

# A Theoretical Study of the Reaction of Methane with Methyl Radical Using Several Different *ab Initio* and Semiempirical Methods

M. T. Rayez-Meume,<sup>1a,b</sup> J. J. Dannenberg,\*<sup>1b</sup> and J. L. Whitten<sup>1c</sup>

*Contribution from the Department of Chemistry, Hunter College of the City University of New York, New York, New York 10021, and the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received January 11, 1977*

**Abstract:** The activation energy for the abstraction of a hydrogen atom from methane by a methyl radical has been calculated by several semiempirical and *ab initio* MO methods with and without configuration interaction. The transition-state geometry was insensitive to the method of calculation, but the activation energy varied considerably with the method used. Among the *ab initio* methods, increasing the basis set or including configuration interaction did not necessarily improve the calculated activation energies. In both cases the main difficulty is in achieving a uniformly accurate description of the transition state and separated reactants. Unless there is evidence for convergence of calculated values, it is concluded that only rough estimates of activation energies of reactions involving bond formation or bond breaking should be expected from calculations involving small and relatively inflexible basis sets.

The energetics of free-radical hydrogen abstractions are relatively free from solvent effects and have been well documented for quite some time.<sup>2</sup> It is, therefore, surprising that very little theoretical study has been directed toward these reactions. Most notably, Dewar et al. have published a MINDO/2 study of the abstraction of a hydrogen from methane by a methyl radical.<sup>3</sup> At the same time, there has been much recent discussion and considerable controversy over the applicability of various *ab initio* and semiempirical techniques to the study of organic reactions.<sup>4</sup> In this paper, we report a study of the reaction of the methyl radical and methane by *ab initio* molecular orbital methods, also including for comparison the results of semiempirical studies, with an aim to documenting the utility of the various methods for this important prototype reaction, as well as adding to our understanding of the reaction itself.

## Methods

The *ab initio* methods used were the STO-3G and 4-31G levels of the Gaussian 70 computer program,<sup>5</sup> and several Gaussian basis sets and programs developed by Whitten.<sup>6</sup> The latter bases consisted of (a) (W1), 1s hydrogen (2 Gaussians), 1s carbon (7 Gaussians), 2s carbon (2 decoupled functions of 3 Gaussians each), and 2p carbon (2 Gaussians); (b) (W1 + BO), constructed by adding two Gaussians per C-H bond to W1 at distances of  $\frac{1}{3}$  and  $\frac{2}{3}$  the bond distance from the carbon in a manner analogous to that used by Schaefer and Rothenberg<sup>7</sup> (Orbital exponents between 0.5 and 1.0 were tried. The former value gave the lowest energies and all subsequent references to this basis are for an orbital exponent of 0.5); (c) (W3 + HPO). Similar to W1 except that 5 Gaussians are used for the carbon 2p orbitals and 4 Gaussian hydrogen 1s orbitals are used; orbitals 2s (3 Gaussians) and 2p (5 Gaussians) were added only to the hydrogen being abstracted. A complete description of the atomic bases has been previously published<sup>6</sup> except for the carbon 2p orbitals of W1 and W1 + BO which are two Gaussian approximations of the larger five Gaussian basis. For separated molecules in the W1 + BO basis, the number of bond basis functions was kept constant. The two bond functions that correspond to the C-H interaction that is not present in the separated species were assigned one to each species.

The adequacy of a single-determinant level of description can be questioned, but in the present activation energy calculation, the reactants and transition state both contain one singly

occupied orbital, and thus correlation energy differences are not as serious as in problems in which a dissociation from closed-shell to open-shell species occurs. Nonetheless, in order to investigate the importance of electron correlation effects, configuration interaction calculations were carried out with the basis set W3 + HPO. All configurations that could be generated by exciting no more than two electrons from the SCF occupied orbitals, excluding the C 1s, were considered. Those configurations with an energy of interaction with the ground state greater than or equal to  $7 \times 10^{-5}$  au were included in the CI calculation. See ref 8 for a complete description of the CI method.

