and 100 g of methanol was heated to reflux for 3 hr. Methanol (75 g) was removed by distillation and the cooled residue was added to water. The solution was extracted repeatedly with ether. The ether solution was dried with magnesium sulfate and distilled giving 8.1 g (68%) of allylcarbinol-*cis*-4-*d*, bp 112–114°.

The allylcarbinol was converted to the tosylate with *p*-toluenesulfonyl chloride in pyridine in the usual fashion. The nmr spectrum of the allylcarbinyl acetate indicated the deuterium to be located in the *cis* position, and showed the presence of 95 ± 3% of one deuterium.

Solvolysis of Allylcarbinyl-*cis*-4-*d* Tosylate. A solution containing 14 g of the tosylate, 200 ml of glacial acetic acid, and 5.5 g of dry sodium acetate was heated to reflux for 96 hr. The cooled solution was poured into ice water and extracted five times with pentane. The pentane solution was washed with sodium carbonate solution and dried over magnesium sulfate. After removal of the pentane, the residue was analyzed by vpc (30-ft DEGS column at 125°). There was found 80% allylcarbinyl acetate, 8% cyclobutyl acetate, and 12% cyclopropylcarbinyl acetate. The mixture was separated by preparative vpc. The 100-MHz spectrum of the allylcarbinyl acetate was identical with that of the acetate prepared in the synthetic sequence indicating no deuterium scrambling. The deuterium content of the cyclopropylcarbinyl acetate was determined by averaging the results of 60 integrations using an HA-100 spectrometer in the field sweep mode. The deuterium distribution was given earlier in the paper.

Organic Quantum Chemistry. XXIV. A Theoretical Study of the Stereochemistry of SE2 and SN2 Reactions[1,2]

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Abstract: The transition states which result when methane undergoes an SN2 or an SE2 reaction, when attacked by hydride ion or by a proton, respectively, have been studied by an SCF method, similar to the PNDO method of Pople. The energies of the transition states have been minimized with respect to all bond lengths and angles, and the results indicate that for the simple (gas phase) reactions, the SN2 reaction prefers an inversion to a retention mechanism by about 0.64 eV, while for the SE2 reaction, the inversion mechanism is preferred by only 0.23 eV.

The Walden inversion mechanism (SN2) has been known for a good many years, and it involves the attack of a Lewis base on a molecule to displace another Lewis base. More often than not, these bases are anions, although other charge types are possible. The transition states have the general structure $CR_1R_2R_3YZ^-$, where the R groups can be hydrogen, alkyl, or various other things, and where Y and Z are the attacking and leaving nucleophiles. Of the hundreds of examples of this reaction type which are known, no evidence has ever been forthcoming to show that any stereochemistry other than inversion occurs during the course of this reaction.[4,5] Certainly, inversion of configuration in the SN2 reactions is one of the most unqualified and absolutely dependable phenomena ever observed in the field of organic stereochemistry. Naturally, many chemists have been led to a consideration of the reasons behind the highly specific stereochemistry of this type of reaction.[6–8] Meer and Polanyi pointed out that the dipole field of a bond such as C–Cl would preferentially direct an anionic reagent like OH^- to the position leading to inversion of configuration. Thus they concluded that this electrostatic effect was sufficient to explain why inversion, rather than retention of configuration, was observed in reactions of this general type. That the situation is actually more complicated than they pictured was shown by the experiments of Read and Walker,[9] who showed that even when hydroxide ion is displacing a trimethylammonium group, and the dipole effects would presumably work in the opposite direction, inversion of configuration was still observed.

Hughes, Ingold, and coworkers[8] looked at these experiments qualitatively from a quantum mechanical point of view, and considered that the conditions which would "minimize the repulsive, exchange energy integrals" would lead to the transition state of lower energy. They considered that this was an effect arising from the exclusion principle; however, this conclusion seems to have been based mainly on intuition. Since one must consider the electronic repulsion integrals, not only between the entering and leaving groups, but between all of the electrons in the molecule, in addition to the nuclear repulsion and the attraction integrals, it is certainly not at all clear in a qualitative way why inversion of configuration is to be preferred. As far as the present authors are able to ascertain, no detailed theoretical study has ever indicated that the SN2 reaction should proceed by inversion of configuration, in spite of the fact that this is a simple fundamental reaction, and the experimental results are not affected by solvent, tem-

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[1] Paper XXIII: J. C. Tai and N. L. Allinger, *Theor. Chim. Acta*, **15**, 133 (1969).

