Potential Energy Surface for Hydrogen Abstraction and Exchange in the H + CH_4 System

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Abstract: Extensive *ab initio* SCF and SCF–CI calculations with minimal and double-ζ (DZ) Slater basis sets have been carried out to determine the potential energy surface, the transition state geometry, and energy for several models of the hydrogen abstraction and exchange reactions in the H + CH_4 system. The DZ SCF–CI values of the potential energy barrier height are 17 kcal/mol for the axial abstraction model, 42 kcal/mol for the inversion exchange model, and 64 kcal/mol for the noninversion exchange model. The results suggest that at lower energy the axial abstraction mechanisms and the inversion exchange mechanism would be most important. At a higher energy the noninversion exchange mechanism as well as others could become important. The surfaces calculated are also compared with the existing empirical potential surfaces.

A large number of experimental studies are available on the chemical reaction between methane and the hydrogen atom.[2–4] This system is unique in that experiments have been done in the thermal energy region as well as with a hot tritium atom created by photochemistry or the nuclear recoil method.

The two main reaction processes are abstraction

$$H' + CH_4 \longrightarrow H'H + CH_3 \qquad (1)$$

and substitution (or exchange)

$$H' + CH_4 \longrightarrow H + CH_3H' \qquad (2)$$

In the thermal region only reaction 1 takes place. The rate constants of both the forward and reverse reactions have been measured with a variety of techniques. The activation energy for the forward process was found to lie in the range of 10–12 kcal/mol[2b,3] with a small exothermicity of $\Delta H = -0.3$ kcal/mol.[2b] Studies with various isotopic species have also been made.

At high energy both reactions 1 and 2 take place. The threshold energy—the minimum relative translational energy of the reactants required for the reaction to be observed—for reaction 2 is found to be about 35 kcal/mol.[4] The abstraction/substitution ratio of the reactive cross sections for T + CH_4 with a relative translational energy near 65 kcal/mol has been measured to be about 4.

The mechanisms and stereochemistry of the hot atom reactions, 1 and 2, have been discussed by Wolfgang,[5] who compared the axial and stripping modes of abstraction and the noninversion and inversion modes of substitution from the point of view of the high translational energy of the T atom. Experimentally, the stereochemistry around the carbon atom appears to be retained in the substitution reaction for methane asymmetrically substituted with heavy atoms or groups.[2a] The implications of this to the unsubstituted methane are not conclusive.

Classical trajectory studies on the reactions have been published. In an early work a three-atom model was used with an atom having a mass 15 to simulate a rigid CH_3 group.[6] Bunker and Pattengill carried out full six-atom trajectory calculations.[7] They used several artificial potential energy surfaces constructed from Morse curves, harmonic potentials, and attenuation factors. The parameters were taken from experiments or adjusted arbitrarily. Their findings are that the experimental abstraction/substitution ratio near 65 kcal/mol cannot be reproduced with their potential surfaces and that Walden inversion may be important in the substitution processes. For a better understanding of the mechanism and kinetics of the reactions, a better knowledge of the potential energy surface appears essential.

The molecular orbital (MO) studies on the potential energy surface for the CH_5 system have been quite limited. Kaufman and Harkins[8] used an extended Hückel method for a limited number of geometries of the axial abstraction model. When the present work was near completion, it became known that Weston and Ehrenson[9] used a modified CNDO method for several models of abstraction and substitution. The CNDO result predicts that CH_5 has several stable configurations which are more stable than the isolated reactants H + CH_4. Consequently, reactions are to take place through intermediates with a small or no potential barrier in between. Such predictions can be ascribed to the inappropriate parametrizations, but some qualitative information obtained in the modified CNDO calculation is still useful.[9] In contrast to the CH_5^+ system,[10] there was no prior *ab initio* calculation for the CH_5 system. More reliable *ab initio* calculations on the system were urgently needed.

The goal of our project is twofold. First, in the present paper, we plan to use the *ab initio* SCF–MO method with and without configuration interaction (CI) to calculate the potential energy surface. For a 6-atom system that has 12 internal degrees of freedom, a complete potential surface calculation is prohibitive. But

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[1] Alfred P. Sloan Research Fellow, 1970–1972.

[2] (a) R. Wolfgang, *Progr. React. Kinet.*, 3, 97 (1965); (b) R. W. Walker, *J. Chem. Soc. A*, 2391 (1968).

[3] M. J. Kurylo and R. B. Timmons, *J. Chem. Phys.*, **50**, 5133 (1969).

[4] C. C. Chou and F. S. Rowland, *ibid.*, 50, 2763, 5133 (1969).

[5] R. Wolfgang, *Accounts Chem. Res.*, **2**, 248 (1969); **3**, 48 (1970).

[6] P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, and W. H. Wong, *J. Chem. Phys.*, **52**, 4654 (1970).

[7] (a) D. L. Bunker and M. D. Pattengill, *Chem. Phys. Lett.*, 4, 315 (1969); *J. Chem. Phys.*, 53, 3041 (1970); (b) M. D. Pattengill, Ph.D. Thesis, University of California, Irvine, Calif., 1969.

[8] J. J. Kaufman, J. J. Harkins, and W. S. Koski, *Int. J. Quantum Chem., Suppl.*, 1, 261 (1967).

[9] R. E. Weston, Jr., and S. Ehrenson, *Chem. Phys. Lett.*, **9**, 351 (1971).

[10] J. L. Gales, *ibid.*, 3, 577 (1969); 4, 408 (1969); W. Th. A. M. van der Lugt and P. Ros, *ibid.*, 4, 389 (1969); J. J. G. Mulder and J. S. Wright, *ibid.*, 5, 445 (1970).

