are not treated adequately by perturbation theory. Therefore, direct computation of these barrier heights is not possible with Møller–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 C_2H_4. Since the barrier for ethylene[10] 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 top of the barrier is a few tenths of a 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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