[2] This research was supported by Grant No. GP 6763 from the National Science Foundation.

[3] All correspondence should be addressed to this author at the Department of Chemistry, University of Georgia, Athens, Georgia 30601.

[4] P. Walden, *Ber.*, **26**, 210 (1893); **28**, 1287, 2766 (1895); **29**, 133 (1896).

[5] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 308; G. W. Wheland, "Advanced Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1960, p 357.

[6] A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933); A. R. Olson and F. A. Long, *J. Amer. Chem. Soc.*, **56**, 1294 (1934); **58**, 393 (1936).

[7] N. Meer and M. Polanyi, *Z. Phys. Chem.*, **B19**, 164 (1932).

[8] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

[9] J. Read and J. Walker, *ibid.*, 308 (1934); *cf.* J. Read, "A Chapter in the Chemistry of Essential Oil," Institute of Chemistry, 1936, p 21.

perature, or catalyst variations, and are beyond question.[10]

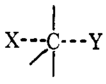
The experimental situation with regard to the SE2 reaction is less clear-cut. The kinds of experimental systems which have been studied most extensively involve mercury as the entering or leaving group, or both. The results with these compounds are that reaction is predominately with retention of configuration. However, it is not clear if one should consider these as typical SE2 reactions, or as reactions which may be peculiar to the element mercury.[11,12] When the entering or leaving groups are protons, and in other cases, it has been found that retention or inversion of configuration, or racemization, or any mixture of these is a possible stereochemical result,[13] depending on the experimental details.

It would seem that these reactions are deserving of some theoretical study, and a variety of approximate ways to solve the Schroedinger equation now exist which could be applied to the problem. One might hope to learn something concerning the geometries of the transition states in these reactions, and also to gain some idea of the magnitude of the energy difference between the transition states corresponding to retention or inversion of configuration in both the SN2 and SE2 cases.

There has recently been considerable effort devoted to the use of molecular mechanics as a method for understanding and predicting various structural features of molecules.[14] In principle these methods are also applicable to transition states, and hence to predictions of reaction rates. In practice, more details (bond lengths, angles, force constants) regarding transition states are needed before that work will show a high probability of being successful, and this paper is aimed at providing details on some simple transition states.

Initially, we carried out some calculations concerning this problem, making use of the then standard Pariser–Parr method.[15] Other work being carried out at the same time[16] led us to note that the two-center exchange-repulsion integrals, when the two centers are located on a common atom, can have very sizable values, and that the neglect of such integrals was probably not desirable, and might be the source of large error. Methods including such integrals had not been applied to other than π systems at that time, but subsequently Pople has shown[17] that such methods are generally applicable and they are now widely used for the study of σ systems. Our method would be considered a PNDO–SCF method in Pople's terminology, because it does include these large two-center exchange-repulsion integrals, when the two centers are on a common atom.

Beginning with the SN2 reaction, we considered two possible transition states, I and II, as shown. Clearly the first of these corresponds to what is observed experimentally, and the second is not (although the second type does correspond to that observed in SNi reaction, and is therefore not of prohibitively high energy). We wished to keep the calculations as simple as possible, and hence we considered the SN2 case where all of the groups attached to carbon were hydrogen; thus the system under consideration is a methane molecule being attacked by a hydride ion to displace a different hydride ion, and yield a different methane molecule. Similarly, the SE2 case involves protons instead of hydride ions. With regard to the transition states, we need to know all of the bond angles and bond lengths, and the total energy of the system in each case. For the case of inversion of configuration (transition state I), all of the bond angles are known at the outset, in that the structure is a trigonal bipyramid. Only the bond lengths need to be determined. For the reaction proceeding with retention of configuration, the situation is more complicated, and we must consider the hydrogens which are not involved directly in the reaction, and those which are. Those three hydrogens which are not directly involved, together with the carbon atom, form a pyramid, which needs an HCH angle in order to completely specify it. For the hydrogens which are involved in the reaction, it is necessary to know the HCH angle and the orientation of this pair of hydrogens with respect to the other three. In addition, it is necessary to know the two different types of C–H bond lengths.