Table I. Exponents Used in the Calculation

Orbital	MZ	DZ
H 1s	1.168	0.97, 1.227
C 1s	5.688	5.2309, 7.96897
C 2s	1.760	1.16782, 1.82031
C 2p	1.760	1.25572, 2.72625

Table II. The Energy (au) and Geometry of Isolated Molecules

	MZ basis set		DZ basis set	
	SCF	SCF–CI	SCF	SCF–CI
H	−0.48589	−0.48589 (1)[a]	−0.49999	−0.49999 (1)
H_2	−1.12773		−1.12833	−1.14319 (4)
(HH 0.742[b])	(HH 0.746[c])		(HH 0.736)	(HH 0.760)
CH_3	−39.46401		−39.54443	−39.59895 (167)
(CH 1.079)	(CH 1.083)		(CH 1.077)	(CH 1.100)
CH_4	−40.12817	−40.20008 (33)	−40.18347	−40.24552 (121)
(CH 1.094)		(CH 1.090) a	(CH 1.089)	(CH 1.089) a
$H_2 + CH_3$	−40.59174		−40.67277	−40.74214
$H + CH_4$	−40.61406	−40.68597	−40.68345	−40.74555
ΔE,[d] au	+0.02232		+0.01069	+0.00336
ΔE, kcal/mol	+14.01		+6.71	+2.11

[a] The number in parentheses is the number of spin eigenfunctions belonging to the irreducible representation of the ground state which were included in the CI calculation. For MZ, all the singly and doubly excited configurations are included. For DZ, see text. [b] The experimental bond distance r_0 (for H_2, r_e) in ångströms: G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950; "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966. [c] The bond distance in ångströms optimized with the specific calculation method. The symbol a was used when the distance was assumed. [d] The calculated energy difference between $H_2 + CH_3$ and $H + CH_4$.

we will examine various models of axial and stripping abstraction and of inversion and noninversion substitution. In the future we would like to construct an analytical potential energy surface based upon these *ab initio* calculations and carry out classical trajectory calculations on the surface to compare with experiments.

Method

Ab initio SCF–MO methods were used throughout the paper with Slater-type orbitals (STO) as the basis functions. Two basis sets are used, the minimal (called MZ) STO set with orbital exponents optimized for CH_4,[11] and a double-ζ (DZ) STO set, with the exponents for carbon taken from Clementi[12] and those for hydrogen chosen arbitrarily. The exponents used are summarized in Table I. These exponents are used without reoptimization for all the calculations including isolated species such as H, H_2, CH_3, and CH_4. No p-type polarization on hydrogen or d-type polarization on carbon was included. This is probably better justified for a neutral system like CH_5 than for an ionic system.

The STO integral and SCF calculations were carried out with the POLYCAL program,[13] which uses Nesbet's approximate SCF method[14] for an open-shell molecule. A value of $\lambda = -0.5$ for the coupling parameter between the Hartree–Fock operator and the open-shell density was used throughout.[15]

The SCF calculation is expected to correctly predict the geometry of transition states and intermediates, if any, but the energy of the barrier (the activation energy in a crude sense) will be sensitive to the correlation energy. To evaluate a more reliable barrier height, CI calculations were carried out by the POLYCI program.[16] The SCF–MO's are used to construct excited configurations. In the DZ calculation the vacant MO's are divided into two classes, the lower four vacant valence MO's and the higher extra MO's resulting from the extended basis functions. Excluding any excitation from the lowest MO, we included all the singly excited configurations and the doubly excited configurations that do not involve excitation of more than one electron into the extra set of vacant MO's. The only doubly excited configurations excluded are those in which two electrons are excited into these extra vacant orbitals. The energies of such configurations are extremely high and the matrix elements connecting them with the ground configuration are usually very small.

Isolated Molecules. H, H_2, CH_3, and CH_4

The calculated results for the isolated molecules are summarized in Table II. For CH_3 and CH_4, D_{3h} and T_d symmetry, respectively, were assumed, and the C–H distance was optimized for each method of calculation. For H_2 the H–H distance was optimized. All the calculations indicate that the MZ–SCF method predicts the geometry of isolated molecules quite accurately. Though we expect the optimal bond distances for MZ–SCF–CI, DZ–SCF, and DZ–SCF–CI calculations to differ from those obtained in the MZ–SCF method, the

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(11) R. M. Stevens, private communication.

(12) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

(13) R. M. Stevens, *ibid.*, **52**, 1397 (1970).

(14) R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).

(15) The method is an approximate restricted Hartree–Fock method utilizing an average between the matrix element for an α electron and that for a β electron. In the closed-shell molecule, this method reduces itself to the exact Hartree–Fock method. In a free radical, the exchange contribution to the Hartree–Fock matrix F_{rs} for the symmetry orbital (SO) pair (r, s), both belonging to symmetry A, from the electron density on the SO pair (t, u), both belonging to symmetry B, is given by $+(\lambda_B{}^C p_{tu}{}^C + \lambda_B{}^O p_{tu}{}^O)(rt|su)$, where $p_{tu}{}^C$ and $p_{tu}{}^O$ are the closed-shell (doubly occupied) part and the open-shell (incompletely occupied) part of the electron density. Without approximation, $\lambda_B{}^C = -0.5$. If symmetry A does not include any closed-shell MO, $\lambda_B{}^O = -1$ without approximation. If A does not include any open-shell MO, $\lambda_B{}^O = -0.5$ without approximation. When symmetry A includes both closed- and open-shell MO's, the method is an approximation and $\lambda_B{}^O$ is to be optimized to give the lowest total energy. We chose $\lambda_B{}^O = -0.5$ without optimization. It is because for a molecule with many electrons the error in the energy by using this approximate method without λ optimization is small (within a few kilocalories per mole in CH_5), because the CI would reduce the error further and because the choice enabled us to compare directly the calculations for various channels with different symmetry.