Semiempirical methods used were INDO<sup>9</sup> and an open-shell version of MINDO/2, using the Pople-Nesbet open-shell method as incorporated in the CNINDO program,<sup>10,11</sup> but with MINDO/2 parameters. This procedure differs somewhat from that used previously by Dewar et al.<sup>3</sup> Complete reaction paths were calculated using a computational procedure that optimizes the geometry of each species (CH<sub>4</sub> and CH<sub>3</sub>) as well as its relative orientation about its own center of mass for a fixed distance between the centers of mass.<sup>12</sup>

For each MO method except (W3 + HPO), the geometries of the starting reactants and the transition state were optimized. Symmetry constraints reduced the optimizations of both CH<sub>4</sub> and CH<sub>3</sub> to those of the respective C-H bond lengths (angles of 109.47 and 120.00°, respectively, were assumed). We assumed the transition state to have a linear C-H-C arrangement with a plane of symmetry perpendicular to the axis passing through the H. This assumption reduces the problem of geometrical optimization to consideration of the C-C distance, one C-H distance, and one H-C-H angle (the central H-C distance is half the C-C distance). These geometrical constraints are supported by the results of the semiempirical studies (see below). Optimizations were performed using the Gaussian 70 program for the STO-3G and 4-31G calculations, by a steepest descent method<sup>13</sup> for the other *ab initio* and semiempirical calculations. The energies of reactants were taken as either the sum of the separated species or as the energy of the supermolecule at least 10 Å separation. When the latter method was used, two points at separations of 10 and 15 Å were calculated and shown to have the same energy within  $6 \times 10^{-4}$  kcal/mol.

## Results and Discussion

The geometries of the relevant species are summarized in

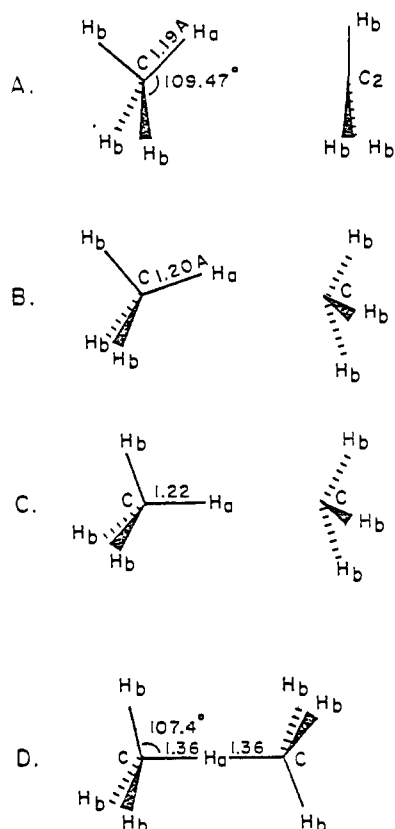


Figure 1. Orientations of methane and methyl radical for various stages along the reaction path as calculated by MINDO/2. The carbon-carbon distances are (A) 4.00, (B) 3.62, (C), 3.06, and (D) 2.73 Å (transition state).

Table I

	CH <sub>4</sub> C-H, Å	CH <sub>3</sub> C-H, Å
INDO	1.116	1.105
MINDO/2	1.198	1.179
STO-3G	1.083	1.078
STO-4-31G	1.086	1.080
W1	1.090	1.090
W1 + BO	1.088	1.087

	H <sub>b</sub> <sup>3</sup> -C-H <sub>a</sub> -CH <sub>b</sub> <sup>3</sup> C-C, Å	C-H <sub>b</sub> , Å	H <sub>a</sub> CH <sub>b</sub> , deg
INDO	2.439	1.116	108.90
MINDO/2	2.731	1.195	107.40
STO-3G	2.621	1.083	106.79
STO-4-31G	2.683	1.087	107.20
W1	2.706	1.090	108.10
W1 + BO	2.695	1.088	108.00

Table II. Total Energies<sup>a</sup>

SCF or CI method	Separated molecules CH <sub>3</sub> + CH <sub>4</sub>	Transition state	Activation energy, kcal/mol
INDO			-40.3
MINDO/2			4.1
STO-3G	-78.8036	-78.7619	26.1
4-31G	-79.6437	-79.5961	29.9
W1	-79.3135	-79.2475	41.4
W1 + BO	-79.3695	-79.3205	30.7
W3 + HPO	-79.5050	-79.4903	9.2
(W3 + HPO) + CI	-76.6200 (187) <sup>b</sup>	-79.6110 (412) <sup>b</sup>	(5.7) <sup>c</sup> (19.0) <sup>d</sup>
Experimental			14.1-14.9 <sup>e</sup>

<sup>a</sup> Hartrees. <sup>b</sup> Number of configurations included. <sup>c</sup> Direct calculation. <sup>d</sup> Corrected for stabilization of CH<sub>3</sub> by hydrogen basis functions (see text). <sup>e</sup> Depending upon whether CH<sub>3</sub> + <sup>14</sup>CH<sub>4</sub> or CD<sub>3</sub> + CH<sub>4</sub> was studied. See ref 2b.