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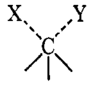

II

Details of the Calculations

Molecular orbital theory approximates the N-electron wave function for a molecule by an antisymmetrized product of doubly occupied molecular orbitals (one-electron functions), which are taken as linear combinations of atomic orbitals.

$$\psi_{\mathrm{i}} = \sum_{\mathrm{v}} \phi_{\mathrm{v}} C_{\mathrm{iv}}$$

where ϕ_{v} are valence state atomic orbitals (1s hydrogen; 2s, $2p_x$, $2p_y$, $2p_z$ for carbon). The subscripts u, v, λ, and σ will be used to denote atomic orbitals in the basis set. For molecules with a closed-shell configuration, variational treatment of the orbital coefficients C_{iv} leads to Roothaan's equations[18]

$$\sum_{\mathrm{v}} F_{\mathrm{uv}} \mathrm{C}_{\mathrm{iv}} = \sum_{\mathrm{v}} S_{\mathrm{uv}} C_{\mathrm{iv}} \epsilon_{\mathrm{i}}$$

where

$$F_{\mathrm{uv}} = H_{\mathrm{uv}} + G_{\mathrm{uv}}$$

$$H_{\mathrm{uv}} = \int \phi_{\mathrm{u}}[-{}^{1}/_{2}\nabla^{2} - \sum_{\mathrm{A}} V_{\mathrm{A}}(r)]\phi_{\mathrm{v}} \mathrm{d}r$$

$$G_{\mathrm{uv}} = \sum_{\lambda,\sigma} P_{\lambda\sigma}[(\mathrm{uv}/\lambda\sigma) - {}^{1}/_{2}(\mathrm{u}\sigma/\mathrm{v}\lambda)]$$

$$P_{\lambda\sigma} = 2\sum_{\mathrm{i}}^{\mathrm{occ}} C_{\mathrm{i}\lambda} C_{\mathrm{i}\sigma}$$

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(10) It has been remarked that a simple MO treatment suggests that an SN2 reaction should proceed with inversion (E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A Morrison, "Conformational Analysis," Interscience Division of John Wiley & Sons, Inc., New York, N. Y., 1965, p 484), and a similar treatment suggests the SE2 reaction should proceed with retention of configuration.

(11) C. K. Ingold, *Rec. Chem. Progr.*, 25, 145 (1964).

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(13) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; D. E. Applequist and G. N. Chmurny, *J. Amer. Chem. Soc.*, 89, 875 (1967).

(14) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, 91, 337 (1969), and references cited therein.

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(16) N. L. Allinger, T. W. Stuart, and J. C. Tai, *J. Amer. Chem. Soc.*, 90, 2809 (1968).

(17) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S 129 (1965); J. A. Pople and G. A. Segal, *ibid.*, 43, S 136 (1965); 44, 3289 (1966).

(18) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

and ϵ_i is the orbital energy for the molecular orbital ψ_i which gives a theoretical estimate of the corresponding ionization potential if the orbital is occupied, while the other symbols have the usual meanings.

