

problems associated with synchronously scanning doubling crystals.

The AS_3 radiation is quite weak ($\ll 50 \mu\text{J}/\text{pulse}$, the lower limit of our power meter), and because it is produced by a highly nonlinear optical process, small pulse-to-pulse variations in the dye laser output are amplified in the AS_3 output. A particular feature of the output is the flaring that occurs on particularly intense input pulses, due to amplification slightly off axis with respect to the main beam. This flaring can give rise to large scattered light signals within the chamber. To eliminate this problem, the AS_3 beam was focused through a 0.5-mm pinhole and recollimated; this effectively filtered out the off-axis contribution.

The excitation beam entered and exited the vacuum chamber at right angles to the jet through 500-mm light-baffled arms fitted with Brewster angle windows to reduce scattered light. A

1000-mm focal length lens was used to produce a beam waist of ~ 0.3 -mm diameter in the region where the laser intersected the jet. Fluorescence was detected at right angles to both the jet axis and the excitation beam. A 50-mm collection lens, situated 100 mm from the laser beam, imaged the fluorescence onto a 3-mm slit which was positioned in front of a high-sensitivity photomultiplier. The photomultiplier output was averaged by use of a PAR 162/165 boxcar averager and displayed on a strip-chart recorder.

The laser power was monitored from a reflection off the input Brewster window using an RCA 1P28 photomultiplier tube and similarly averaged by use of a PAR 162/165 boxcar averager and recorded with a chart recorder.

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Theoretical Study of the Potential Energy Surface Governing the Stereochemistry in ClC_2H_4 Reactions

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Large-scale multireference configuration interaction calculations in a double- ζ -type AO basis including polarization functions are carried out for the potential surface of the ClC_2H_4 system. The charge distribution for various extreme points of the surface is discussed. The absolute minimum is found for an asymmetric ClC_2H_4 structure. The symmetrical bridged nuclear conformation is also found to be stable with respect to dissociation into $Cl + C_2H_4$. The activation energy for rotation about the C-C axis is calculated to be around 18 kJ/mol, which is comparable to that for the 1,2 migration (around 26 kJ/mol). The stereochemistry is governed by the fact that addition of Cl to C_2H_4 (or dissociation) is a two-step reaction proceeding through a symmetrical intermediate. The direct addition pathway possesses a small barrier of about 8 kJ/mol.

Introduction

In a previous paper¹ an extended study of the potential surface of the system $F-C_2H_4$ has been performed including dissociation and 1,2-fluorine migration, whereby most geometrical parameters have been optimized for all points of the surface. Generally such reactions of ethylene with radicals containing one unpaired electron have been of wide theoretical and experimental interest (see ref 1 and references therein). In the series of $X-C_2H_4$ radicals with $X = H, F, Cl, Br, \text{ and } I$ the question arises whether an unsymmetrical or a symmetrical structure should be used to describe the system and how to interpret the observed 1,2 migrations, control of stereochemistry, dissociation, formation, enhanced reactivities, and other characteristics of these systems.

In 1962 Thaler² reported the unexpected preponderance of 1,2-dibromobutane in the product mixture from the radical bromination of 1-bromobutene (not observed in chlorination or bromination of 1-chlorobutene) and attributed this result to a rate-enhancing effect of the bromo substituent on the vicinal position. Since then many studies to clarify this behavior have been undertaken.³ All exhibit a smaller effect if bromine is

replaced by chlorine, while the radical reactions involving fluorine behave in an entirely normal fashion.

Skell and co-workers extended the Thaler observations and also found these substituents could control stereochemistry. They interpreted the unexpected behavior of the iodine, bromine, and chlorine compounds by invoking a bridged XC_2H_4 radical. For this bridged radical they discussed two possible structures: a symmetrically bridged radical with a single equilibrium position and an unsymmetrical bridged structure in which the bridging atom performs a fast shuttling motion between the two carbon centers.^{3,4}

The experimental evidence does not distinguish these two possibilities when the substituent is β -bromo, or β -iodo, the conclusion being that they are either symmetrical, or undergo rapid shuttling. An unambiguous decision in favor of an unsymmetrical structure was made for β -chloroalkyl radicals, since here the barrier for shuttling is sufficiently large to permit trapping of the radical faster than shuttling. This interpretation is not free from dispute, and an alternative has been suggested.⁵ In the series,

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(3) A good summary of the experimental results is contained in: *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, Chapter 26.

(4) See, for example: Skell, P. S.; Traynham, J. G. *Acc. Chem. Res.* **1984**, *17*, 160, and references therein.

(5) See, for example: Tanner, D. D.; Darwish, D.; Mosher, M.; Bunce, N. *J. Am. Chem. Soc.* **1969**, *91*, 7398. Tanner, D. D.; Mosher, W. M.; Das, N. C.; Blackburn, E. V. *J. Am. Chem. Soc.* **1971**, *93*, 4802. Examination of these and other criticisms can be found in ref 3 and 4.

H, F, Cl, and Br the hydrogen and fluoro substituents show none of the bridging characteristics associated with the heavier substituents.

The addition/elimination reactions, $X + C_2H_4 = XC_2H_4$, have generally been described without consideration of a symmetrical intermediate, or the 1,2 migration. It is known that the dissociation energy for ClC_2H_4 is 87 kJ/mol.⁶ The possibility of the 1,2 migration has been investigated for the ethyl radical by theoretical methods.^{7,8}

The investigation by ESR spectroscopy^{9,10} has been restricted to β -substituted radicals where the substituent is H, F, Cl, S, Si, Sn, etc., but with lack of success to Br and I. Except for H and F, these radicals have structures in which the β -substituent sits in the same plane as the half-filled p orbital, in an asymmetric structure, distorted to varying degrees toward the symmetric structure, and an enhanced rotational barrier.

There is confusion regarding the definition, or significance of the title "bridged". From the experimental side it was used to encompass all the radicals that have certain unexpected properties, such as control of stereochemistry, rearrangement, enhanced barrier to rotation, and enhanced reactivity in the preparation of these radicals. It was clear that these characteristics did not indicate a unique structure, even if they were written symbolically with the bridge atom symmetrically disposed. The theoretical studies are directed to a more precise description of these radicals to determine if there is a structural uniqueness to which the title bridging might be applied.

Various studies have been carried out using theoretical methods. Hopkinson et al.¹¹ studied the equilibrium structure and the rotation around the CC axis using the UHF method in a minimal and a split-valence shell basis. They find no evidence of a bridging from chlorine. An analysis of the dissociation process from the absolute asymmetric minimum into $Cl + C_2H_4$ and $H + C_2H_3Cl$ was performed by Schlegel et al.¹² with emphasis on the transition-state region in the dissociation process. They also employed UHF calculations followed by second-order Møller-Plesset perturbation procedures in a 3-21G and 6-31G* basis set and found a barrier toward dissociation. They did not consider a shuttling motion. Finally, Hoz et al.^{13,14} investigated the equilibrium structure and the dissociation process in the symmetric nuclear conformation employing UHF and MCSCF procedures in a split-valence AO basis with one d polarization function on chlorine. They found the $Cl-C_2H_4$ curve to be repulsive in this geometry. None of the investigations studied the entire surface important for dissociation, bridging, and rotation, taking into account electron correlation for geometrical conformations, and none made a comparison with the analogous FC_2H_4 system.