(16) K. Morokuma and H. Konishi, *J. Chem. Phys.*, **55**, 402 (1971).

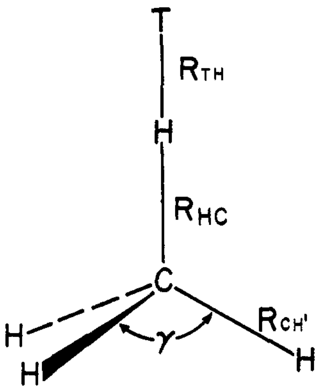

Figure 1. Axial abstraction model. C_{3v} symmetry is assumed.

error in the energy incurred by using the MZ–SCF bond distances rather than optimized distances is found to be within a few kilocalories per mole. Therefore, in the calculation of potential surfaces, the geometry found with the MZ–SCF method is sometimes used without reoptimization for more elaborate calculations.

The current experimental value of the heat of reaction 1 is $\Delta H = -0.3$ kcal/mol[2b] (older value, −2 kcal/mol).[17] The calculated energy difference between $H_2 + CH_3$ and $H + CH_4$ is sensitive to the basis set and CI (Table II). The DZ–CI value +2.11 kcal/mol is quite reasonable in the sense that $H + CH_4$ and $H_2 + CH_3$ have almost identical energy.

The above results suggest that the MZ–SCF calculation gives reasonable values of geometrical parameters, while the energy difference is often overestimated. The DZ–SCF–CI calculation results in a realistic energy difference.

Axial Abstraction Model

(A) Model. The first model we considered for the CH_5 system is the axial model in which the incoming hydrogen atom (denoted by T) approaches one of the hydrogen atoms of CH_4 from the extension of the C–H axis. T then abstracts the hydrogen atom from CH_4 and leaves in the direction from which it approached. In the process the residual CH_3 group will relax to a planar methyl radical. Assuming that the C_3 symmetry is to be retained throughout the reaction, the four parameters that describe the model completely are shown in Figure 1. They are R_{TH}, the distance between the incoming T atom and the H atom to be abstracted; R_{HC}, the distance between this H atom and the carbon; $R_{CH'}$, the nonreactive C–H distance; and γ, the HCH angle of the CH_3 group (109.47° for $CH_4 + H$ and 120° for $CH_3 + H_2$). In the following calculations, unless specifically mentioned $R_{CH'} = 1.088$ Å, an approximate C–H equilibrium distance for CH_4, and $\gamma = 109.47°$ are assumed.

(B) Minimal STO–SCF Calculations. In order to find out the overall characteristics and the approximate saddle point geometry of the potential surface, MZ–STO–SCF calculations were carried out for a wide range of R_{TH} and R_{HC}. The potential surface shown in Figure 2 was constructed from the calculations of approximately 100 geometries.[18] The interpolated saddle point is at $R_{HT} = 0.873$ Å and $R_{HC} = 1.365$ Å with a barrier height of 37.5 kcal/mol above $H + CH_4$. The barrier height is more than three times larger than experimentally observed activation energy (10–12 kcal/mol),[2b,3] but this is anticipated in the MZ–SCF calculation. Nevertheless the general feature of the potential surface including the saddle point geometry is expected to be qualitatively acceptable. (See section C for further confirmation.)

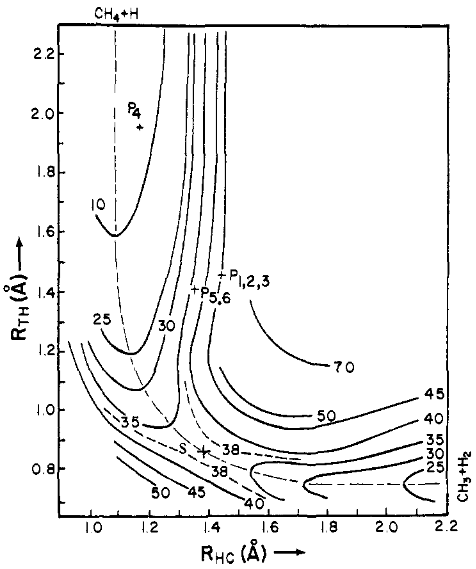

Figure 2. Potential surface for the axial model in the MZ–SCF method. The methane values of $R_{CH'}$ and γ are assumed. The contours are in kilocalories per mole from $H + CH_4$. The dashed line is the reaction coordinate. The point S is the calculated saddle point, and the points $P_{1,2,3}$, P_4, and $P_{5,6}$ are saddle points by Bunker and Pattengill.[7]

It is worth mentioning that this saddle point geometry ($R_{TH} = 0.873$ Å, $R_{HC} = 1.365$ Å) is very different from those used by Bunker and Pattengill in their empirical potential surfaces;[7] their surfaces 1, 2, and 3 had the saddle point at $R_{TH} = 1.45$, $R_{HC} = 1.45$ Å, surfaces 5 and 6 at 1.40, 1.40 Å, and surface 4 at 1.95, 1.17 Å. The present saddle point has the R_{TH} and R_{CH} values much closer to the hydrogen molecule R_{TH} value ($R_{TH}{}^{0}$) and the methane R_{CH} value ($R_{CH}{}^{0}$) in comparison to the Pattengill–Bunker saddle points. At the present saddle point, $R_{TH} - R_{TH}{}^{0}$ is smaller than $R_{CH} - R_{CH}{}^{0}$, indicating that the barrier is located closer to the products than to the reactants. This might be attributed partly to the instability of the $H_2 + CH_3$ product in the MZ calculation ($\Delta H = 14$ kcal/mol), but the DZ–SCF–CI calculations (see section C) confirm the present finding. The reaction path is smooth with no well near the top of the path. On the reaction coordinate before the saddle point, R_{CH} does not increase significantly from $R_{CH}{}^{0}$ until R_{TH} becomes 1.4 Å or less; after the saddle point, R_{TH} reaches $R_{TH}{}^{0}$ as soon as R_{HC} becomes 1.7 Å or longer.

