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Bauschlicher Jr., Charles W.

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Charles W. Bauschlicher Jr., Charles F. Bender, and
Henry F. Schaefer III

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Transition States for the Abstraction Reactions of Triplet Methylene
with Hydrogen and Methane *

Charles W. Bauschlicher Jr., Charles F. Bender,** and Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory

University of California, Berkeley, California 94720

* Work performed under the auspices of the U. S. Energy Research
and Development Administration.

** Lawrence Livermore Laboratory, University of California, Livermore,
California 94550.

Abstract

The transition states and barrier heights for the reactions $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ and $\text{CH}_2(^3\text{B}_1) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3$ have been predicted using nonempirical electronic structure theory. Earlier work on the $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ reaction has been extended by (a) the addition of polarization functions to the earlier double zeta basis set, and (b) the consideration of five additional degrees of freedom in the potential surface. The earlier conclusions remain essentially unchanged: the transition state occurs for a C_{2v} structure and the barrier height is ~ 15 kcal/mole. For the methane abstraction reaction a barrier height ~ 7 kcal/mole higher was found, implying that neither reaction should occur to a significant degree at room temperature. This conclusion is consistent with the BEBO calculations of Carr but in disagreement with the MINDO predictions of Dewar.

Introduction

We have recently suggested¹ that the abstraction and insertion reactions of triplet and singlet methylene with H_2 may be representative of the analogous reactions of CH_2 with saturated hydrocarbons. More specifically, based on ab initio theoretical studies it has been predicted² that $CH_2(^3B_1)$ should not react (via abstraction) with saturation hydrocarbons due to sizeable activation energies (~ 15 kcal/mole). However, $CH_2(^1A_1)$ should insert into the CH bonds of saturated hydrocarbons via non-least motion pathways involving little or no activation energy.³

The validity of $CH_2 + H_2$ as a prototype has been given substantial support by the empirical Bond-Energy Bond-Order⁴ (BEBO) calculations of Carr⁵ for $CH_2(^3B_1)$ abstraction reactions. In agreement with our ab initio prediction^{1,2} (which, however, came after Carr's work), he finds large activation energies for the $CH_2(^3B_1) + RH$ reactions. For H_2 and the saturated hydrocarbons CH_4 , C_2H_6 , C_3H_8 , and $n-C_4H_{10}$, Carr predicts E_a values of 19.7, 25.6, 15.7, 14.2, and 13.1 kcal/mole respectively.

For the reactions of triplet methylene with hydrogen and methane, semi-empirical calculations have been carried out⁶ using the modified intermediate neglect of differential overlap (MINDO) methods of Dewar.⁷ For $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$, MINDO/3 appears to predict no barrier at all, while for $CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3$, a barrier of only 3.8 kcal/mole was reported using MINDO/2. Thus it would appear that MINDO will predict small barriers for the abstraction reactions of $CH_2(^3B_1)$ with saturated hydrocarbons. This conclusion is of course quite the opposite

of that reached by BEBO and the ab initio methods. Since MINDO appears to be one of the most promising semi-empirical methods currently available, it is important to establish whether or not the conflict with the a priori theory is a real one.

In the present paper, we remove some of the limitations of our earlier study of the $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ reaction. In addition the validity of $\text{CH}_2 + \text{H}_2$ as a prototype is tested via ab initio calculations on the $\text{CH}_2(^3\text{B}_1) + \text{CH}_4$ reactions.

Perhaps the most serious deficiency in our earlier calculations¹ was the absence of polarization functions in the chosen basis set. For example, in the case of $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$, polarization functions lower the predicted barrier height⁸ from 5.7 to 1.7 kcal/mole. Therefore we added to the earlier double zeta basis a set of d-like functions $[x^2e^{-\alpha r^2}, y^2e^{-\alpha r^2}, z^2e^{-\alpha r^2}, xye^{-\alpha r^2}$ (actually, this function was deleted since it is of a_2 symmetry and will not contribute to any of the occupied molecular orbitals), $xze^{-\alpha r^2}$, and $yme^{-\alpha r^2}]$ centered on carbon. The orbital exponent $\alpha = 1.0$ was chosen on the basis of previous experience.⁹ Similarly, a set of p functions with $\alpha = 1.0$ were centered on each hydrogen atom. Results obtained using the larger basis set are summarized in Table I, which includes the earlier results for comparison. Figure 1 shows the coordinate system used here and earlier. These new results are very encouraging in that the predicted barrier height is only 0.2 kcal/mole lower than the previous double

-3-

zeta result and the transition state geometries are nearly indistinguishable.

