An *Ab Initio* LCGO–MO–SCF Calculation of the Potential Energy Surface for an SN2 Reaction

Calvin D. Ritchie and George A. Chappell

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received October 23, 1969*

Abstract: An *ab initio* LCGO–MO–SCF study of the SN2 displacement of hydride ion by hydride ion on methane has been carried out. The portion of the potential energy surface for the CH_5^- system for which the approach of the hydride ion is toward the back side of the carbon, on line with the C–H bond to be broken, was explored. A single saddle point in this portion of the surface is found, corresponding to the CH_5^- system with D_{3h} symmetry, apical C–H distance of 3.30 au, and equatorial C–H distances of 2.01 au. The electron density on the carbon atom is found to decrease on going from methane to the saddle point.

The SN2 displacement reactions have been of considerable interest to both organic and inorganic chemists for a number of years. Stereochemical studies of these reactions have indicated a general back-side displacement process resulting in inversion of configuration about the atom on which the displacement occurs. It is generally assumed that the SN2 radio-exchange on saturated carbon compounds passes through a transition state with trigonal-bipyramidal geometry, but this assumption is open to question.[1]

In a continuation of our previous work on the *ab initio* calculations of potential energy surfaces,[2] we have now explored a portion of the surface for the reaction of hydride ion with methane in which the product results from an SN2 displacement.

Methods and Results

The program used for the calculations has been described.[2] The Gaussian basis set used for all of the present work is the small basis set previously reported.[3] It consists of four simple s-type functions, one "frozen core", and three of each p-type functions on carbon, and three s-type functions on each of the hydrogens.

The study was begun by locating the D_{3h} configuration of lowest energy. A minimum energy was found for this geometry having an apical C–H distance of 3.30 au and equatorial C–H distances of 2.01 au. Since this latter distance is only slightly less than that for methane, it was decided to carry out all further calculations with these "nonreacting" C–H distances constant at 2.06 au.

One calculation was carried out for a configuration with C_{3v} symmetry and with the incoming and outgoing hydrogens at equal distances from the carbon. The energy for this configuration is higher than that for D_{3h} symmetry.

Further calculations were restricted to configurations with C_{3v} symmetry. This restriction, along with the constancy of the "nonreacting" C–H distances, still leaves us with a surface on which the energy is a function of three variables: the angles between the "nonreacting" C–H bonds, the distance of the entering hydrogen from carbon, and the distance of the leaving hydrogen from carbon.

Calculations were carried out for three angles, spaced 1° apart, for each chosen pair of C–H distances. The minimum energy with respect to angle variation was then obtained by fitting the three points to a harmonic equation. In most cases, we were able to bracket the optimum angle in the three guesses, and the values obtained by the interpolation are highly reliable. In a few cases, however, our guesses were fairly far from the extrapolated optimum values. In these cases, notably points 5, 12, and 13 in Table I, the values for optimum angle and minimum energy may be in error by several degrees and perhaps 0.002 au, respectively.

The data obtained are reported in Table I, and a contour diagram of the surface constructed from these points is shown in Figure 1. A "reaction coordinate" diagram, obtained by interpolation of the points on the surface, and corresponding to the dashed line in Figure 1, is shown in Figure 2. The distance along the reaction coordinate in Figure 2 is defined as the perpendicular distance of the point from the 1,1 axis of Figure 1 (*i.e.*, $D_{RC} = 2^{-1/2}[D(CH_1) - D(CH_2)]$). The energy difference between separated methane plus hydride and the saddle point is 0.078 au = 48.7 kcal/mol.[4]

Gaussian and harmonic equation fits to the reaction coordinate are shown in Figure 2. It is interesting that the Gaussian function gives a far better fit than does the harmonic equation.

Mulliken population analyses of the wave functions for several configurations on, or near, the reaction coordinate are reported in Table II.

The reliability of calculations of the present type for constructing potential energy surfaces has been discussed thoroughly in earlier papers.[2]

Discussion

Only a small portion of the total potential energy surface for the CH_5^- system has been explored in this work. It seems pertinent to inquire, then, if we have explored the important regions for an SN2 process. Several lines of argument indicate that we have.