In the above calculations, the nonreacting CH_3 group was assumed to be rigid. The product CH_3 radical will be in the planar form, while in the intermediate region the HCH angle will be larger than 109.47°. The HCH angle was relaxed in two calcula-

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(17) T. A. Cottrell, "The Strength of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

(18) Individual calculations, omitted for brevity, are available from the authors upon request.

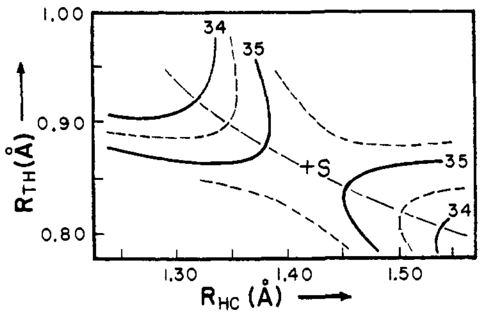

Figure 3. The potential surface near the saddle point for the axial model in the DZ–SCF method. The methane values of $R_{CH'}$ and γ are assumed. The energy is in kilocalories per mole from H + CH_4. The dashed line through the saddle point S is the reaction coordinate.

tions, one at the saddle point and another at the product limit CH_3. The results are shown in Table III. At the saddle point the optimum (interpolated) HCH angle is 113.2°, with a barrier height of 36.4 kcal/mol, 1.1 kcal/mol lower than the unrelaxed value of 37.5 kcal/mol. At infinite separation between H_2 and CH_3, the energy difference between the most stable planar conformation (Table II) and the tetrahedral conformation was found to be 3.4 kcal/mol. We have not optimized the C–H′ distance during the reaction. This is justified by recognizing in Table II that the optimum C–H distance in CH_3 is not very much different from CH_4.

Table III. The Effect of Geometry Change in the Nonreactive CH_3 Group for the Product ($CH_3 + H_2$) and at the Saddle Point of the Axial Model in the MZ–SCF Method

Geometry	Angle,[a] deg	∠HCH, γ, deg	Energy, au
Saddle point	Tetrahedral	Tetrahedral	−40.5542
	105	113.55	−40.5560
	100	117.05	−40.5528
$CH_3 + H_2$	Tetrahedral	Tetrahedral	−40.5863
	90	120	−40.5917

[a] Angle between T and the nonreactive CH.

Table IV. Axial Model in DZ–SCF and DZ–SCF–CI Calculation

R_{TH}, Å	R_{HC}, Å	E(SCF), au	E(CI), au
0.989	1.331	−40.62936	
0.936	1.279	−40.63044	−40.71769
0.936	1.384	−40.62750	−40.71618
0.883	1.226	−40.62783	
0.883	1.331	−40.62815	
0.883	1.437	−40.62724	−40.71473
0.883	1.543	−40.62673	−40.71444
0.831	1.384	−40.62680	−40.71244
0.831	1.490	−40.62818	−40.71390
0.778	1.437	−40.62592	
0.778	1.543	−40.62943	−40.71295

(C) Double-ζ STO–SCF and CI Calculations. The MZ–STO–SCF calculation usually predicts the geometries of molecules and saddle points reasonably well. However, the potential energy barrier height is sensitive to the basis set and also to the correlation energy. To obtain more reliable information on the barrier height and the saddle point geometry, we have carried out several double-ζ (DZ) STO–SCF and SCF–CI calculations in the neighborhood of the MZ saddle point. The CI calculation included 692 doublet functions contributing to the A_1 symmetry of the C_{3v} group as specified in the Method section. The results are shown in Table IV and Figure 3. The saddle point geometry and the barrier height from various calculations are summarized in Table V. The DZ–SCF–CI calculations do not cover the saddle point exactly, but we can make a reasonable estimate of its geometry and energy. The barrier height changes little from 38 kcal/mol for MZ–SCF to 35 kcal/mol for DZ–SCF, but the DZ–SCF–CI value is about 18 kcal/mol. The difference between the DZ–SCF–CI and DZ–SCF results is mainly due to the correlation energy, because the error due to the use of Nesbet's approximate SCF method at the saddle point is estimated to be within a few kilocalories per mole.

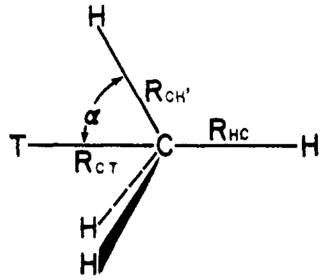

Figure 4. Inversion exchange model. C_{3v} symmetry is assumed.

Table V. Saddle Point for Axial Model in Various Calculations

	MZ-SCF	DZ-SCF	DZ-SCF-CI
R_{TH}, Å	0.87	0.86	$\sim$0.95
R_{HC}, Å	1.37	1.42	$\sim$1.48
ΔE, kcal/mol[a]	37.5	35.2	$\sim$18

[a] Barrier height from the CH_4 + H limit.