Note that we have not carried out configuration interaction (CI) calculations using the double zeta plus polarization basis. However the SCF results using the two basis sets are so similar that it is not unreasonable to assume that a CI calculation using the larger basis would also yield a barrier of ~ 15 kcal/mole. Our best estimate is that the true barrier height for $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ is in the range 10-15 kcal/mole.

The remainder of the new calculations on $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ were carried out to explore the importance of degrees of freedom not previously considered. For example, in the previous work¹ the CH separations were fixed at 2.06 bohrs = 1.090 Å. Here the CH separation was optimized for methylene (2.030 bohrs), for the saddle point (2.035 bohrs), and the methyl radical (2.028 bohrs). The barrier height changes only slightly (from 25.7 to 25.8 kcal/mole, a reasonable result since the optimized CH distance for reactants is farther from 2.06 than that for the saddle point) and the exothermicity from 4.1 to 4.3 kcal/mole. Thus the approximation of a fixed CH separation is quite valid for this reaction.

The next new degree of freedom considered was the angle α depicted in Figure 2. This corresponds to an upward movement of the far H atom in H_2 , while the near H atom remains on the line which bisects the CH_2 bond angle. With the angle α constrained to be 20° , the transition state in terms of R , r , and θ was determined and is seen in Table II. There we see that the constrained barrier height is 1.0 kcal/mole greater than the original C_{2v} approach. Although this adds to the justification of the

-3a-

original reaction coordinate, it is clear that the potential surface is rather flat for values of α near zero.

The angle β corresponds to an out of the plane (of the original Figure 1 coordinate system) movement of the far H atom. As seen in Figure 3, this far hydrogen remains on the plane which bisects the methylene HCH bond angle. Constrained saddle points were determined for both $\beta = 20^\circ$ and $\beta = 45^\circ$. Although the energy is only slightly higher (1.2 kcal/mole) for $\beta = 20^\circ$, a more sizeable increase (6.3 kcal/mole) is found for $\beta = 45^\circ$.

The angle γ , depicted in Figure 4, corresponds to rotating the H-H-C axis about the position of the carbon nucleus. Thus all five atoms remain coplanar but the point group symmetry is reduced to C_s . Thus while the angle α is related to the original C_{2v} pathway by the upward displacement of one H atom, γ allows the entire H_2 molecule the freedom of an upward movement. For $\gamma = 10^\circ$, the constrained saddle point lies 1.4 kcal/mole higher than the original C_{2v} constrained transition state.

Finally, we have considered the angle δ , seen in Figure 5. This angle corresponds to an out of the plane rotation of the entire H_2 molecule. As seen in Table II, the choice of $\delta = 10^\circ$ yields a barrier only 0.1 kcal/mole higher than the original one. Further, $\delta = 20^\circ$ raises the energy by an additional 0.3 kcal and $\delta = 40^\circ$ yields a barrier of 27.4 kcal/mole. Thus the potential energy surface is very flat in this region, a result predicted intuitively by Hoffmann¹⁰ several years ago. We conclude that although the barrier for $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$ is high (10-15 kcal/mole), the surface is relatively flat in a large region surrounding the transition state and hence reagents with the necessary total energy should typically lead to reaction.

This reaction is of special interest since it is the simplest of methylene with an actual saturated hydrocarbon. In addition, the contrast between the BEBO (25.6 kcal)⁵ and MINDO (3.8 kcal)⁶ barrier height predictions is especially striking.