Table I, and total energies and activation energies are given in Table II. The reaction path depicted in Figure 1 shows that the methane becomes oriented so that one of its C-H bonds becomes coaxial with the initially singly occupied p orbital of the methyl radical as the species approach. This observation tends to justify the linear C-H-C constraint used for the optimization of the ab initio transition state. It was assumed that a fixed orientation of the methyls would have no appreciable effect on the energy of the transition state (the barrier to internal rotation was calculated by MINDO/2 to be 0.03 kcal/mol). The results in Table I show that all of the ab initio SCF methods predict very similar geometries for the transition state. The MINDO/2 geometry agrees as well if 0.1 Å is subtracted from each of the normal C-H bonds (according to the normal usage<sup>3</sup>) but not from the C-H bonds involving the central hydrogen.

The C-C distance predicted in the transition state corresponds to a rather stretched central C-H bond, although the two species are well within the separation predicted by the sum of their van der Waals radii. The angle distortion upon going to the transition state is much greater for the methyl radical (18°) than for methane (1°) as expected from the presumably shallow well for planar to pyramidal distortion of the former.

Of the ab initio calculations in Table II, all except (W3 + HPO) and (W3 + HPO) + CI predict a significantly higher barrier than the experimental value. Going from STO-3G to 4-31G raised rather than lowered the activation energy. Adding the bond orbitals to the W1 basis, giving the basis (W1 + BO), markedly improves the calculated activation energy. The highest singly occupied MO in this basis is of some interest. In this orbital, the two bond orbitals on the axis to each side of the central hydrogen have opposite signs, and each has a stabilizing interaction with the adjacent carbon 2p and 2s  $\sigma$  orbitals. Thus, these two bond orbitals act much like a hydrogen 2p orbital. The other two bond orbitals on the central axis have opposite signs from the first pair and detract from the positive interaction on each side. These, presumably, act to correct the electron density distributions on each side of the central H.

In summary, on improvement of the simplest bases, STO-3G and W1,  $E_{act}$  increases and decreases, respectively, but the final values are  $\sim 30$  kcal/mol in both cases (4-31G and W1 + BO). Before proceeding further, however, it is worthwhile to discuss the likelihood that all of the high values are simply artifacts of the small basis calculations. Several general arguments support this contention. First, flexibility of the atomic orbital basis for the central hydrogen and carbon  $\sigma$ -type orbitals is clearly desirable for the description of the transition state in which the internuclear distance from each of the carbons to the central hydrogen is considerably lengthened. In the STO-3G and W1 bases, however, the atomic orbitals are constrained to be the same as in the free atoms except (in the

case of W1) for a scaling of the hydrogen orbital exponent appropriate to methane. Inclusion of additional, bond orbital, basis functions for each CH bond in the W1 + BO basis alleviates the constraint. Thus, the activation energy calculated with the W1 + BO basis (see Table II) improves (decreases) by 10 kcal/mol. In addition, the change in correlation energy due to the variability of the ionic/covalent character of the central CH bonds is important in view of differences in bond lengths between the transition state and separated reactants. These effects are not treated by the STO-3G, W1, and W1 + BO methods which are at the SCF level.

Another factor influencing the relative accuracy of the transition state calculations is the use of small-size Gaussian expansions of the atomic orbitals. In the calculation W1 + BO, the carbon orbitals and the terminal CH bonds will utilize the bond orbitals of the central CH bonds to a greater extent than would be the case if near Hartree-Fock atomic orbitals were used. Thus, the atomic orbitals themselves are improved by utilization of the extra bond basis functions. It, therefore, follows that there is an arbitrariness due to the uncertainty in the assignment of the central CH bond functions to the separated species, CH<sub>4</sub> and CH<sub>3</sub>.

Finally, there is an additional basis effect not directly related to the nature of the central C-H-C bonding. If the basis is imbalanced such that the polarities of the terminal CH bonds are not properly described, the resulting errors in charge densities can affect the relative stability of the transition state and separated species. Two of the calculations in this study exhibit this effect. Upon going from the STO-3G basis to the more flexible 4-31G basis, the carbon atoms become more negatively charged, as indicated by an increase in orbital energies of the inner shell orbitals. The corresponding activation energy increases slightly by 3.8 kcal/mol. The same effect was noted for another basis, not reported in Table II, in which carbon p orbitals were improved by adding more Gaussians, but hydrogen 1s orbitals were left the same as in the W1 + BO basis. In this case the carbon atoms again become more negative and an increase in activation energy of 6 kcal/mol was calculated.