The present paper contains a theoretical study of the entire potential surface for the $Cl-C_2H_4$ system, in close analogy to what has been undertaken for the related $F-C_2H_4$ compound.¹ The emphasis lies on the reaction of the Cl and C_2H_4 itself, on the chlorine 1,2 migration and on the rotation around the CC axis which is a competitive motion to the 1,2 migration. All calculations employ a multireference CI treatment. In the previous paper on FC_2H_4 the influence of the excited states on the ground-state potential surface has been discussed only briefly. Since the spacing between ground and excited states becomes smaller in the heavier systems, their interaction becomes stronger and consequently more influential on the ground-state hyper-

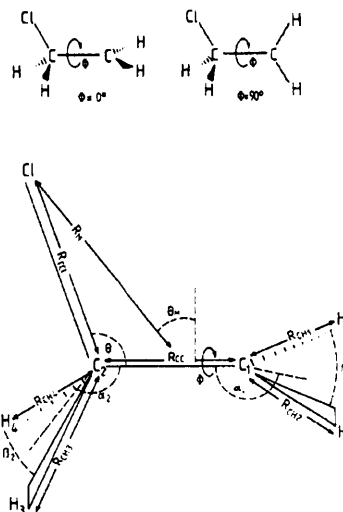


Figure 1. Coordinate system employed in the present study.

surface. The results for the chlorine system will be compared to those for $F-C_2H_4$ in order to explain differences between the two systems. Finally, a third paper in this series¹⁵ will show details of the corresponding $Br-C_2H_4$ system and an overall comparison of the three systems, in particular the relation to the various experiments available.

Technical Details

The coordinate system employed in the present work is given in Figure 1. The calculations were carried out using for the chlorine atom the standard (12s8p) basis by Dunning and Hay,¹⁶ augmented by one d function with exponent $\alpha(d) = 0.6$. For the carbon atoms the (9s5p) set of Gaussians given by Huzinaga in the [4s2p] contraction suggested by Dunning¹⁷ was used. For the description of polarization and correlation effects a d function with an exponent of 0.7 was added. For the hydrogen center, the five-component expansion by Whitten¹⁸ was used in the [2s] contraction with a scaling factor of $\eta^2 = 2.0$.

In order to obtain an adequate description of the CC bond, an additional s-bond function with exponent $\alpha(s) = 1.4$ was located between the two carbon atoms. Similarly an s-type bond function with exponent 1.2 was placed in the CCl bond. The total number of contracted Gaussians was thus 66.

Several types of configuration interaction calculations are undertaken. In the first calculation only a single reference configuration is employed (standard notation SD-CI) while the second CI generally used a large number of reference configurations. Such a multireference CI treatment is generally necessary as soon as the state in question cannot be represented by a single configuration. This is normally the case if a bond is broken, i.e., for nuclear geometries away from the minimum. In order to test the influence of an excited state on the ground state, simultaneous configuration selection was undertaken with respect to both states in some instances. Such a procedure is sometimes necessary if the character of the ground state changes considerably along the reaction path, as has been shown in detail for various ionic diatomic molecules.¹⁹ These calculations are referred to as two-root calculations (since selection is undertaken for two eigenvalues of the Hamiltonian matrix).

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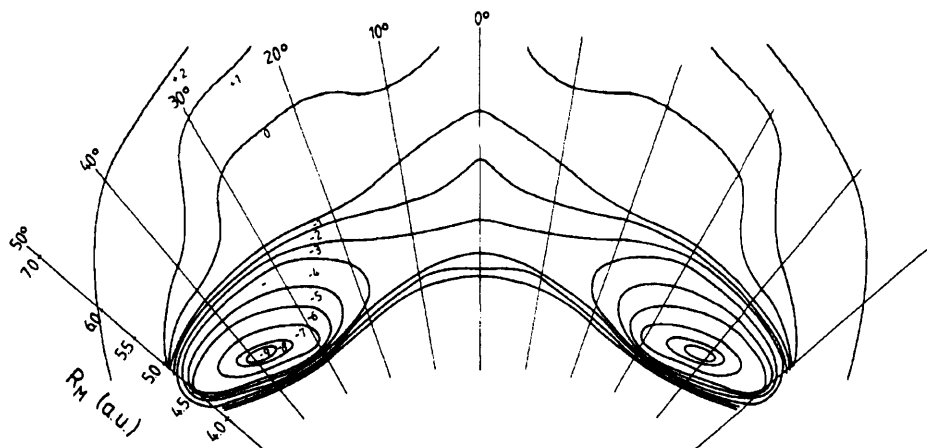


Figure 2. Potential energy hypersurface for the $\text{Cl} + \text{C}_2\text{H}_4$ system. All points are obtained from the 17M1R calculations; estimated full CI values are plotted. For each pair of θ_M , R_M values the other coordinates, R_{CC} , α_2 , β_2 are optimized. Relative energies in kcal/mol.

The total MRD-CI configuration space which arises from single and double excitations with respect to the reference configurations was in the order of 800 000; the SD-CI space (one reference configuration) was around 100 000. The MRD-CI and estimated full CI energies are evaluated in the standard manner.²⁰ The values given in the tables are always the estimated full CI results since they incorporate the influence of the higher excitations not explicitly included in the MRD-CI. The difference between the estimated full CI and MRD-CI values is quite small, however, so that it does not seem necessary to give both.

Because of the size of the system, not all geometrical parameters have been fully optimized. First the values for α_1 and β_1 are set to their corresponding values in ethylene, i.e., 180° and 118° , respectively, which can be justified by the small dependence of the total energy on these parameters.¹ Test calculations at the absolute minimum as well as at the migration saddle point employing $\alpha_1 = 160^\circ$ or $\alpha_1 = 200^\circ$ (instead of $\alpha_1 = 180^\circ$) both lead to higher energy values. In analogy to the FC_2H_4 system it is expected that an optimization of α_1 and β_1 may change the total energy by no more than 1–2 kJ/mol. The effect is even smaller for the outer regions ($R_{\text{CCl}} > 5.0$ au).

The angle Φ is also kept to zero for all points on the surface and varied only at the absolute minimum to obtain the CH_2 rotational barrier. Furthermore, all CH bond lengths are chosen to be equal to 2.052 au after test calculations had shown that variations in the CH bond length have a minor influence on the total energy. All other parameters (α_2 , R_{CC} , and β_2) are varied and optimized for each value of θ_M , R_M , which are the leading coordinates in describing the shuttling motion and the dissociation process.

The Potential Surface of ClC_2H_4

A contour plot of the calculated potential energy for the ClC_2H_4 system is shown in Figure 2. The important data of the system are contained in Table I.

The shape of the potential surface shows an asymmetric structure for the absolute minimum and a saddle point for $\theta_M = 0^\circ$. The bent skeleton ClCC conformation with a bond angle around 110° is expected on the basis of qualitative MO theory in the Mulliken–Walsh model²¹ and is typical for molecules with a triatomic skeleton in their electronic ground states and possessing 19 valence electrons. The optimal structure calculated by using the MRD-CI treatment has the following parameters: $R_{\text{CC}} = 1.48$ Å, $\alpha_2 = 130^\circ$, $R_M = 2.25$ Å, $\theta_M = 38^\circ$, and $\beta_2 = 110^\circ$. The total SCF energy is -537.4996 hartrees, the MRD-CI energy is -537.863 hartrees and the estimated full CI energy is -537.910

TABLE I: Extreme Points on the Hypersurface for the Systems FC_2H_4 and ClC_2H_4 , Taken Relative to the Dissociation Limit (Estimated Full CI Energies Used)

	FC_2H_4	ClC_2H_4
absolute minimum energy, kJ/mol	-165	-41
XC distance, Å	1.44	1.86
θ , deg	108	112
R_{CC} , Å	1.50	1.48
β_1 , deg	118	118
α_2 , deg	130	130
β_2 , deg	110	110
α_1 , deg	190	180 ^a
barrier to direct dissociation, kJ/mol	0	7.9
shuttling motion minimum for $\theta_M = 0^\circ$ (transition state)	-41	-14 to -16
XC distance, Å	1.83	2.98
R_{CC} , Å	1.38	1.38
activation energy of 1,2 migration	115–130	25–27
ΔE (absolute minimum, min $\theta_M = 0^\circ$), kJ/mol	115–130	25–27
activation energy of Φ rotation, kJ/mol	11–17	17–18

^a Value assumed; see text.

hartrees. In analogy to what has been observed for the FC_2H_4 system the minimum in the symmetric $\theta_M = 0^\circ$ approach relative to dissociation is obtained only by the CI calculations.