The relaxation of the HCH angle at the saddle point will reduce the barrier by about 1.2 kcal/mol if the MZ value is assumed to be applicable here. The best value of the barrier height is about 17 kcal/mol. This value is still larger than the kinetically determined activation energy E_a of 10–12 kcal/mol. Two comments can be made on this difference. One might expect that a further improved basis set including p orbitals on H and d orbitals on C will lower the barrier by a few kilocalories per mole. Another point is that there is no *a priori* reason why a kinetic quantity E_a has to be equal to the static quantity of the energy barrier and could well be smaller than the barrier.[19] The geometry of the saddle point is again very different from those used by Bunker and Pattengill.[7]

Inversion Substitution Model

(A) Model. This is a Walden inversion model in which T approaches the carbon atom from behind one of the C–H bonds, maintaining C_{3v} symmetry. Four parameters describe the model completely (Figure 4),

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(19) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, 43, 3259 (1965). On this potential surface, which has the saddle point in the product valley, the bobsled effect might raise E_a, while the tunneling effect might lower E_a.

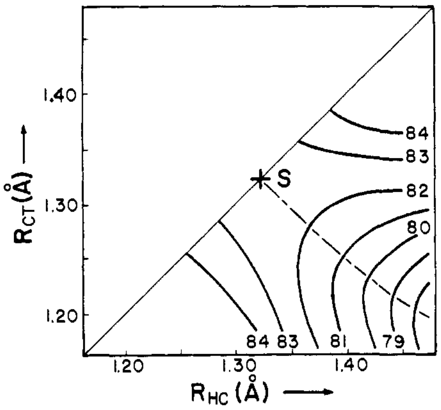

Figure 5. The potential energy surface for the inversion model in the MZ-SCF method. $R_{CH'}$ = 1.094 Å and α = 90° are assumed. The contours are in kilocalories per mole from H + CH_4. The dashed line through the saddle point S is the reaction coordinate. The surface is symmetric with respect to the inversion at R_{CT} = R_{HC}.

R_{CT}, R_{HC}, $R_{CH'}$ (nonreactive C–H distance), and α (TCH′ angle). In most calculations, α = 90° was assumed.

(B) Minimal STO–SCF Calculations. The results of MZ–SCF calculations are shown in Table VI. In the first ten calculations, the symmetric structure (D_{3h}, α = 90°) was optimized with respect to the reactive C–H distance $R_{HC} = R_{CT}$, then to the nonreactive $R_{CH'}$ distance, and finally again to $R_{HC} = R_{CT}$. The optimal symmetric geometry thus obtained has R_{HC} = R_{CT} = 1.320 Å and $R_{CH'}$ = 1.094 Å with an energy of −40.48250 au or a barrier of 82.6 kcal/mol. Additional calculations were carried out to show that this optimal symmetric structure actually corresponds to a saddle point (transition state) for the inversion substitution process. A calculation with $R_{HC} = R_{CT}$ = 1.320 Å, $R_{CH'}$ = 1.094 Å, and α = 80° (not shown in Table VI) gives the energy −40.47329 au, which is 5.8 kcal/mol above the α = 90° value. The second half of Table VI and Figure 5 shows that the potential energy surface is smooth, so that no local minimum appears to exist in a slightly nonsymmetric region, as was found in a CNDO calculation.[9]

Table VI. Inversion Substitution Model in MZ–SCF Method[a]

R_{HC}, Å	R_{CT}, Å	R_{CH}, Å	E, au
1.249	1.249	1.049	−40.47362
1.301	1.301	1.049	−40.47745
1.354	1.354	1.049	−40.47753
1.407	1.407	1.049	−40.47451
1.329	1.329	1.049	−40.47792
1.329	1.329	1.102	−40.48224
1.329	1.329	1.155	−40.47434
1.329	1.329	1.094	−40.48246
1.303	1.303	1.094	−40.48232
1.356	1.356	1.094	−40.48179
1.373	1.373	1.094	−40.48095
1.373	1.426	1.094	−40.47961
1.373	1.479	1.094	−40.47875
1.320	1.320	1.094	−40.48250
1.320	1.373	1.094	−40.48249
1.320	1.426	1.094	−40.48268
1.267	1.267	1.094	−40.48077
1.267	1.320	1.094	−40.48235
1.267	1.373	1.094	−40.48380
1.267	1.426	1.094	−40.48543
1.267	1.479	1.094	−40.48743
1.214	1.320	1.094	−40.48152
1.214	1.373	1.094	−40.48432
1.214	1.426	1.094	−40.48726
1.162	1.320	1.094	−40.47934
1.162	1.373	1.094	−40.48337
1.162	1.479	1.094	−40.49173

[a] α = 90° is assumed.