The total electronic energy of the valence electrons is

$$E_{\text{electronic}} = {}^1/_2 \sum_{u,v} P_{uv}(H_{uv} + F_{uv})$$

The total energy of the molecule (relative to separated valence electrons and isolated cores) is obtained by adding to the electronic energy the repulsion energy between cores. The latter can be well approximated by a point-charge model so that

$$E_{\text{total}} = E_{\text{electronic}} + \sum_{A<B} Z_A Z_B / R_{AB'}$$

where Z_A is the core charge of atom A and R_{AB} is the A–B internuclear distance. According to Goeppert-Mayer and Sklar,[19] the term H_{uv} can be written as

$$H_{uv} = U_{uv} + \sum_{B}(u|V_B|v)$$

when u = v, U_{uv} is the energy of the electron in orbital u due to the core A. This is the familiar $-I_u$ term in the π-electron calculations, I_u being the valence state ionization potential. Pople and Segal[17] have used another approximation to the term U_{uv} which involves also the valence state electron affinity A_u. They gave the relation

$$-{}^1/_2(I_u + A_u) = U_{uu} + (Z_A - {}^1/_2)\gamma_{AA}$$

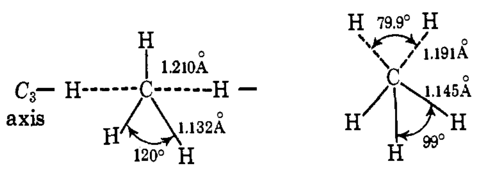
which we adopted in our present work. When u and v are different but on the same center A, U_{uv} becomes identical with zero.

Theoretical values of the repulsion integrals and the overlap integrals are calculated by formulas given by Roothaan.[18] The values of the average ionization potential ${}^1/_2(I_u + A_u)$ are calculated from spectral data by Pople and Segal.[17] The values of the average ionization potentials calculated for hydrogen and for carbon 2s and 2p, together with that of the core charge, the β-proportionality constants β^0's, and the exponent for the Slater type atomic orbitals used in the present work are summarized in Table I. Note that the self-consistent field orbital exponent of 1.2 is used for hydrogen.

Table I. Parameters Used in PNDO Calculations

Orbital	"Averaged" ionization potential, eV	Core charge	Slater exponent	β-proportionality constant
C, 2s	14.051	4	1.625	21
C, 2p	5.572	4	1.625	21
H, 1s	7.176	1	1.2	9

The PNDO approximation (a modified CNDO-2 method[16]) provides a method for greatly simplifying the above equations while still retaining the essential features of the treatment of the electron repulsion. The approximations used were as follows. (1) The ϕ_v are treated as if they form an orthonormal set; *i.e.*, the overlap integrals S_{uv} are put equal to zero unless u = v, in which case they are unity. (2) All two-electron integrals which depend on the overlapping charge densities of basis orbitals on different atoms are neglected. Thus $(uv/\lambda\sigma)$ is zero unless u,v belong to the same atom A and λ,σ are centered on a common atom B. (3) The term $(u|V_B|u)$ is set equal to zero when u and v are on different centers. When u and v are on the same atom A, this integral represents the nuclear attraction between the core B and an electron in the charge cloud A. If penetration integrals are neglected



SN2 inversion SN2 retention

Figure 1. The calculated transition states of the SN2 reaction. For the SN1 reaction, the gross transition state structures are similar to those for the SN2 reaction, but the numbers differ as discussed in the text.

$$(u|V_B|v) = Z_B(\delta_B\delta_B|u_A v_A)$$

where Z_B is the charge on core B, and δ_B is the p-type orbital of atom B. The neglect of penetration integrals in this type of calculation is desirable, as discussed by Pople and Segal.[17] (4) Off-diagonal core matrix elements between atomic orbitals on different atoms are estimated by the formula

$$H_{uv} = \beta_{uv} = \beta^0_{AB} S_{uv}$$

with $\beta^0_{AB} = {}^1/_2(\beta^0_A + \beta^0_B)$, where β^0_A and β^0_B are parameters which depend only on the nature of A and B, respectively, and are determined empirically.

Using the parameters specified in this way, the LCAO–SCF equations are solved in the following steps. (1) An initial set of molecular orbital coefficients C_{iu} is obtained from a Hückel-type calculation in which F_{uu} is replaced by the average ionization potential $-{}^1/_2(I_u + A_u)$ and F_{uv} by $\beta^0_{AB}S_{uv}$. (2) Electrons are assigned in pairs to the molecular orbitals with lowest energies (*i.e.*, lowest eigenvalues of F_{uv}). (3) The population matrix P_{uv} is calculated from the molecular orbital coefficients (C_{iu}'s) and is then used to form a new Hartree–Fock matrix F_{uv}. (4) New coefficients C_{iu} are derived from this F_{uv} and the process is repeated from step 2 until self-consistency is achieved on electronic energy with a tolerance of 0.0003 eV.