The shape of the potential surface is qualitatively similar to that for the FC_2H_4 system. A more quantitative comparison of important values on the two surfaces can be extracted from Table I. In the ClC_2H_4 system the absolute minima is only -41 kJ/mol below the separated $\text{Cl} + \text{C}_2\text{H}_4$ species in comparison to the large value of -165 kJ/mol in the FC_2H_4 system. The stabilization of the symmetric minimum—relative to dissociation into Cl and C_2H_4 along the path with $\theta_M = 0^\circ$ —is only -16 kJ/mol; i.e., along this coordinate the binding character is also small in comparison to the fluorine system (-41 kJ/mol).

In comparison to the experimentally determined dissociation energy of 87 kJ/mol, the calculated ClC_2H_4 minimum is not deep enough. This is not surprising since a larger AO basis, in particular one that includes more polarization/correlation functions (of d and f type, for example), is required if the dissociation energy is to be obtained with an accuracy within a few kilojoules per mole. Normally the separated fragments are described somewhat better (the correlation energy error is smaller) than the combined system, and hence the dissociation energy is calculated too low. This break in the accuracy of the description is expected to take place at large separations of Cl and C_2H_4 . Hence the shape of the potential surface for the combined system should be reliable in the AO basis used over a large range of nuclear conformations, in particular the relative behavior for the intramolecular arrangements including rotation, shuttling, and the calculated barrier to dissociation (as will be discussed in the pathway for $\theta_M = 40^\circ$). The extra com-

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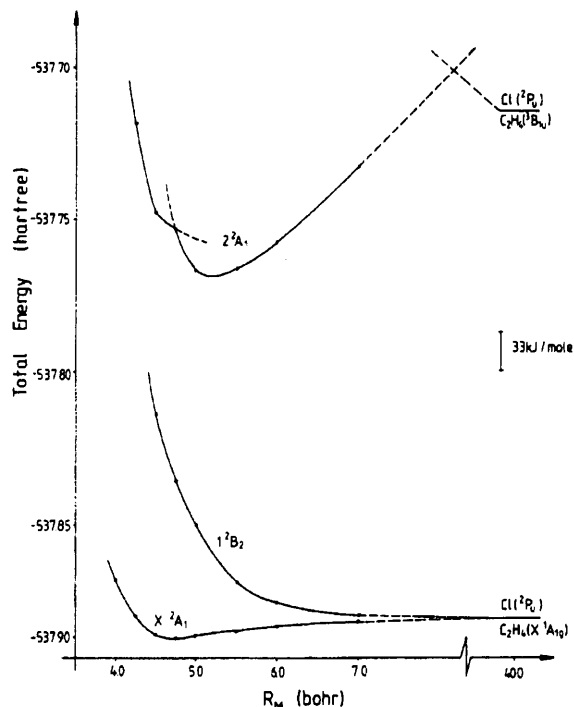


Figure 3. Calculated sections of the potential surface for Cl-C₂H₄ abstraction along a symmetrical pathway. The ground and first excited states are given. The estimated full CI values of the 13M2R calculation are employed.

computational effort that would have been necessary for employing a larger AO basis thus did not seem to be justified.

Apart from these quantitative differences between the fluorine and chlorine systems, a qualitative difference is only seen in the potential curve of the Φ variation. The present calculations give an optimal angle of 0°, a pattern that will be discussed later. The geometrical values obtained for the absolute minima are in excellent agreement with those of other calculations.¹¹⁻¹⁴ This is not surprising since the structure is an essentially one-configuration conformation at equilibrium and as such should be found within small differences by all types of ab initio methods.

Separation into Cl + C₂H₄

The separation of ClC₂H₄ into ethylene and chlorine will be discussed in analogy to the previous work dealing with FC₂H₄ along two extreme pathways: first for $\theta_M = 0^\circ$, i.e., dissociation maintaining the symmetric C_{2v} structure, and second $\theta_M = 40^\circ$ relating the minimum structure with the separated products.

Pathway $\theta_M = 0^\circ$. The bonding interaction between Cl and C₂H₄ at $\theta_M = 0^\circ$ is not only due to polarization effects. The same qualitative situation has also been found for FC₂H₄. Only with CI, but not with SCF, calculations, does one find a minimum along this pathway, which is an indication that correlation effects are important or, in an alternative description, that interaction of the ground state with higher states is effective. If the latter picture is assumed, qualitative arguments predict that the state mixing is more important in Cl-C₂H₄ than in the related fluorine system because the states are closer in energy in the heavier compound. Figure 3 contains the potential energy curves obtained from the MRD-CI calculations together with some important excited states that have been taken into account. Because the ground-state binding energy is quite small (14–16 kJ/mol) along this pathway, the actual form of the potential depends somewhat on the theoretical treatment. Various calculations have been performed including those in the lower C_v symmetry in order to assess the errors; a sample of results is contained in Table II. It is seen that the SCF treatment gives a very shallow minimum (1.4 kJ/mol) at large separations which disappears in the more appropriate CI treatments. The CI treatments with fewer reference

TABLE II: Relative Minima in the $\theta_M = 0^\circ$ Dissociation Pathway as a Function of Theoretical Treatment (Estimated Full CI Energies Used)

treatment ^a	minimum	
	R ₀ , bohrs	E, kJ/mol
SCF	7	1.4
Cl, 1M1R, C _v symmetry	5.6	11.8
Cl, 17M1R, C _v symmetry	4.8	14.5
Cl, 6M1R, C _{2v} symmetry	5.1	13.8
Cl, 13M2R, C _{2v} symmetry	4.8	15.5

^a xMyR denotes that x reference configurations are employed in the MRD-CI calculations and that configuration selection is carried out according to y roots.

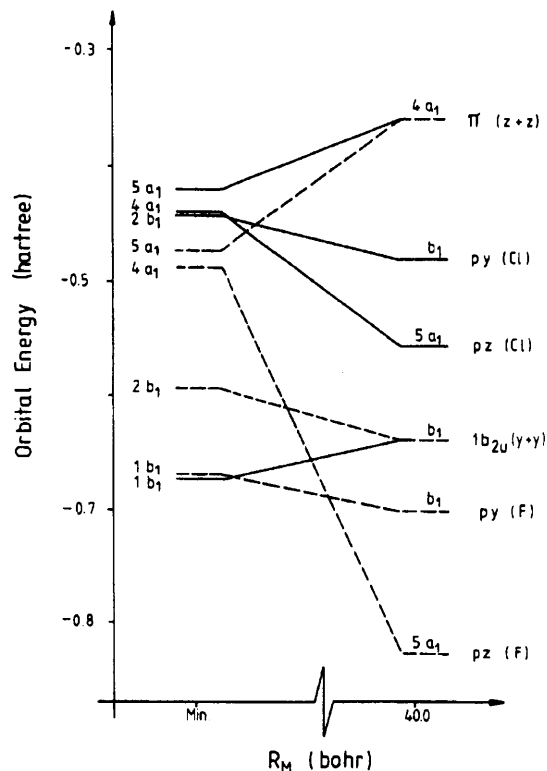


Figure 4. Orbital energies of ClC₂H₄ and FC₂H₄ for relevant orbitals involved in the binding (symmetric approach, C_{2v} symmetry). Dashed lines correspond to FC₂H₄, and solid connecting lines correspond to ClC₂H₄.

configurations (one or six) give somewhat smaller potential depths and larger bond lengths than the more extensive treatments. The difference in results between the 17M1R treatment in C_v symmetry and the 13M2R treatment in C_{2v} symmetry is quite small; the most reliable results should be those of the 13M2R treatment, which have actually been plotted in Figure 3.