(C) Double-ζ STO–SCF and CI Calculations. Table VII shows the results of DZ–SCF and DZ–SCF–CI calculations. R_{HC} and R_{CT} are varied independently around the MZ optimum values. The deviation of these distances from the MZ values is extremely small. The DZ–SCF saddle point has the geometry R_{HC} = R_{CT} = 1.349 Å and $R_{HC'}$ = 1.086 Å, with the barrier height from H + CH_4 of 63.7 kcal/mol. A CI calculation, which included 692 doublet spin eigenfunctions belonging to A_1 in D_{3v} symmetry, was carried out at this geometry to obtain the best barrier height, 41.7 kcal/mol. This value now compares well with the observed threshold energy, 35 kcal/mol, of the substitution reaction, though it is not certain whether the actual substitution follows this inversion mechanism. There exists an argument against this inversion mechanism based on the kinetic consideration,[2a,5] but a trajectory study suggests the possibility of this mechanism.[7]

Table VII. Inversion Substitution Model in DZ–SCF and DZ–SCF–CI Methods[a]

$R_{HC} = R_{CT}$, Å	$R_{CH'}$, Å	E, au
1.267	1.094	−40.57877
1.320	1.094	−40.58138
1.373	1.094	−40.58148
1.320	1.147	−40.57478
1.320	1.041	−40.57774
1.349	1.085	−40.58193
1.349	1.085	(−40.67897)

[a] α = 90° is assumed. The energy E is for SCF except for the last row in parentheses, which is the SCF–CI energy.

Noninversion Replacement Model

(A) Model. The simplest model for the hydrogen exchange reaction without inversion is one in which T approaches one of the C–H bonds. A stripping-type abstraction reaction can also take place through a similar attack from the side.

It may be assumed for simplicity that the nonreacting CH_3 group retains C_{3v} symmetry and the plane defined by T, C, and H always contains the C_3 axis. Then, as is shown in Figure 6, the geometry of the system can be described by seven parameters: R_{TC} and R_{HC} (two reacting C–H bond distances), θ_1 (the TCX angle where X is the extension of the threefold axis toward the reacting bonds), θ_2 (the HCX angle), $R_{CH'}$ (the nonreacting C–H distance), α (the H′CX angle), and ϕ (the angle between the TCH plane and one of the nonreactive H′CX planes). The simplest model of the transition state for the noninversion exchange reaction will be symmetric ($R_{TC} = R_{CH}$ and $\theta_1 = \theta_2$) with respect to T and H. We carried out extensive calculations to find out the optimum symmetric structure using a fixed methane value for $R_{CH'}$ and α and a fixed ϕ = 30°

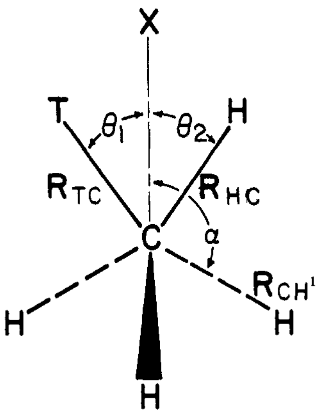

Figure 6. Noninversion replacement model. C_{3v} symmetry of the nonreactive CH_3 group and the coplanarity of T, C, H, and X (the extension of the C_{3v} axis) are assumed.

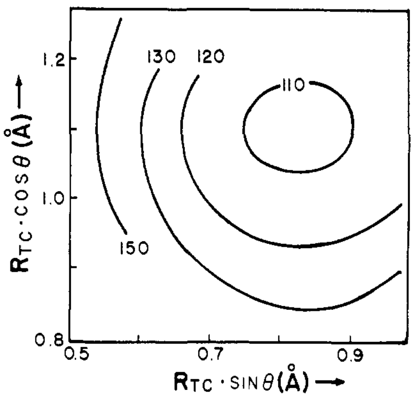

Figure 7. The potential energy surface near the saddle point for the replacement model. The system is symmetric ($\theta_1 = \theta_2$, $R_{TC} = R_{HC}$). The methane values of $R_{CH'}$ and α and $\phi = 30°$ are assumed.

(Table VIII). With a few additional calculations, the effects of the relaxation of $R_{CH'}$ and α were examined as well as the effects of ϕ (the rotation of the THC plane around the threefold axis) (Table IX). But no serious effort has been made to confirm that the symmetric structure is actually the saddle point.

Table VIII. Symmetric Noninversion Replacement Model in MZ-SCF Calculation

$R_{TC} = R_{CH}$, Å	$\theta_1 = \theta_2$, deg	E, au
1.143	45.0	−40.39552
1.217	45.0	−40.41116
1.292	45.0	−40.41802
1.367	45.0	−40.41817
1.442	45.0	−40.41322
1.332	45.0	−40.41882
1.145	41.25	−40.40764
1.152	37.54	−40.41276
1.154	36.98	−40.41287
1.164	33.68	−40.41003
1.332	37.0	−40.43982
1.332	34.0	−40.43863
1.334	40.0	−40.43570
1.332	36.18	−40.44006
1.425	21.41	−40.34743
1.376	22.62	−40.35844
1.303	23.96	−40.36556
1.231	25.46	−40.36740
1.160	27.15	−40.36223
1.248	25.09	−40.36752
1.216	21.70	−40.29829
1.284	28.30	−40.40911
1.323	31.33	−40.43130
1.366	34.18	−40.43989
1.412	36.84	−40.43882

(B) Minimal STO-SCF Calculations. Table VIII and Figure 7 show the results of MZ-SCF calculations for symmetric structures with a fixed geometry of the nonreactive CH_3 group. The minimum was obtained at $R_{TC} = R_{CH} = 1.332$ Å, $\theta_1 = \theta_2 = 36.18$ Å, and therefore $R_{TH} = 1.572$ Å with an energy of 109.2 kcal/mol above the reactants, $CH_4 + H$. Several additional calculations in Table VIII confirm that there is no other local minimum around the one obtained above and that the symmetric structure with a shorter R_{TH} ($\sim$1.06 Å) has even higher energy. The above barrier height is larger than that for the inversion (82.6 kcal/mol).

Table IX summarizes the effects of the relaxation of the nonreactive CH distance $R_{CH'}$ and the XCH′ angle α. It shows that these relaxation effects are extremely small. The last row of Table IX indicates that at the symmetric transition state the rotation of the CH_3 group around the X axis is essentially free.