As Pearson and Burwell have pointed out,[1] there is no *a priori* reason to assume that the reaction path for an SN2 process passes through a structure with D_{3h}

---

(1) R. G. Pearson and R. L. Burwell, *J. Phys. Chem.*, **70**, 300 (1966).

(2) C. D. Ritchie and H. F. King, *J. Amer. Chem. Soc.*, **90**, 825, 833, 838 (1968).

(3) C. D. Ritchie and H. F. King, *J. Chem. Phys.*, **47**, 564 (1967).

(4) In our earlier papers, we referred to this quantity loosely as the activation energy. This careless usage has been properly criticized: M. Menzinger and R. Wolfgang, *Angew. Chem. Intern. Ed. Engl.*, **8**, 438 (1969).

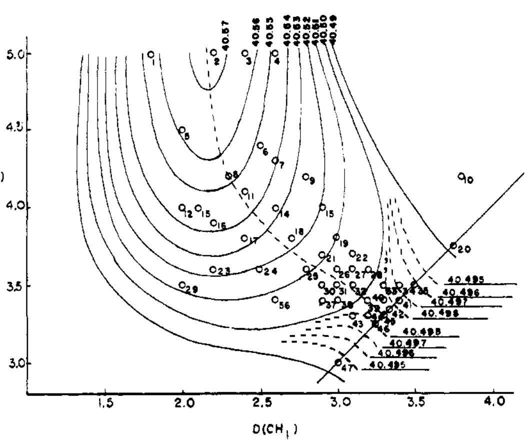


Figure 1. Potential energy surface contour diagram constructed from data in Table I.

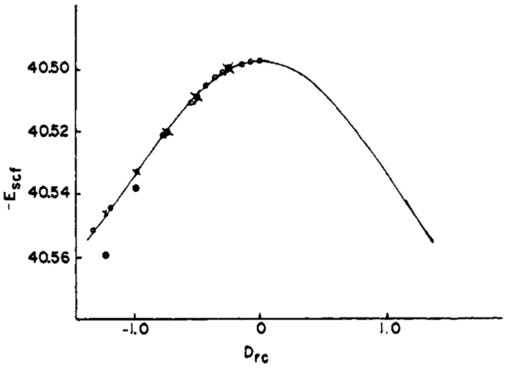
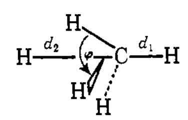


Figure 2. Reaction coordinate diagram: open circles, experimental points from Table I; filled circles, calculated from the equation, $E + 40.498 = -0.040D^2$; crosses, calculated from the equation, $E + 40.576 = 0.078 \exp(-0.26D^2)$.

Table I. Potential Energy Surface Points for S_N2 Reaction of Hydride with Methane[a]