An analysis of the MO's during the Cl-C₂H₄ separation process shows that there are only quantitative but no qualitative differences relative to the situation in the fluorine compound. The p orbitals of chlorine transform according to the A₁(p_z), B₂(p_x), and B₁(p_y) irreducible representation, whereby p_z is the open-shell orbital. The relevant ethylene orbitals are the unoccupied $\pi^*(z-z)$ of B₂ symmetry and the occupied orbitals $\pi(A_1)$, the two in-plane CH binding orbitals of A₂ and B₁ symmetry, respectively, and the CC (p_z) bonding MO 3a_g(x+x) of A₁ symmetry. A noticeable mixing in the combined system occurs only between the two orbitals π and p_z of A₁ symmetry (4a₁ and 5a₁ in valence electron notation). No mixing is possible in the A₂ symmetry. Mixing between the 1b_{2u} and p_y of B₁ symmetry (1b₁, 2b₁) is small because of the larger difference in orbital energy and likewise between π^* and p_x in the B₂ irreducible representation. Details have been discussed in connection with the approach of fluorine to C₂H₄.

TABLE III: Orbital Energies of the Inner Shells in ClC₂H₄ for the Three Extreme Points of the Potential Energy Hypersurface (Energies in hartrees)^a

orbital	$\theta_M = 40^\circ$		Δ_1	$\theta_M = 0^\circ$		
	ϵ_i (minima)	ϵ_i ($R_M = 40$ au)		ϵ_i (minima)	Δ_2	Δ_3
1s	-104.8112	-104.8788	-0.0676	-104.8513	-0.0274	0.0403
2s	-10.5368	-10.6023	-0.0655	-10.5750	-0.0273	0.0382
2p _x	-8.0023	-8.0674	-0.0651	-8.0400	-0.0274	0.0377
2p _y	-8.0000	-8.0639	-0.0639	-8.0367	-0.0272	0.0367
2p _z	-8.0000	-8.0639	-0.0639	-8.0367	-0.0272	0.0367
σ_g (ethylene)	-11.3051 ^b	-11.2379	0.0672	-11.2521	0.0142	-0.0530
σ_u (ethylene)	-11.2498 ^b	-11.2363	0.0135	-11.2505	0.0142	0.0007

^a Δ_1 refers to the difference between the separated species and ClC₂H₄ in its absolute minimum ($\theta_M = 40^\circ$), Δ_2 refers to the energy differences between separated species and the symmetric ($\theta_M = 0^\circ$) minimum, and Δ_3 refers to the difference between the orbital energies of the relative C_{2u} and the absolute minimum. ^b In the absolute minimum σ_g corresponds to the 1s orbital at C₂ while σ_u becomes the 1s orbital of the terminal carbon C₁.

The strength of the mixing, in particular when comparing ClC₂H₄ and FC₂H₄, can be seen from Figure 4, which contains the orbital energies of the relevant MO's involved in the binding. It is clear that the type of binding is similar in both systems but that there are definite quantitative differences; on the basis of this MO analysis one expects a weaker bonding between the halogen and ethylene in the ClC₂H₄ compound. Similar arguments will also hold for the situation at the absolute minimum.

Since the binding effects are quite small, a consideration of the influence of higher states is also important. The ground state for $\theta_M = 0^\circ$ is X²A₁ in C_{2v} symmetry with the valence electron configuration ...4a₁²5a₁1b₁²2b₁²1b₂²2b₂²1a₂² in C_{2v} notation or ...6a²7a¹1a¹23a² in C_s symmetry. It dissociates into the lowest channel Cl(²P_u) and C₂H₄(X¹A_{1g}). Around the minimum, and even more strongly for smaller R_M values, the electron configuration possesses some ionic Cl⁻C₂H₄⁺ character, which is represented by the 2²A₁ state at larger separations (Figure 3). This situation is wholly analogous to that in the FC₂H₄ system.

The ionic character can most easily be seen from the orbital energies of the inner shells given in Table III. Generally it can be stated that the higher the K shell energy the more negative is the surrounding of the atom under consideration. The reduction in 1s orbital energy goes from -104.8788 hartrees in the separated chlorine to -104.8513 hartrees in the relative C_{2u} minimum and reaches finally -104.8112 hartrees at the absolute minimum of the ClC₂H₄ compound. This shows a definite charge transfer toward the chlorine which is still small in the first step (from fragments to the $\theta_M = 0^\circ$ minimum) but considerable in the minimum structure. Conversely the charge reduction at the carbon sites is also obvious from the σ_g and σ_u orbital energies of ethylene which exhibits also the most dramatic effect when the absolute minimum is reached. Hence these data show already at the SCF level the definite change from the neutral Cl + C₂H₄ conformation toward a configuration with partial Cl⁻C₂H₄⁺ character. As expected, this ionic behavior is even more present in the corresponding fluorine compound which exhibits changes of $\Delta_2 = 0.0284$ for the ethylene inner shells compared to the present values of 0.0142 hartree.

From a theoretical point of view the change in character indicates that configuration interaction is important and that possibly a two-root CI treatment is necessary. For this reason the important excited states of ClC₂H₄ are also investigated, at least to the extent that their influence on the ground-state surface can be evaluated. The results are contained in Figure 3. A more accurate description would probably be necessary if the main purpose were to obtain the proper spectroscopic data, i.e., reliable values for the transition energies and intensities, but within the present context the calculations undertaken most probably suffice.

A characterization of states is contained in Table IV. The first two excited states with the same dissociation limit as the ground state are ²B₂ and ²B₁. In the dissociation limit they correspond to the electronic configuration $\pi^2 p_x^2 p_y^2 p_z^2$ (B₁) and $\pi^2 p_x^2 p_y^2 p_z^2$ (B₂), respectively, whereby the ground state has the $\pi^2 p_x^2 p_y^2 p_z^2$ (A₁) occupation. The ²B₁ state possesses different symmetry not only for the symmetric C_{2v} chlorine-ethylene approach but also for all asymmetric (A'') pathways and is therefore not of interest in the present context, which is concerned with the influence of excited

TABLE IV: Characterization of the Low Excited States of ClC₂H₄ of Interest in the Present Context

state		excitation	fragments
C _{2v}	C _s		
X ² A ₁	X ² A'	... $\pi^2 p_x^2 p_y^2 p_z^2$ ground state	Cl + C ₂ H ₄
¹ 2B ₂	² 2A'	p _x (Cl) → p _x (Cl)	Cl + C ₂ H ₄
¹ 2B ₁	¹ 2A''	p _y (Cl) → p _y (Cl)	Cl + C ₂ H ₄
² 2A ₁	³ 2A'	π (C ₂ H ₄) → p _x (Cl)	Cl ⁻ + C ₂ H ₄ ⁺
² 2B ₂	⁴ 2A'	{ p _x (Cl) → π^* (C ₂ H ₄)	{ Cl ⁺ + C ₂ H ₄ ⁻
³ 2B ₂	ⁿ 2A'	{ π (C ₂ H ₄) → π^* (C ₂ H ₄)	{ Cl + C ₂ H ₄ [*]

states on the ground-state potential. The ²B₂ state has no direct influence on the X²A₁ ground state along the symmetric C_{2v} approach but possesses the same symmetry (²A') as the ground state for all C_s nuclear conformations and plays therefore a role in determining the ground-state hypersurface. This will be discussed in the next section. At smaller internuclear separations the ²B₂ state results from excitation out of the 2b₂(3a') valence orbital into the 5a₁(7a') valence orbital which is a combination of π and p_x in this range; the state is repulsive in the range of internuclear separations calculated (Figure 3).