Table IX. Effects of Nonreactive CH_3 Bond Length and Angle Relaxation for the Symmetric Noninversion Model in MZ-SCF Method[a]

$R_{CH'}$, Å	α, deg	ϕ, deg	E, au
1.088	109.47	30	−40.44010
1.141	109.47	30	−40.43761
1.194	109.47	30	−40.42525
1.088	105	30	−40.42522
1.088	100	30	−40.39991
1.088	109.47	0	−40.44011

[a] The optimized values of reactive coordinates, $R_{TC} = R_{CH} = 1.332$ Å and $\theta_1 = \theta_2 = 36.18°$ from Table VIII were used throughout.

In Table X a nonlinear variation of the axial model was examined. In this model $\beta = 0$ corresponds to the transition state of the axial model ($R_{TH} = 0.873$ Å, $R_{HC} = 1.365$ Å, and unrelaxed CH_3). Then T is moved off the axis toward a staggered THCH′ geometry by an angle β with the rest of the system fixed. The calculations suggest that for the abstraction reaction the nonlinear approach of T, commonly called the stripping model, has a higher energy than the axial model.

Table X. Nonlinear Variation of Axial Model[a]

β, deg	E, au
0	−40.55419
45	−40.54123
90	−40.47274

[a] With $R_{TH} = 0.873$ Å, $R_{HC} = 1.365$ Å, and unrelaxed CH_3. β is angle of deviation of the TH bond from linearity with the CH bond.

(C) Double-ζ STO-SCF and CI Calculations. The DZ-SCF calculations around the minimum of the MZ-SCF calculations for the symmetric replacement model are shown in Table XI. The interpolated mini-

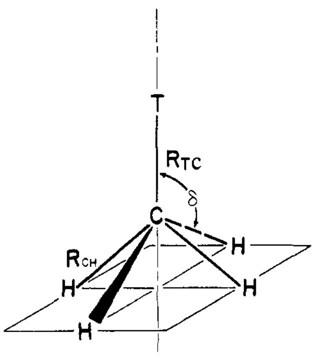

Figure 8. The C_{4v} intermediate in the pseudorotation model.

mum at $\theta_1 = \theta_2 = 35.6°$, $R_{TC} = R_{CH} = 1.36$ Å, $R_{TH} = 1.59$ Å is not very different from the MZ minimum. Its energy is now 86.6 kcal/mol above the $H + CH_4$ limit. The only CI calculation was carried out near this minimum with 1284 doublet spin eigenfunctions belonging to A'' of C_s symmetry. The energy of the minimum is reduced to 64.2 kcal/mol, which is about 22 kcal/mol larger than the corresponding value of 41.7 kcal/mol for the inversion model.

Table XI. Symmetric Noninversion Replacement Model in DZ-SCF and CI Calculations

$R_{TC} = R_{CH}$, Å	$\theta_1 = \theta_2$, deg	R_{TH}, Å	E(SCF), au	E(CI), au
1.279	36.18	1.510	−40.54302	
1.332	36.18	1.572	−40.54536	
1.385	36.18	1.634	−40.54545	−40.64322
1.437	36.18	1.697	−40.54374	
1.332	37.18	1.609	−40.54500	
1.332	35.18	1.534	−40.54535	

The C_{4v} Structure

Weston and Ehrenson examined a racemization mechanism by means of pseudorotation involving an intermediate of C_{4v} symmetry.[9,20] A few similar calculations were included in our *ab initio* studies. The geometry of the C_{4v} system is described by three parameters (Figure 8), R_{TC}, R_{CH}, and δ (the TCH angle). The four equivalent C–H distances R_{CH} were assumed to be 1.090 Å, the calculated CH_4 equilibrium distance. The results of the calculations for several values of R_{TC} and δ are shown in Table XII. Even at the minimum, $R_{TC} = 1.088$ Å and $\delta = 103°$, the system has a very high energy, −40.43574 au, which is 112 kcal/mol above the $H + CH_4$ limit. This barrier height is an overestimate, as in all other MZ-SCF calculations. But it is noticed that the 112-kcal/mol barrier is comparable to the 109-kcal/mol MZ barrier for the replacement (noninversion) exchange model. No DZ calculation has been carried out for the model, but it is not unreasonable to presume that the DZ-SCF-CI barrier would be comparable to that for the replacement model, 64 kcal/mol.

Table XII. The C_{4v} Structures in the MZ-SCF Method

R_{TC}, Å	δ, deg	E, au
1.323	90	−40.37499
1.164	90	−40.39625
1.111	90	−40.39800
1.058	90	−40.39570
1.115	90	−40.39800
1.115	95	−40.41697
1.115	100	−40.43338
1.115	102	−40.43507
1.115	103	−40.43519
1.115	104	−40.43480
1.141	103	−40.43362
1.088	103	−40.43574
1.062	103	−40.43514

Thus it is possible that this pseudorotation model as well as the replacement model contribute in the actual high-energy reactions.

Discussion

Ab initio molecular orbitals calculations have revealed several interesting properties of the potential energy surface for $H + CH_4$ reactions.

Table XIII summarizes the calculated heights of the potential energy barrier for four models. It is quite striking to notice that the experimental activation energy for the abstraction process, 10–12 kcal/mol,[2b,3] is reasonably close to the potential barrier height, 17 kcal/mol, in the DZ-SCF-CI axial model, and also that the experimental threshold energy for the exchange process, 35 kcal/mol,[4] is not far from the DZ-SCF-CI barrier for the inversion model.