Pople has discussed in detail how one should take special care to ensure invariance in transformation, so that the properties of the system are independent of the coordinates chosen. Our present method satisfies this requirement.

Results and Conclusions

For each of the transition states in question, when the energy was minimized by varying all of the bond lengths and bond angles, the results obtained are as indicated in Figure 1.

For the SN2 reaction with retention of configuration, it was found that the minimum of energy was obtained when the bond angle between the hydrogens not involved in the reaction was 99°, corresponding to the hybridization of $sp^{6.39}$. The HCH angle involving the

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(19) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

Table II

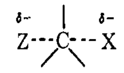
	Atomic coordinates (relative to carbon at origin) x	y	z	Bond lengths	Bond angles
				(A) For SN2-sp^2	
1	−0.98031	0.56600	0	$R_{CH_1} = R_{CH_2} = R_{CH_3} = 1.132$ Å	$H_1CH_4 = H_2CH_4 = H_3CH_4 = 90°$
2	0.0	−1.13200	0	$R_{CH_4} = R_{CH_5} = 1.210$ Å	$H_1CH_5 = H_2CH_5 = H_3CH_5 = 90°$
3	0.98031	0.56600	0		$H_2CH_3 = H_2CH_3 = H_3CH_1 = 120°$
4	0	0	1.21000		
5	0	0	−1.21000		
				(B) For SN2-sp$^{6.39}$ (retention)	
1	0.87066	0.50267	−0.54800	$R_{CH_1} = R_{CH_2} = R_{CH_3} = 1.145$ Å	$H_1CH_2 = H_2CH_3 = H_3CH_1 = 99°$
2	0	−1.00535	−0.54800	$R_{CH_4} = R_{CH_5} = 1.191$ Å	$H_1CH_4 = H_3CH_5 = 83° 46'$
3	−0.87066	0.50267	−0.54800		$H_2CH_4 = H_2CH_5 = 112° 30'$
4	0.78810	−0.10300	0.88700		$H_4CH_5 = 79° 51'$
5	−0.78810	−0.10300	0.88700		$H_1CZ = 118° 36'$
				(C) For SE2-sp^2 (inversion)	
1	−0.97165	0.56100	0	$R_{CH_1} = R_{CH_2} = R_{CH_3} = 1.122$ Å	$H_1CH_2 = H_2CH_3 = H_3CH_1 = 120°$
2	0	−1.12200	0	$R_{CH_4} = R_{CH_5} = 1.131$ Å	$H_1CH_4 = H_2CH_4 = H_3CH_4 = 90°$
3	0.97165	0.56100	0		$H_1CH_5 = H_2CH_5 = H_3CH_5 = 90°$
4	0	0	1.13100		
5	0	0	−1.13100		
				(D) For SE2-sp$^{4.46}$ (retention)	
1	0.87540	0.50541	−0.48000	$R_{CH_1} = R_{CH_2} = R_{CH_3} = 1.119$ Å	$H_1CH_2 = H_2CH_3 = H_3CH_1 = 102° 57'$
2	0	−1.01082	−0.48000	$R_{CH_4} = R_{CH_5} = 1.142$ Å	$H_2CH_4 = H_2CH_5 = 111° 4'$
3	−0.87540	0.50541	−0.48000		$H_4CH_5 = 74° 27'$
4	0.69091	0.02300	0.90900		$H_1CZ = 115° 24'$
5	−0.69091	0.02300	0.90900		$H_1CH_4 = H_3CH_5 = 81° 54'$