The ²2A₁ state lies about 3.5 eV above the ground state; it can in principle interact with the ground state in both symmetries, the symmetric C_{2v} as well as the asymmetric C_s nuclear arrangement. The present calculations predict binding character for this state. The electronic configuration around its minimum is ...4a₁²5a₁²1b₁²2b₁²1b₂²2b₂²1a₂² and corresponds to an ionic structure Cl⁻C₂H₄⁺. At smaller Cl-C₂H₄ separations (approximately 4.8 au) the calculations find a crossing with another state of ²A₁ symmetry. Since the ²2A₁ state dissociates into the first excited channel Cl(²P) + C₂H₄^{*}(π, π^*) with three open shells, a crossing with a further state must take place beyond R_M = 7.0 au. Both crossings are not pertinent to the present study, and therefore further examination of this situation has not been undertaken. The calculations show a certain mixing between the ²2A₁ and the X²A₁ ground state in the range between R_M = 4.5 and 5.3 au. For larger separations the ionic character is found in the upper state while the ground state dissociates into the neutral fragments. The difference in the results obtained from the MRD-CI calculations in which selection is undertaken simultaneously for both states or only for the ground state (see also Table II) is quite small. This is an indication that most of the state mixing has already occurred on the MO level.

The higher ²B₂ state which arises from an excitation from the open-shell p_x chlorine orbital into the π^* ethylene orbital leads to the electron distribution Cl⁺ + C₂H₄⁻ and is thus less important. Another ²B₂ state arises from $\pi \rightarrow \pi^*$ excitation. This state is important in the lower C_s symmetry since there it possesses the same symmetry as the ground state and correlates with the first excited dissociation channel. In the molecule the orbitals p_x on chlorine and π mix (Figure 4) and hence the two ²B₂ states cannot be distinguished uniquely anymore. Further mixing with the ¹2B₂ state might occur at small values of R_M as has been found for the related Br-C₂H₄ compound¹⁵ and has also been discussed by Hoz et al.¹⁴ for ClC₂H₄. But again this interaction is not of interest for the $\theta_M = 0^\circ$ pathway since in this symmetry ²B₂ does not

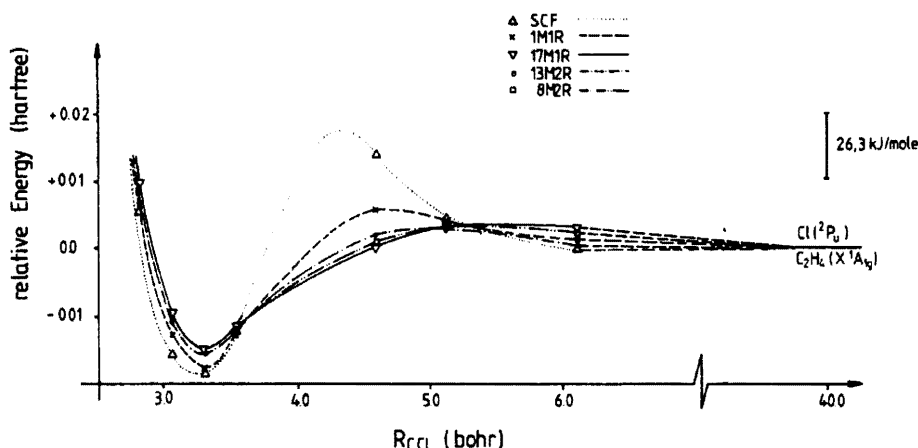


Figure 5. Section of the $\theta_M = 40^\circ$ pathway from the ClC_2H_4 equilibrium to the separated fragments $\text{Cl} + \text{C}_2\text{H}_4$ obtained by several treatments. The estimated full CI values are given.

TABLE V: Conversion Table between R_M and R_{CCl} in ClC_2H_4 (See Figure 1)^a

R_M , au	$R_{\text{CCl}}(\theta_M=0^\circ)$, au	$R_{\text{CCl}}(\theta_M=40^\circ)$, au
3.75	3.97 (2.60)	3.05 (2.80)
4.00	4.21 (2.60)	3.28 (2.80)
4.25	4.44 (2.60)	3.52 (2.80)
4.50	4.68 (2.60)	3.76 (2.80)
4.75	4.91 (2.53)	4.02 (2.70)
5.00	5.16 (2.53)	4.26 (2.70)
5.50	5.64 (2.53)	4.77 (2.60)
6.00	6.13 (2.53)	5.28 (2.53)
7.00	7.11 (2.53)	6.26 (2.53)

^aThe optimized values of R_{CCl} , which were used in the conversion calculation, are given in parentheses.

interact with the X^2A_1 ground state.

In summary the present MRD-CI calculations definitely show a minimum in the $\theta_M = 0^\circ$ pathway. The angle α_2 has been kept fixed at the same value as α_1 , i.e., 180° . An optimization of both parameters is expected to lower the binding energy by at most 1–2 kJ/mol (if at all), on the basis of the experience with the calculations on FC_2H_4 , in which the energy surface between $\alpha = 180^\circ$ and 170° is very flat (changes of the order of 1 kJ/mol) and shows a definite rise for α values on either side of these two points. Hence the best prediction for the minimum in the symmetric $\text{Cl}-\text{C}_2\text{H}_4$ approach is 14–16 kJ/mol according to the present behavior.

This prediction is in contrast to earlier work of Hoz et al.¹⁴ Their MO analysis is in principle quite similar to that given here. On the other hand, they find that all geometrical points for the symmetrically bridged structure lie above the $\text{C}_2\text{H}_4 + \text{Cl}$ dissociation energy limit in an MCSCF framework even though UHF calculations show a very shallow minimum of 3.8 kJ/mol at long $\text{Cl}-\text{C}_2\text{H}_4$ (7.8 au) separations. In light of the present analysis, which also finds an essentially repulsive curve in the SCF treatment (Table II), we believe that use of proper configuration interaction is essential for obtaining the correct results.

Pathway $\theta_M = 40^\circ$. The section of the potential energy with a fixed value of $\theta_M = 40^\circ$ contains the absolute minimum of the ClC_2H_4 system. Figure 5 shows the results of SCF and various CI calculations which have been undertaken to investigate whether there exists a barrier toward dissociation or not. The parameter R_M (see Figure 1), which is the best choice for describing the shuttling motion, is replaced in this consideration by R_{CCl} , which is the distance between the carbon atom and the chlorine atom and could be looked upon as reaction coordinate in this $\text{Cl}-\text{C}_2\text{H}_4$ separation. Table V is the conversion table from R_M to R_{CCl} for $\theta_M = 0^\circ$ and $\theta_M = 40^\circ$.