Point no.	d_1, au	d_2, au	φ, deg	$-E$, au
1	1.80	5.00	109.5	40.5554
2	2.20	5.00	109.5	40.5713
3	2.40	5.00	109.5	40.5625
4	2.60	5.00	109.5	40.5494
5	2.00	4.50	106.1[b]	40.5630
6	2.50	4.40	110.8[b]	40.5476
7	2.60	4.30	111.8[b]	40.5399
8	2.30	4.20	109.7[b]	40.5514
9	2.80	4.20	113.1[b]	40.5264
10	3.80	4.20	115.0	40.4754
11	2.40	4.10	110.7[b]	40.5444
12	2.00	4.00	108.3[b]	40.5444
13	2.10	4.00	108.0[b]	40.5471
14	2.60	4.00	112.4[b]	40.5321
15	2.90	4.00	115.1[b]	40.5176
16	2.20	3.90	110.7[b]	40.5417
17	2.40	3.80	111.8[b]	40.5325
18	2.70	3.80	114.4[b]	40.5213
19	3.00	3.80	116.8[b]	40.5095
20	3.75	3.75	120.0	40.4895
21	2.90	3.70	116.6[b]	40.5109
22	3.10	3.70	118.0[b]	40.5046
23	2.20	3.60	110.1[b]	40.5248
24	2.50	3.60	113.9[b]	40.5198
25	2.80	3.60	116.4[b]	40.5110
26	3.00	3.60	117.8[b]	40.5056
27	3.10	3.60	118.5[b]	40.5031
28	3.20	3.60	119.5[b]	40.5009
29	2.00	3.50	110.3[b]	40.5125
30	2.90	3.50	117.7[b]	40.5054
31	3.00	3.50	118.4[b]	40.5033
32	3.10	3.50	119.3[b]	40.5015
33	3.30	3.50	119.5[b]	40.4982
34	3.40	3.50	119.5	40.4968
35	3.50	3.50	120.0	40.4964
36	2.60	3.40	116.1[b]	40.5072
37	2.90	3.40	118.4[b]	40.5024
38	3.00	3.40	119.2[b]	40.5011
39	3.20	3.40	119.5[b]	40.4990
40	3.30	3.40	120.0	40.4981
41	3.40	3.40	120.0	40.4978
42	3.34	3.34	120.0	40.4981
43	3.10	3.30	119.5[b]	40.4979
44	3.20	3.30	120.0	40.4978
45	3.30	3.30	120.0	40.4982
46	3.25	3.25	120.0	40.4980
47	3.00	3.00	120.0	40.4920
42b[c]	3.34	3.34	119.0	40.4958
46 (1.94)[d]	3.25	3.25	120.0	40.4968
46 (2.00)[d]	3.25	3.25	120.0	40.4997
46 (2.12)[d]	3.25	3.25	120.0	40.4922
46 (2.18)[d]	3.25	3.25	120.0	40.4839
∞[e]	2.12	∞	109.5	40.576

[a] Unless specified otherwise, the three identical nonreacting carbon–hydrogen bonds have a distance of 2.06 au. [b] Optimum angle obtained from interpolation or extrapolation as described in text. [c] This point establishes that the D_{3h} geometry of the transition state is stable toward the motion into C_{3v} symmetry. [d] In these calculations, the nonreacting carbon–hydrogen bond distances are varied. The distances are given in the parentheses. [e] This value, for separate methane and hydride systems, was reported in an earlier study, ref 2.

symmetry. It is quite possible that such a path is not the one of lowest energy. The possibility of paths involving structures of very low symmetry cannot be ruled out by the present work. We believe, however, that paths involving a C_{4v} configuration, or a path passing through a configuration with C_{3v} symmetry and equal distances between carbon and both leaving and entering group, can be ruled out.

The latter statement is based on a comparison of the energies calculated for points 42 and 42b of Table I. The movement of the three equatorial hydrogens away from their positions in the configuration with D_{3h} symmetry raises the energy considerably.

Our belief that a path involving C_{4v} symmetry can be ruled out is based on the arguments recently presented by Pearson.[5] It was argued there that two factors are of prime importance in determining the relative stabilities of D_{3h} and C_{4v} configurations for XY_5 molecules. These two factors are the symmetry species of the highest occupied and lowest unoccupied molecular orbitals, and the difference in orbital energies for these same orbitals.

Our calculations give the MO order: $(1A_1')^2(1E')^4(1A_2'')^2(2A_1')^2(2A_2'')^0$ for the valence shell of the CH_5^- species with D_{3h} symmetry (*i.e.*, point no. 45). The highest occupied orbital has an orbital energy of −0.023 au, and the lowest unoccupied orbital has an energy of +0.425 au. The direct product of A_1' and A_2'' does not contain E', the symmetry species of the vibration carrying D_{3h} into C_{4v} configuration. It is informative to note that the A_2'' transition symmetry is consistent

(5) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

Table II. Mulliken Population Analyses

Point no.	Center population: C	H_E[a]	H_L[b]	H_{NR}[c]	Bond orders: CH_L[b]	CH_E[a]	CH_{NR}[c]	d_1[d]	d_2[e]
∞	6.54	2.00	0.869	0.869	0.387	0.00	0.387	2.06	∞
14	6.36	1.904	1.187	0.853	0.254	−0.05	0.411	2.60	4.00
21	6.27	1.818	1.359	0.852	0.184	−0.006	0.417	2.90	3.70
26	6.24	1.773	1.422	0.851	0.161	0.008	0.418	3.00	3.60
32	6.23	1.730	1.484	0.851	0.137	0.035	0.419	3.10	3.50
39	6.22	1.691	1.532	0.852	0.115	0.055	0.420	3.20	3.40
45	6.22	1.613	1.613	0.852	0.086	0.086	0.420	3.30	3.30