entering and leaving hydrogens was 79° 51′. The hydrogens not involved in the reaction had a bond length of 1.145 Å, while the entering and leaving hydrogens had bond lengths of 1.191 Å, respectively. The energy of this configuration was 0.646 eV (14.9 kcal/mol) above that of the minimum energy geometry for the inversion transition state. This result is certainly consistent with the fact that SN2 reactions are always associated with inversion of configuration at carbon. For the minimum energy geometry corresponding to inversion of configuration in the SN2 reaction, the entering and leaving hydrogens are calculated to have bond lengths of 1.210 Å, while those not involved in the reaction have bond lengths of 1.132 Å. It may be noted that all of these bond lengths are slightly greater than those calculated for methane itself by the same method (1.10 Å). In each case, the hydrogens coming and going have longer C–H bond lengths in the transition state than do those not directly involved in the reaction. These data are summarized in Table II.

Turning now to the SE2 reaction, the transition states are superficially analogous to those in Figure 1, and we see that again the transition state corresponding to inversion of configuration is of lower energy than that corresponding to retention, and that the difference is much smaller than it was in the SN2 case (5.3 kcal/mol *vs.* 14.9 kcal/mol). This would indicate that the SE2 reaction might be expected to go by inversion of configuration in simple cases (in the gas phase), but that since the energy difference is much smaller than in the SN2 case, exceptions to the general rule might well be much more commonplace. For the inversion of configuration, the geometry is not greatly different from that calculated for the SN2 case. The details are summarized in Table II. Here the hydrogens not involved in the reaction are calculated to have a bond length of 1.122 Å, while those which are coming and going have bond lengths of 1.131 Å. For the retention of configuration transition state, the bond lengths are all quite a bit smaller than they were in the SN2 case, but still larger than they were for methane itself, being 1.142 Å for the hydrogens which are coming and going, and 1.119 Å for those which are not reacting. The bond angles for the retention mechanism are also different from those which were calculated in the SN2 case, with the angle between the hydrogens not reacting being 102° 57′, and the angle between the entering and leaving hydrogens being 74° 27′. This corresponds to a hybridization of sp$^{4.46}$.

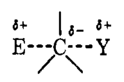
The next question to ask is whether or not we can develop a simple physical picture of these calculations.

From the population matrices (Table III), we can see that in each of these transition states the carbon atom is close to neutral. The bulk of the charge (negative in the SN reactions, and positive in the SE reactions) is on the hydrogens. Again, in each case, the hydrogens entering and leaving bear a greater charge (− or +) than do the remaining hydrogens. Thus the usual way of writing the SN2 transition state

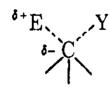


is the best simple way of expressing it.

For the SE2 transition states, the positive charge is more evenly distributed among the hydrogens than is the negative charge in the SN2 case, and there is some excess negative charge on carbon. These transition states are therefore less accurately represented by single pictures, but the best pictures are



and



The gross physical picture is simple enough. If there is excess charge, negative or positive, it tends to locate itself on the peripheral atoms (hydrogens). The quantitative details of the transition states are less easy to in-