In contrast to the $\theta_M = 0^\circ$ section of the potential surface the binding in this asymmetric $\text{Cl}-\text{C}_2\text{H}_4$ is already obtained in the SCF calculation. It is seen, however, that in this theoretical

TABLE VI: Comparison of Orbital Energies (in hartree) for ClC_2H_4 and FC_2H_4 in Their Absolute Minima and the Dissociation Channel (Valence Electron Notation)

	ClC_2H_4	FC_2H_4	Cl	F	C_2H_4
1a''	-0.668	-0.692			-0.641 (1b _{2g})
4a'	-0.592	-0.652	-0.481 (p)	-0.75 (p)	
5a'	-0.532	-0.623			-0.574 (3a _g)
2a''	-0.546	-0.589	-0.481 (p _y)	-0.705 (p _y)	
6a'	-0.428	-0.527			-0.372 (π)
3a''	-0.422	-0.513			-0.505 (1b _{1g})
7a''	-0.372	-0.388	-0.564 (p)	-0.825 (p)	

^aNote that 7a' are the open-shell orbitals.

approach a large barrier toward dissociation appears. If the more appropriate CI techniques are employed, similar to what has been done for the $\theta_M = 0^\circ$ section, the immediate barrier following the minimum disappears but a small barrier of about 7–8 kJ/mol remains at larger (slightly above $R_{\text{CCl}} = 5$ bohrs) internuclear separation (Figure 5). Because this barrier is quite small, there is the question whether this finding is of chemical significance or whether it is an artifact of the theoretical treatment. In this connection one notes that the ab initio calculations of Schlegel et al.¹² using UHF and MP2 treatments in a 6-31G* AO basis also find a small barrier; on the other hand, these types of calculations find also a barrier in the $\text{F}-\text{C}_2\text{H}_4$ system which is removed entirely if extended CI is employed as shown in our previous work. In favor of a reality of the barrier is the observation that our calculations do not show a barrier in the $\theta_M = 0^\circ$ approach of chlorine to ethylene, although the quality is the same for the $\theta_M = 0^\circ$ and $\theta_M = 40^\circ$ approach. Furthermore, studies on unsaturated hydrocarbons in the gas phase indicate that the rate of addition of chlorine atoms to olefins is affected little by the nature of the hydrocarbon.²² The barrier of reaction is small (6 ± 2 kJ/mol) or zero for a wide variety of chlorinated olefins.

In order to clarify this question for ClC_2H_4 , additional calculations together with a more detailed analysis was undertaken. First, the MO analysis with respect to composition along the reaction coordinate is qualitatively the same as for $\text{F}-\text{C}_2\text{H}_4$ and has been discussed earlier in detail. The relative energies of the various orbitals given in Table VI differ in the same manner as discussed for the $\theta_M = 0^\circ$ approach (Figure 4). The barrier in the SCF calculation is caused by the interaction of the ground state X^2A_1 with the 3^2A_1 which corresponds to a $\pi \rightarrow \pi^*$ excitation and the 4^2A_1 which leads to the $\text{Cl}-\text{C}_2\text{H}_4^+$ ionic structure. In the

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flourine system a MRD-CI calculation based on a single-root selection (namely, the ground state) removed the SCF barrier entirely. In the chlorine counterpart an equivalent treatment removes the barrier at the SCF location but shows a 7–8 kJ/mol barrier about 1 bohr further to the dissociation limit.

Contrary to the C_{2v} symmetry, in this $\theta_M = 40^\circ$ section the $2^2A'$ state (which is 2^2B_2 for $\theta_M = 0^\circ$) can also interact with the X^2A' ground state. It retains its character (at least from about the minimum of X^2A' to the dissociation limit) so that coupling with the ground state is expected primarily at larger $\text{Cl}-\text{C}_2\text{H}_4$ separations due to the proximity in energy of the two states. If two states couple strongly, a two-root calculation is the adequate treatment from a theoretical point of view. Hence two further calculations were undertaken, one in which the simultaneous configuration selection was undertaken for X^2A' and $2^2A'$ (referred to as 13M2R in Figure 5) and the other for X^2A' and $4^2A'$ (referred to as 8M2R). Both calculations give results almost identical (variations up to 3 kJ/mol) with those of the MRD-CI calculation with 17 references configurations in which configuration selection was carried out only with respect to the X^2A' root (denoted 17M1R in Figure 5); only the SCF and the 1M1R treatment differ markedly from the others. From this computational experimentation and the fact that the $2^2A'$ can couple in this $\theta_M = 40^\circ$ geometry and not in $\theta_M = 0^\circ$ in which no barrier is found, it is concluded that it is very likely that the long-range barrier of 7–9 kJ/mol is real.

If one considers the minimum energy path for this process of $\text{Cl}-\text{C}_2\text{H}_4$ separation, it is *not* a direct dissociation from the ClC_2H_4 equilibrium to the separated fragments, as has been found for FC_2H_4 , but rather a shuttling motion to $\theta_M = 0^\circ$ and then dissociation taking place from this saddle point of the 1,2 migration with only the endothermicity as the barrier to dissociation. This is different from FC_2H_4 in which no barrier exists for $\theta_M = 40^\circ$. In order to obtain a more quantitative confirmation of this behavior, calculations of the dynamics of the system would have to be carried out which are not the subject of the present paper.

Rotation around the CC Bond

A motion competitive to the 1,2 migration is the rotation around the CC bond. The migration can easily take place for $\Phi = 0^\circ$ (see Figure 1) but is strongly hindered for $\Phi = 90^\circ$ since the H atom of the C_1 carbon prevents an approach of the chlorine atom. The calculated potential curve for the rotation around the CC axis is given in Figure 6. In this case the parameters of the absolute minimum in energy have been employed without accounting for further relaxation, and α_1 was fixed at 180° . In addition a somewhat smaller AO basis (without the d polarization function but the rest unaltered) has been employed in this calculation, which does not show any symmetry element in most parts of the rotational movement. Generally it is found²⁴ that a small AO basis without d polarization functions underestimate the calculated rotational barrier. On the other hand, the present basis is fairly large and the lack of d polarization functions is compensated to some extent by the use of bond functions so that the presently calculated barrier should be fairly realistic on theoretical grounds.

In contrast to the fluorine system (for which Φ is around 40° in MRD-CI calculations) the present calculations predict $\Phi = 0^\circ$ to be the absolute minimum and $\Phi = 90^\circ$ the maximum of rotation at every level of treatment. The predicted barrier height increases from 13 kJ/mol in the SCF calculation to 17–18 kJ/mol if correlation effects are taken into account. This value of 17–18 kJ/mol is in excellent agreement with the experimental results of Chen, Elson, and Kochi,¹⁰ who derived a value of approximately 17 kJ/mol on the basis of ESR measurements.

The present calculations agree qualitatively with those carried out by Hopkins et al.¹¹ and Hoz et al.,¹³ quantitatively the present

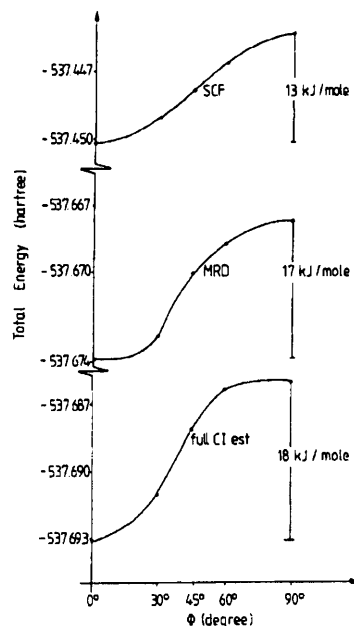


Figure 6. Calculated potential energy curves for rotation of the CH_2 groups around the C–C axis in ClC_2H_4 . Note that a smaller AO basis is employed in this case.

barrier is higher than in the earlier calculations. This is understandable since AO basis set differences affect the barrier heights; in particular a flexible description of the π system, normally by addition of d function, is necessary.