[a] H_E is the entering hydrogen, *i.e.*, the hydrogen farthest from the carbon. [b] H_L is the leaving hydrogen, *i.e.*, the hydrogen along the H_E–C bond extension. [c] H_{NR} refers to the nonreacting hydrogens. [d] The distance between C and H_L is d_1. [e] The distance between C and H_E is d_2.

with the symmetry of the vibration carrying CH_5^- into $CH_4 + H^-$.

Assuming that we have explored the path corresponding to an SN2 reaction, it is interesting to note the population analyses in Table II. The interesting feature is that the electron densities on both carbon and the nonreacting hydrogens decrease on going from methane to the saddle point. This rather surprising result appears to be consistent with the experimental observation that electron donating substituents on carbon increase the rates of SN2 reactions.[6]

Quite recently, Berthier[7] has reported *ab initio* LCGO-MO-SCF calculations pertaining to the SN2 reaction of F^- with CH_3F. Only the two regions corresponding to reactants and D_{3h} species were examined closely. In agreement with the present study, it was found that the electron densities on carbon and on the hydrogens decrease on going from reactants to "transition state." The density on carbon decreased by 0.123 unit, and the densities on each of the hydrogens decreased by 0.008 unit. In the present study, the corresponding decreases are 0.32 and 0.017 unit, respectively.

In contrast to the present results, Berthier finds the $CH_3F_2^-$ transition state to be 8.8 kcal/mol more stable than the separated reactants. It should be recalled that the same situation was encountered in our earlier work[2] on the reactions of H^- and F^- with hydrogen molecules. The H^- reaction showed a transition state less stable than separated reactants, while the F^- reaction gave the opposite result. We are still unable to understand the origin of these unusual results, but note that positive "excitation energies" have been found for ion–molecule reactions only in the cases where hydride ion is both the entering and leaving group.

Acknowledgments. We are grateful to the Computer Center, State University of New York at Buffalo, for the donation of massive amounts of computer time.

(6) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 3 ff; C. K. Ingold, *Quart. Rev.* (London), **11**, 1 (1957).

(7) G. Berthier, D. J. David, and A. Viellard, *Theor. Chim. Acta*, **14**, 329 (1969).

A Semiempirical Description of the Diamagnetic Susceptibilities of Aromatic Molecules

Patricia S. O'Sullivan[1] and H. F. Hameka

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania. *Received September 10, 1969*

Abstract: A semiempirical description of the diamagnetic susceptibilities of conjugated organic molecules has been derived. The susceptibility is represented as a sum of three terms, namely the contributions from the σ electrons and from the π electrons and the contribution from σ–π interactions. The π-electron contribution is derived from London's theory and the other terms are expressed in terms of atomic susceptibilities, bond susceptibilities, and bond–bond interactions. As an example the polyacenes are discussed, where satisfactory agreement with experiment is obtained.

In previous work[2] the authors have put forward a semiempirical theory of the diamagnetic susceptibilities of saturated organic molecules. The present paper extends this theory to conjugated molecules.

It should be noted that in deriving the theory for saturated molecules we made a few assumptions which are not valid in the case of conjugated systems and it is therefore necessary to reconsider the theoretical derivation. The first assumption was that the molecular eigenfunctions of the ground and excited states may be approximated as single-determinant LCAO–MO functions. The second assumption was that the

(1) Supported by the National Science Foundation Undergraduate Participation Program.

(2) (a) H. F. Hameka, *J. Chem. Phys.*, **34**, 1996 (1961); (b) P. S. O'Sullivan and H. F. Hameka, *J. Amer. Chem. Soc.*, **92**, 25 (1970).