The same double zeta basis set¹ used for $\text{CH}_2 + \text{H}_2$ was used for $\text{CH}_2 + \text{CH}_4$. Based on the present confirmation of the C_{2v} transition state (Figure 1) for $\text{CH}_2(^3\text{B}_1) + \text{H}_2$, the present geometry search was limited to four variables, depicted in Figure 6. Of these, the methylene angle θ is identical to that used for $\text{CH}_2 + \text{H}_2$. R plays an analogous role, but is now the (methylene carbon - leaving hydrogen) separation. Also playing an analogous role to the $\text{CH}_2 + \text{H}_2$ system is r , now the (methane carbon - leaving hydrogen) separation. The new degree of freedom ϕ is the (leaving hydrogen - methane carbon - other hydrogen) angle. For the reactants ϕ is the tetrahedral angle, while it will be 90° for the products, since CH_3 is planar or very nearly so.¹¹

If one assumes the reaction of triplet methylene with H_2 to be a valid model for $\text{CH}_2(^3\text{B}_1) + \text{CH}_4$, then the transition state geometry can be predicted without a single calculation. If one labels the coordinates for the hydrogen and methane reactions with the subscripts H and M, respectively, we have

$$\frac{r_M^{\text{SP}}}{r_M^{\text{RX}}} = \frac{r_H^{\text{SP}}}{r_H^{\text{RX}}}$$

$$\frac{R_M^{\text{SP}}}{R_M^{\text{PR}}} = \frac{R_H^{\text{SP}}}{R_H^{\text{PR}}}$$

$$\frac{\theta_M^{\text{SP}}}{\theta_M^{\text{RX}}} = \frac{\theta_H^{\text{SP}}}{\theta_H^{\text{RX}}} \text{ or } \frac{\theta_M^{\text{SP}}}{\theta_M^{\text{PR}}} = \frac{\theta_H^{\text{SP}}}{\theta_H^{\text{PR}}};$$

where the superscripts SP (saddle point), RX (reactants), and PR (products) are self-explanatory. In this way we predict $r_M^{SP} = 2.52$ bohrs. The values of R and θ are trivially predicted to have the same values as for the $CH_2 + H_2$ reaction, namely $R = 2.52$ bohrs and $\theta = 124.8^\circ$. As will be seen, these simple predictions are quite accurate.

Our principal result is an SCF prediction of 33.3 kcal/mole for the barrier height. If we allow, analogous to our findings for $CH_2 + H_2$, a correlation energy lowering of 10-15 kcal/mole, the final prediction is $E_a \sim 18-23$ kcal. Clearly this conclusion is consistent with the BEBO results and in disagreement with the MINDO approach. For the purpose of future comparisons, we note that the total energies of $CH_2(^3B_1) + CH_4$ and the saddle point structures are -78.0988 and -79.0458 hartrees, respectively.

For $\text{CH}_2(^3\text{B}_1) + \text{H}_2$, the SCF and CI saddle point structures were quite similar.¹ This, combined with the large body¹² of ab initio structure predictions for stable molecules, suggests that the present transition state prediction (see Table III) should be quite reliable. Carr⁵ and Dewar⁶ do not report transition state geometries from the BEBO and MINDO studies. As expected¹⁵ for a nearly thermoneutral reaction, the transition state lies about halfway between reactants and products. The reaction is actually exothermic by 5 ± 1 kcal/mole,¹⁶ while the present calculations predict -0.5 kcal/mole for this quantity.

Concluding Remarks

The failure of MINDO methods to predict relatively high barriers for these triplet methylene abstraction reactions is undoubtedly due to the fact that MINDO is parameterized for stable molecules, not transition states. Thus the situation is reminiscent of the $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ isomerization, where MINDO/2 predicts¹³ a spurious¹⁴ minimum between reactants and products. Since MINDO has a number of very impressive characteristics, we are hopeful that reliable ab initio transition state information will be incorporated in future parameterizations of MINDO. More generally we feel that one of the primary goals of careful ab initio studies should be to provide guidelines for the inherently simpler semi-empirical methods.

Acknowledgments

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References

1. C. P. Baskin , C. F. Bender, C. W. Bauschlicher, and H. F. Schaefer, J. Am. Chem. Soc. 96, 2709 (1974).
2. H. F. Schaefer, Chemistry in Britain 11, 227 (1975).
3. C. W. Bauschlicher, H. F. Schaefer, and C. F. Bender, to be published.
4. H. S. Johnston and C. Parr, J. Am. Chem. Soc. 85, 2544 (1963).
5. R. W. Carr, J. Phys. Chem. 76, 1581 (1972).
6. N. Bodor, M. J. S. Dewar, and J. S. Wasson, J. Am. Chem. Soc. 94, 9095 (1972); the MINDO/3 study of $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ was carried out by Dr. Robert C. Haddon of the Australian National University, Canberra.
7. M. J. S. Dewar, Chemistry in Britain 11, 97 (1975).
8. C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, Science 176, 1412 (1972).
9. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Massachusetts, 1972).
10. R. Hoffmann, Dallas ACS Meeting, Spring 1972.
11. G. Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1966).
12. See, for example, W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, Progress in Physical Organic Chemistry, 11, 175 (1974).
13. M. J. S. Dewar and M. C. Kohn, J. Am. Chem. Soc. 94, 2705 (1972).