The previous calculations employing the STO-3G, 4-31G, W1, and W1 + BO bases, all of which produce activation energies in the range 26–41 kcal/mol, illustrate the importance of considering the several factors discussed above: flexibility of the orbital basis in the central C-H-C bonding region, balance of the basis, and variability of ionic/covalent character in forming the transition state from the separated reactants. In the final series of calculations, configuration interaction was employed along with an improved carbon and hydrogen basis plus additional 2s and 2p functions on the central hydrogen (the basis W3 + HPO). The latter functions allow for both radial changes in shape and polarization of orbitals in the bonding region. The calculated results in Table II show an activation energy of 9.2 kcal/mol at the SCF level, and 5.7 kcal/mol after CI on both the transition state and separated CH<sub>4</sub> and CH<sub>3</sub>. The latter value is 9 kcal/mol lower than the experimental value of 15 kcal/mol.

Since the basis is still relatively inflexible, it is suggested that a correction of the above calculation is needed to achieve comparable accuracy in the calculation of the transition state

and separated species. As it now stands, the central basis functions are assigned to CH<sub>4</sub> on separation of the reactants; therefore, these functions are not available to stabilize CH<sub>3</sub>. In order to take into account this stabilization, an additional SCF calculation on CH<sub>3</sub> was performed including hydrogen 2s and 2p functions positioned at the same distance from CH<sub>3</sub> as in the transition state. The SCF energy of CH<sub>3</sub> is lowered by 13.3 kcal/mol on inclusion of these functions and if the separated species energy is corrected by this amount an activation energy of 19.0 kcal/mol is obtained.

In summary, the observation is that all of the semiempirical and ab initio results are in qualitative agreement as far as the geometry of the transition state is concerned, with the exception of the INDO calculation, which differs more substantially as shown in Table I. For the activation energy, the different methods, excluding the INDO calculation, give values ranging from 4 to 41 kcal/mol. Some of these results can be discarded on the basis of the uncertainties discussed above, and the calculations that appear most reliable are MINDO/2 ( $E_{act} = 4.1$  kcal/mol) and the ab initio calculation using the (W3 + HPO) + CI basis, corrected by improvement of the CH<sub>3</sub> description, which gives  $E_{act} = 19.0$  kcal/mol. In general, however, given the wide range in ab initio results, it is concluded that such small basis calculations should not be relied upon to give more than rough estimates of activation energies unless there is supporting evidence for convergence of calculated values. Geometrical optimization of the transition state is an absolute necessity as there are no experimental geometries to use. It is clearly not economically feasible at present to optimize the geometries of the transition states of any but the simplest reactions in a basis sufficiently flexible to allow us to have quantitative confidence in a calculated activation energy. In addition, the increasingly common practice of optimizing geometries with an STO-3G basis and using these geometries to calculate hopefully more accurate activation energies using the 4-31G basis is of doubtful value in light of the above discussion.

## References and Notes

- (1) (a) Équipe de Recherches Associée au CNRS, No. 312, Laboratoire de Chimie Physique A, Université de Bordeaux I, 33405 Talence, France; (b) Hunter College of the City University of New York; (c) State University of New York at Stony Brook.
- (2) (a) F. S. Dainron, K. J. Ivin, and F. Wilkinson, *Trans. Faraday Soc.*, **55**, 929 (1959); (b) G. A. Creak, F. S. Dainron, and K. J. Ivin, *ibid.*, **58**, 326 (1962).
- (3) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).
- (4) J. A. Pople, *J. Am. Chem. Soc.*, **97**, 5306 (1975); W. H. Hehre, *ibid.*, **97**, 5308 (1975); M. J. S. Dewar, *ibid.*, **97**, 6591 (1975); J. L. Whitten, *Acc. Chem. Res.*, **6**, 238 (1973); J. J. Dannenberg, *Angew. Chem., Int. Ed. Engl.*, **15**, 519 (1976).
- (5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971); The program is available from the Quantum Program Exchange, Department of Chemistry, University of Indiana, Bloomington, Ind. (Program No. 236).
- (6) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966); **39**, 349 (1963).
- (7) S. Rothenberg and H. F. Schaefer III, *J. Chem. Phys.*, **54**, 2764 (1971).
- (8) J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.*, **51**, 5584 (1969).
- (9) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
- (10) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1974).
- (11) Available from the Quantum Chemistry Program Exchange, Department of Chemistry, University of Indiana, Bloomington, Ind. (Program No. 141).
- (12) J. C. Rayez and J. J. Dannenberg, to be published.
- (13) A. Dargelos, D. Liotard, and M. Chaillet, *Tetrahedron*, **28**, 5595 (1972); to be published.