Table XIII. Calculated Barrier Heights (kcal/mol) for Four Models of $T + CH_4$ Abstraction and Exchange Reactions

Model	Axial (abstraction)	Inversion (exchange)	Replacement (exchange)	C_{4v} (exchange)
MZ-SCF	36	83	109	112[a]
DZ-SCF	34	64	87[a]	
DZ-SCF-CI	17	42	64[a]	

[a] Geometry not fully optimized.

Even though the calculated energies may still involve an error of a few to several kilocalories per mole, a qualitative prediction can be made on the reaction mechanisms of the system. At the thermal energy only the axial abstraction process should predominate, in agreement with experiments. In the energy range of 40 kcal/mol, only the axial abstraction and the inversion exchange mechanisms are energetically allowed. The experimental threshold, 35 kcal/mol, for the exchange appears to be determined by the barrier for the inversion mechanism. Up to this energy, the potential energy would be the main factor determining the mechanisms of reactions ("potential energy dominant" region). At around 65 kcal/mol, in addition to the above two channels, the noninversion exchange channel and possibly the pseudorotation channel will become available. Also possibly important is the stripping type abstraction mechanism which might be considered to take place through a high-energy wall of the potential surface on which the axial model corresponds to the lowest path. Of two exchange mechanisms the inversion mechanism is more favored energetically but less favored in the steric angles available for the approach of the hydrogen atom. Therefore,

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(20) S. Ehrenson, *Chem. Phys. Lett.*, 3, 585 (1969).

Table XIV. The Bond Distance Differences between the Transition State and the Isolated Molecules in the Axial Model

	Method	ΔR_{TH},[b] Å	ΔR_{HC},[b] Å
Ab initio	MZ-SCF	0.13	0.26
	DZ-SCF	0.22	0.33
	DZ-SCF-CI	0.19	0.39
Empirical[a]	Surfaces 1, 2, 3	0.71	0.36
	Surfaces 4	1.21	0.08
	Surfaces 5, 6	0.66	0.31

[a] Reference 7. [b] $\Delta R_{TH} = R_{TH}$(saddle point) − $R_{TH}(H_2$ equilibrium); $\Delta R_{HC} = R_{HC}$(saddle point) − $R_{HC}(CH_4$ equilibrum).

it is possible that at this energy the two mechanisms are important almost to the same extent (transition between the "potential energy dominant" and "collision dynamics dominant" regions). At even higher energy as is expected in the recoil T + CH_4 reaction, all the examined models become available. There could be other possibilities which were not included in our simplified models. At such a high energy, where most paths become energetically easily accessible, the dynamic factor would play the most important role in determining the relative importance of different mechanisms ("collision dynamics dominant"). Then the inversion model might well become essentially forbidden dynamically, as discussed by Wolfgang,[5] because the collision time is so short that the CH_3 group does not have enough time to invert. To obtain a more quantitative picture of the mechanisms, especially at higher energy, a classical trajectory study on the calculated potential energy surface has to be awaited.

It is worthwhile now to compare the characteristic of our *ab initio* surface with empirical surfaces of Bunker and Pattengill (BP).[7] All the BP surfaces excluded the inversion exchange mechanism. With these surfaces they found that the experimental abstraction/exchange ratio of 4 could not be reproduced and suspected that the inversion mechanism might be important. *Ab initio* calculations clearly suggest that such mechanism is energetically favored and should be included. In the axial model, BP's saddle point geometries are very different from those of *ab initio* calculations (see Figure 2). Table XIV shows $\Delta R_{TH} = R_{TH}$ (saddle point) − R_{TH} (H_2 equilibrium) and $\Delta R_{HC} = R_{HC}$ (saddle point) − R_{HC} (CH_4 equilibrium). On *ab initio* surfaces the TH distance at the saddle point is only about 0.2 Å larger than the H_2 equilibrium value, while on BP's surfaces it is 0.7–1.2 Å larger. Consequently, the reaction coordinate in *ab initio* surfaces has to make a much sharper turn near the saddle point than that in BP surfaces. The kinetic implication of this difference is not obvious, but a sharper turn might be anticipated to decrease the reactive cross section by reflecting more trajectories back to the initial state.

In order to obtain detailed kinetic information for the system, a trajectory study has to be carried out on the calculated surface. Our *ab initio* calculations have been extensive in the MZ-SCF method but are quite limited in the DZ-SCF-CI method where the energy is more reliable. In any case a table of discrete values of the potential energy is not convenient for any trajectory calculation. It is most convenient to have an analytical form of the surface, which could be a least-squares polynomial fit or a semiempirical construction built from diatomic potential functions. The parameters of the fit should be taken to satisfy the general characteristics of the extensive MZ-SCF calculations, but with the barrier height scaled down to the DZ-SCF-CI value or some experimental value. Such work is underway in this laboratory.[21]

Acknowledgment. The authors are grateful to Dr. R. M. Stevens for the use of his POLYCAL program. They also wish to thank Drs. D. L. Bunker, R. Wolfgang, and S. Ehrenson for sending preprints of their work prior to publication. They are also indebted to Drs. Bunker, F. S. Rowland, and M. D. Newton for helpful discussions. One of the authors (R. E. D.) was supported during the summer of 1970 by a fellowship from an Eastman Kodak Company grant to the Department of Chemistry. The numerical calculations were carried out at the Computing Center of the University of Rochester, which is in part supported by National Science Foundation Grant No. GJ-823.

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(21) D. L. Bunker (private communication) also is now using empirical surfaces including the inversion mechanism and partly taking into account the characteristics of the present *ab initio* energy surfaces.