Possibility of the 1,2 Migration

The earlier studies of Hopkinson et al.¹¹ and of Hoz et al.^{13,14} have not found a definite stabilization of the symmetric ClC_2H_4 ($\theta_M = 0^\circ$) compound relative to the separated fragments $\text{Cl} + \text{C}_2\text{H}_4$. The UHF calculations of Hoz et al.¹⁴ find a shallow minimum at $R_{\text{CCl}} \sim 6.0\text{--}7.7$ au that disappears if the more reliable MCSCF method is employed. Hence they could not support an intramolecular migration process passing a saddle point for $\theta_M = 0^\circ$ which is indicated by experiments.²⁵ In order to overcome the differences between experiment and theory, Hoz et al.¹⁴ invoked a loose association between chlorine and ethylene for a transition state whereby it is argued that in solution cage effects will stabilize this type of complex further. In contrast to this general view our calculations predict a relative minimum in the $\theta_M = 0^\circ$ pathway toward dissociation so that 1,2 migration can occur.

Whereas in the fluorine system the 1,2 migration is possible but highly improbable because of the high activation barrier (115–130 kJ/mol), in the chlorine system the barrier is only 25–27 kJ/mol, making it an accessible pathway. The competitive process of rotation about the C–C axis has a lower barrier (17–18 kJ), however.

Summary

The global minima for ClC_2H_4 and FC_2H_4 are similar, exhibiting unsymmetrical structures, essentially those written in the classical manner; they differ mainly in the preferred angle of rotation about the C–C axis, the former with $\Phi = 0^\circ$ and a rotation barrier of 18 kJ/mol and the latter with around 40° and a rotation barrier between 11 and 17 kJ/mol, and the magnitude of the barriers to shuttling, 115–130 kJ/mol for fluorine and 25–27 kJ/mol for chlorine. The molecular orbital analysis shows that differences between the two compounds are only of a quantitative nature; from the electronic structure point of view the bond formation is the same in both compounds. The smaller stability of ClC_2H_4 (with respect to $\text{Cl}-\text{C}_2\text{H}_4$ separation) can be traced to the different stabilities of the fluorine–carbon and chlorine–

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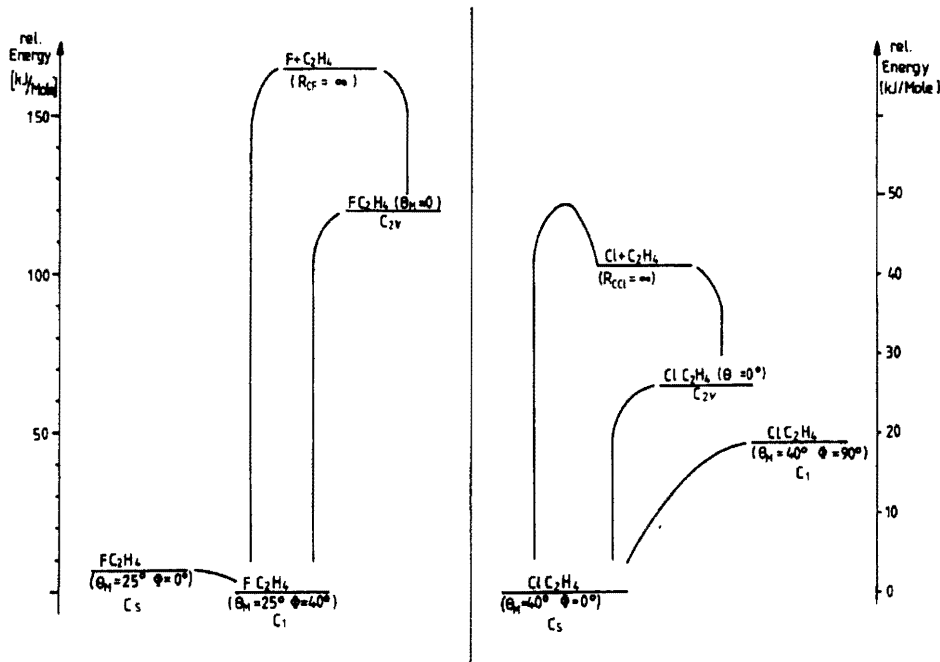


Figure 7. Summary of energies and activation energies in the possible pathways on the FC_2H_4 and ClC_2H_4 energy surfaces. The symmetry of the corresponding point groups is also indicated.

carbon bonds. The analysis of the charge distribution shows that the terminal carbon C_1 is considerably more negative than carbon C_2 , but both carbon atoms are less negative in the global minimum of ClC_2H_4 than in the separated C_2H_4 fragment. In other words, a definite charge transfer to the Cl center has taken place whereby the neighboring C_2 center is understandably most affected. In comparison to the FC_2H_4 compound it is found that the charge at the terminal carbon is almost the same (based on the 1s energies of -11.2465 in FC_2H_4 vs -11.2498 in ClC_2H_4) but that considerably more charge has been transferred from C_2 toward the F center (-11.3244 in FC_2H_4 vs -11.3051 in ClC_2H_4).

During rotation very little change in the total charge transfer is observed. The open-shell orbital, on the other hand, becomes localized solely on the terminal carbon as discussed for FC_2H_4 .

The symmetrical bridged structures are saddle points on the entire potential surface for both FC_2H_4 and ClC_2H_4 systems with a 1.38-\AA C-C bond length, whereby the stability relative to dissociation is larger in the FC_2H_4 compound. For this symmetrical structure a charge transfer occurs also from the carbons to the halogen center but is smaller than in the total minimum. Interestingly the transfer in the fluorine compound is not larger than in ClC_2H_4 . (The 1s orbital energies at the carbon centers are -11.251 in ClC_2H_4 and -11.244 in FC_2H_4 indicating a slightly more negative carbon surrounding in FC_2H_4). The large difference in energies relative to the unsymmetrical minima account for the divergent behaviors exhibited in these two systems, the symmetrical FC_2H_4 lying about 120 kJ/mol above the ground state and the ClC_2H_4 only around 26 kJ/mol , so that shuttling between the carbons is a readily accessible pathway for the latter, but not the former.

The energies and activation energies are summarized in Figure 7; they make it apparent that addition of Cl to C_2H_4 and the dissociation of ClC_2H_4 are two-step reactions proceeding through the symmetrical intermediate. The direct path to (or from) the unsymmetrical intermediates has a higher activation barrier. For the analogous fluorine case there is no basis for distinguishing between the direct and the two-step pathways since both have "zero" barriers.

The two steps in the minimal energy path for the $\text{Cl} + \text{C}_2\text{H}_4$ combination are, in principle, first the symmetric approach of the chlorine to ethylene along the attractive part of the potential surface to the local symmetric minimum (which is at the same

time the transition state for the 1,2 migration) followed by the pathway to the absolute asymmetric minimum, which is part of the shuttling motion. Details of the actual pathway taken by the system can only be obtained from dynamical calculations which are not the goal of the present work.

Aside from the understandable (vide supra) difference between calculated and experimental dissociation energies, the agreements between calculations and experiments are remarkable. The experimental barrier to rotation about the C-C axis of 17 kJ/mol for ClC_2H_4 , determined from changes of line broadenings with temperature, agrees with the calculated value of $17\text{--}18\text{ kJ/mol}$. There is no experimental value for the shuttling barrier in ClC_2H_4 , but the rate of 1,2 migration of $(\text{CH}_3)_2\text{CCl-CH}_2$ to $(\text{CH}_3)_2\text{C-CH}_2\text{Cl}$, 10^{10} s^{-1} , yields a 15 kJ/mol barrier (assume $\log A = 12.5\text{ s}^{-1}$) for this energetically more favorable rearrangement. In work that will be presented elsewhere, the rate of shuttling in the 3-chloro-2-butyl radical is 10^9 s^{-1} , corresponding to a shuttling barrier of 20 kJ/mol . Consequently the shuttling barrier of $25\text{--}27\text{ kJ/mol}$ for ClC_2H_4 can be considered to be in accord with experimental values.