Table III

	1s (H1)	1s (H2)	1s (H3)	1s (H4)	1s (H5)	2s	$2p_x$	$2p_y$	$2p_z$
Charge–Density and Bond-Order Matrix for SN2-sp^2 Inversion									
1s (H1)	1.07550	0.09217	0.09217	−0.21046	−0.21046	0.47142	−0.70701	0.40820	0
1s (H2)		1.07551	0.09217	−0.21048	−0.21048	0.47147	0	−0.81638	0
1s (H3)			1.07550	−0.21046	−0.21046	0.47142	0.70701	0.40820	0
1s (H4)				1.34087	0.30005	0.40215	0	0	0.70652
1s (H5)					1.34087	0.40215	0	0	−0.70652
2s						1.09924	0	0	0
$2p_x$							1.01667	0	0
$2p_y$								1.01667	0
$2p_z$									0.95918
Charge–Density and Bond-Order Matrix for SN2 Retention									
1s (H1)	1.19174	−0.01360	−0.25278	−0.26161	0.22017	0.46027	0.53399	0.41169	−0.34024
1s (H2)		0.97935	−0.01360	−0.01892	−0.01892	0.43518	0	−0.81162	−0.38778
1s (H3)			1.19174	0.22017	−0.26161	0.46027	−0.53399	0.41169	−0.34024
1s (H4)				1.28042	−0.30171	0.43434	0.46314	−0.03100	0.55583
1 (H5)					1.28042	0.43434	−0.46314	−0.03100	0.55583
2s						0.09710	0	0.00988	−0.00956
$2p_x$							0.97334	0	0
$2p_y$								1.01596	0.00495
$2p_z$									0.98992
Charge–Density and Bond-Order Matrix for SE2 Inversion									
1s(H1)	0.71593	−0.10863	−0.10862	0.16841	0.16841	0.43913	−0.69614	0.40192	0
1s (H2)		0.71592	−0.10863	0.16841	0.16841	0.43913	0	−0.80383	0
1s (H3)			0.71593	0.16841	0.16841	0.43913	0.69614	0.40192	0
1s (H4)				0.59638	−0.25512	0.44490	0	0	0.69927
1s (H5)					0.59638	0.44490	0	0	−0.69927
2s						1.16007	0	0	0
$2p_x$							1.17544	0	0
$2p_y$								1.17544	0
$2p_z$									1.14850
Charge–Density and Bond-Order Matrix for SE2 Retention									
1s (H1)	0.66980	0.01342	0.13249	0.21509	−0.20844	0.45546	0.55070	0.40047	−0.33532
1s (H2)		0.77310	0.01342	−0.00991	−0.00991	0.46685	0	−0.78969	−0.32619
1s (H3)			0.66980	−0.20844	0.21509	0.45546	−0.55070	0.40047	−0.33532
1s (H4)				0.61988	0.28603	0.41197	0.43409	0.01199	0.57061
1s (H5)					0.61988	0.41197	−0.43409	0.01199	0.57061
2s						1.15972	0	−0.01631	−0.04424
$2p_x$							1.12885	0	0
$2p_y$								1.23451	−0.00956
$2p_z$									1.12466
Charge–Density and Bond-Order Matrix for CH_4									
1s (H1)	0.87201	−0.01805	−0.01805	−0.01805		0.49164	−0.49697	0.49697	0.49697
1s (H2)		0.87201	−0.01805	−0.01805		0.49164	0.49697	−0.49697	0.49697
1s (H3)			0.87201	−0.01805		0.49697	0.49697	0.49697	−0.49697
1s (H4)				0.87201		0.49164	−0.49697	−0.49697	−0.49697
2s						1.18214	0	0	0
$2p_x$							1.10994	0	0
$2p_y$								1.10994	0
$2p_z$									1.10990

terpret. It is interesting to note that the exact geometries for the transition states are not strongly dependent on the number of electrons present (angles same, bond lengths different by only about 0.01 Å in the SN2 as compared to the SE2 case for inversion; angles same ± 5°, bond lengths to within 0.01 Å for retention).

While one would like to know something of the details of these reactions when chlorine or bromine are leaving groups, the additional approximations required would introduce further uncertainties, and these calculations involve too much labor to be feasible at this time. It is perhaps instead worthwhile to note that in the transition states the bond lengths of the entering and leaving atoms are only 10% (or less) longer than in the initial ground state. This is probably a reasonable approximation for molecular mechanics calculations for carbon–halogen bonds too.[20]

Appendix

All calculations were carried out on an IBM-7074 computer. The program was written to carry out the SCF calculations with an initial assumed geometry, and then to change in increments the various angles and lengths and repeat the calculation. The constraint placed on the system to keep the transition state from collapsing to product was that the bond lengths for the entering and leaving hydrogens be equal. The population matrices for the minimum energy transition states are given in Table III.

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(20) After this paper was submitted, a study by A. Gamba, G. Morosi, and M. Simonetta, *Chem. Phys. Lett.*, 3, 20 (1969), became available to us which described calculation of the energies of the CH_5^+ ion by the CNDO-2 method. These authors concluded that the geometry of C_s symmetry was more stable than that of D_{3h} symmetry by about 10 kcal/mol. The different conclusions reached by the two different calculational methods warrent further study.