14. D. H. Liskow, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. 57, 4509 (1972).
15. G. S. Hammond, J. Am. Chem. Soc. 77, 334 (1955).
16. D. R. Stull and H. Prophet, JANAF Thermochemical Tables, Second Edition, NSRDS-NBS 37 (Superintendent of Documents, Washington, D.C., 1971).

TABLE I. Effect of polarization basis functions on the transition state and barrier height for $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$. See Figure 1 for a definition of the geometrical parameters employed.

Calculation	Transition State Geometry			Total Energy (hartrees)	Barrier Height (kcal/mole)	Exothermicity (kcal/mole)
	R(bohrs)	r(bohrs)	θ (degrees)			
Double Zeta SCF	2.52	1.69	124.8	-39.9990	25.7	4.1
Double Zeta CI ^a	2.64	1.70	126.5	-40.1040	15.5	5.4
Double Zeta Plus Polarization	2.51	1.69	124.4	-40.0181	25.5	3.8

^a Reference 1. In the present work a more dense grid ($R = 2.3, 2.4, 2.5, 2.6, 2.7$; $r = 1.5, 1.6, 1.7, 1.8, 1.9$; $\theta = 110^\circ, 120^\circ, 130^\circ$) was employed than in reference 1. As a result the SCF barrier found here (25.7 kcal/mole) is slightly greater than that (25.1 kcal/mole) reported earlier.¹

TABLE II. Summary of $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ calculations with nonzero values of the angles α , β , γ , and δ defined in Figures 2-5. Each line represents the result of a constrained transition state geometry determination. Note that the effect of electron correlation is to lower all these barriers by ~ 11 kcal/mole.

α	β	γ	δ	R(bohrs)	r(bohrs)	θ	Barrier Height (kcal/mole)
0°	0°	0°	0°	2.52	1.69	124.8°	25.7
20°	0°	0°	0°	2.54	1.70	124.8°	26.7
0°	20°	0°	0°	2.53	1.70	124.8°	26.9
0°	45°	0°	0°	2.55	1.75	124.3°	32.0
0°	0°	10°	0°	2.51	1.71	124.2°	27.1
0°	0°	0°	10°	2.53	1.69	124.7°	25.8
0°	0°	0°	20°	2.53	1.70	124.6°	26.1
0°	0°	0°	40°	2.53	1.72	123.9°	27.4

TABLE III. Geometry predictions for $\text{CH}_2(^3\text{B}_1) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3$,
and the transition state connecting them.

	$\text{CH}_2(^3\text{B}_1) + \text{CH}_4$	Saddle Point	$\text{CH}_3 + \text{CH}_3$
R(bohrs)	∞	2.50	2.06
r(bohrs)	2.06	2.50	∞
θ	130.3°	122.1°	120°
ϕ	109.4°	105.2°	90°

Figure Captions

- Figure 1. Coordinate system used in original¹ study of $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$.
- Figure 2. Illustration of the angle α used in constrained saddle point studies of $\text{CH}_2(^3\text{B}_1) + \text{H}_2$.
- Figure 3. Illustration of the angle β used in constrained saddle point studies of $\text{CH}_2(^3\text{B}_1) + \text{H}_2$.
- Figure 4. Illustration of the angle γ used in constrained saddle point studies of $\text{CH}_2(^3\text{B}_1) + \text{H}_2$. Note that if γ were constrained to be e.g., 20° along the entire path from reactants to products, the resulting CH_3 radical would be vibrationally excited.
- Figure 5. Illustration of the angle δ used in constrained saddle point studies of $\text{CH}_2(^3\text{B}_1) + \text{H}_2$.
- Figure 6. Coordinate system used to study the abstraction reaction $\text{CH}_2(^3\text{B}_1) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3$.

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

XBL759-3994

Figure 6

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