The structure with C-Cl lying in the same plane as the half-occupied p orbital was initially proposed to explain stereochemical control and subsequently used to account for the ESR spectra. A further consequence of the analysis of the ESR spectra was the placement of the Cl at some intermediate position between $\theta_M = 38^\circ$ and 0° . Here there seems to be lack of accord, in that calculations indicate $\theta_M = 38^\circ$ (Figure 2) at the global minimum. On the other hand, the θ_M value of the global minimum does not correspond directly to the θ_M value for ClC_2H_4 in its lowest vibrational state. The broad and asymmetric characteristic of the potential well (Figure 2) indicates that the maximum in the vibrational wave function, i.e., the average position of the Cl, lies at θ_M values smaller than the calculated global minimum. Thus, there is no lapse of accord here either.

Finally, we must address the structural origin of the reaction properties brought together under the rubric "bridged". The broad, shallow well, opening toward the symmetric position shown by ClC_2H_4 at the global minimum, results in a $v = 0$ vibrational state which places the chloro closer to that of the C_{2v} condition, a state with shortened C-C bond, approaching that of a double bond with its very large barrier to rotation. Thus, the origin of bridging acquires this more concrete description, associating it with the

interaction which is set up when a chloro (bromo, iodo, etc.) and a half-filled orbital are in the same plane on adjacent atoms, resulting in a diminished shuttling barrier and the consequent relaxation in the direction of the C_{2v} configuration, with increase in the rotational barrier. Thus, all aspects that have been associated with the bridging phenomenon are readily understandable with this construct.

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Electron Paramagnetic Resonance Spectra and Structures of $\text{Cu}[\text{C}_2\text{H}_4]$, $\text{Cu}[\text{C}_2\text{H}_4]_2$, and $\text{Cu}[\text{C}_2\text{H}_4]_3$ in Hydrocarbon Matrices¹

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Two mononuclear π -complexes, $\text{Cu}[\text{C}_2\text{H}_4]$ and $\text{Cu}[\text{C}_2\text{H}_4]_2$, have been positively identified by EPR spectroscopy from reaction of Cu atoms and ethylene at 77 K in inert hydrocarbon matrices on a rotating cryostat. The spectra of these copper(0) complexes are consistent with dative bonding for both species and with a C_{2v} structure for $\text{Cu}[\text{C}_2\text{H}_4]$ and a D_{2h} structure for $\text{Cu}[\text{C}_2\text{H}_4]_2$. Spectra of $\text{Cu}[\text{C}_2\text{H}_4]_3$ are consistent with these assignments. A third complex is formed in both adamantane and cyclohexane that could be $\text{Cu}[\text{C}_2\text{H}_4]_2$ with a structure other than D_{2h} but is more likely to be the mononuclear trisligand complex $\text{Cu}[\text{C}_2\text{H}_4]_3$ with a D_{3h} structure. In the absence of a well-resolved isotropic spectrum of $\text{Cu}[\text{C}_2\text{H}_4]_3$, this assignment must however be taken as tentative.

Introduction

There have been several spectroscopic (EPR, IR, resonance Raman, and UV-visible) studies of the reaction of Cu atoms with ethylene under matrix-isolation conditions at cryogenic temperatures (≤ 77 K).³⁻⁷ Ozin and co-workers^{3,5} suggested that three mononuclear zero-valent copper complexes are formed with one, two, and three ethylene ligands, i.e., $\text{Cu}[\text{C}_2\text{H}_4]$, $\text{Cu}[\text{C}_2\text{H}_4]_2$, and $\text{Cu}[\text{C}_2\text{H}_4]_3$. Each complex displays intense visible charge-transfer and ultraviolet absorptions that red and blue shift, respectively, with increasing ethylene stoichiometry. IR bands have been assigned to the C=C stretching and CH_2 deformation and wagging modes of $\text{Cu}[\text{C}_2\text{H}_4]$ and $\text{Cu}[\text{C}_2\text{H}_4]_2$ while positive stoichiometric assignment of $\text{Cu}[\text{C}_2\text{H}_4]_3$ has proved difficult because of complications due to isotopic band overlap.

EPR studies of the $\text{Cu}/\text{C}_2\text{H}_4$ system in argon⁶ have identified two spectra, one with a large Cu hyperfine interaction (hfi) assigned to $\text{Cu}[\text{C}_2\text{H}_4]$ and one with a much smaller Cu hfi assigned to $\text{Cu}[\text{C}_2\text{H}_4]_2$. There was no evidence of an EPR spectrum in argon that could be assigned to $\text{Cu}[\text{C}_2\text{H}_4]_3$.

A recent resonance Raman and infrared study in pure ethylene and ethylene/argon mixtures⁷ confirmed the formation of the three copper/ethylene complexes and provided sound evidence for the formation of the dimer, $\text{Cu}_2[\text{C}_2\text{H}_4]_2$. The stability of these complexes was found to increase in the order $\text{Cu}[\text{C}_2\text{H}_4] < \text{Cu}[\text{C}_2\text{H}_4]_2 < \text{Cu}[\text{C}_2\text{H}_4]_3$.

We have performed an EPR study of the reaction of Cu atoms with C_2H_4 in inert hydrocarbon matrices on a rotating cryostat

at 77 K and report here tentative spectral evidence for the formation of $\text{Cu}[\text{C}_2\text{H}_4]_3$ as well as positive evidence for the mono- and diligand complexes.

Experimental Section

The rotating cryostat and instruments used to record and calibrate EPR spectra have been described previously.⁸

Copper oxide enriched to 99.89% in the isotope ^{63}Cu was obtained from Oak Ridge National Laboratory, TN. It was reduced to the metal by hydrogen at 500 °C. Ethylene (C_2H_4) was obtained from Matheson, and $^{13}\text{CH}_2\text{CH}_2$ (99 atom % ^{13}C) was obtained from MSD, Montreal. The inert hydrocarbon matrices used were adamantane and cyclohexane and were obtained from Aldrich. $\text{Cu}:\text{C}_2\text{H}_4:\text{matrix}$ ratios were typically 1:~40:500; i.e., there was an excess of reactant over metal atom. While the metal and matrix fluxes were generally kept constant, the C_2H_4 inlet pressure was varied by a factor of 10 but the exact amount of C_2H_4 deposited was not determined.

Values of a_{\parallel} and g_{\parallel} were obtained from directly measured transitions and are accurate to ± 2 MHz and ± 0.0006 , respectively, while a_{\perp} and g_{\perp} values were obtained by computer simulation and are probably accurate to about 5 MHz and 0.0015, respectively.

Results

Adamantane. ^{63}Cu atoms (25 mg) and C_2H_4 (0.07 Torr) in adamantane (1 g) gave a dark red deposit, the EPR spectrum of which at ~ 4 K consisted of an almost isotropic quartet 1 with $a_{63} = 3730$ MHz and $g = 1.9930$ and a more intense central feature 3 (Figure 1a) that was indicative of a species with $a_{\parallel} \gg a_{\perp}$. This central feature was not the same as the central feature given by $\text{Cu}/\text{C}_2\text{H}_4$ in Ar.⁶ A satisfactory simulation of this spectrum (Figure 1b) was obtained by using the magnetic parameters $a_{\perp} = 60$ MHz, $a_{\parallel} = 152.2$ MHz, $g_{\perp} = 2.0121$, $g_{\parallel} = 2.0021$, and $P_{\perp} = 10$ MHz, i.e., the carrier of the spectrum had

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