Transition States for the Abstraction Reactions of Triplet Methylene with Hydrogen and Methane[1]

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Abstract: The transition states and barrier heights for the reactions $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$ and $CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3$ have been predicted using nonempirical electronic structure theory. Earlier work on the $CH_2(^3B_1) + H_2$ reaction has been extended by (a) the addition of polarization functions to the earlier double ζ 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/mol. For the methane abstraction reaction a barrier height ~7 kcal/mol 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.

We have recently suggested[2a] 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 predicted[2b] that $CH_2(^3B_1)$ should not react (via abstraction) with saturated hydrocarbons due to sizable activation energies (~15 kcal/mol). 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-order[4] (BEBO) calculations of Carr[5] 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/mol, respectively.

For the reactions of triplet methylene with hydrogen and methane, semiempirical calculations have been carried out[6] 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/mol 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 semiempirical 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 $CH_2(^3B_1) + H_2$ reaction. In addition the validity of $CH_2 + H_2$ as a prototype is tested via ab initio calculations on the $CH_2(^3B_1) + CH_4$ reactions.

$CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$

Perhaps the most serious deficiency in our earlier calculations[1] was the absence of polarization functions in the chosen basis set. For example, in the case of $F + H_2 \rightarrow HF + H$, polarization functions lower the predicted barrier height[8] from 5.7 to 1.7 kcal/mol. Therefore we added to the earlier double ζ 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 for point group C_{2v}), $xze^{-\alpha r^2}$, and $yze^{-\alpha r^2}]$ 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 $\alpha = 1.0$ was 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/mol lower than the previous double ζ result and the transition state geometries are nearly indistinguishable.

Note that we have not carried out configuration interaction (CI) calculations using the double ζ 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/mol. Our best estimate is that the true barrier height for $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$ is in the range 10-15 kcal/mol.

The remainder of the new calculations on $CH_2(^3B_1) + H_2$ was carried out to explore the importance of degrees of freedom not previously considered. In light of the above C_{2v} results, these calculations were performed using the original[2a] double ζ basis set. In the previous work[2a] 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/mol, 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/mol. 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/mol greater than the original C_{2v} approach. Although this adds to the justification of the 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 $\beta = 20°$ and $\beta = 45°$. Although the energy is only slightly higher (1.2 kcal/mol) for $\beta = 20°$, a more sizable increase (6.3 kcal/mol) is found for $\beta = 45°$.

The angle γ, depicted in Figure 4, corresponds to rotating

Table I. Effect of Polarization Basis Functions on the Transition State and Barrier Height for $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$[a]

Calculation	Transition state geometry			Total energy, hartrees	Barrier height, kcal/mol	Exothermicity, kcal/mol
	R, bohrs	r, bohrs	θ, deg			
Double ζ SCF	2.52	1.69	124.8	−39.9990	25.7	4.1
Double ζ CI[b]	2.64	1.70	126.5	−40.1040	15.5	5.4
Double ζ plus polarization	2.51	1.69	124.4	−40.0181	25.5	3.8

[a] See Figure 1 for a definition of the geometrical parameters employed. [b] Reference 2a. 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; θ = 110°, 120°, 130°) was employed than in ref 2a. As a result the SCF barrier found here (25.7 kcal/mol) is slightly greater than that (25.1 kcal/mol) reported earlier.[2a]

Table II. Summary of $CH_2(^3B_1) + H_2$ Calculations with Nonzero Values of the Angles α, β, and δ Defined in Figures 2-5[a]

α, deg	β, deg	γ, deg	δ, deg	R, bohrs	r, bohrs	θ, deg	Barrier height, kcal/mol
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

[a] 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/mol.

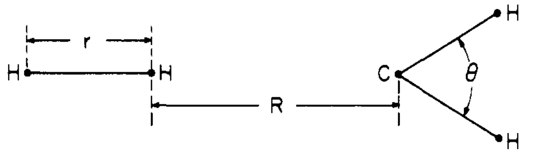

Figure 1. Coordinate system used in the original[2a] study of $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$.

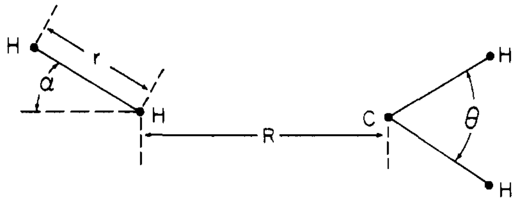

Figure 2. Illustration of the angle α used in constrained saddle point studies of $CH_2(^3B_1) + H_2$.

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 γ = 10°, the constrained saddle point lies 1.4 kcal/mol 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 δ = 10° yields a barrier only 0.1 kcal/mol higher than the original one. Further, δ = 20° raises the energy by an additional 0.3 kcal and δ = 40° yields a barrier of 27.4 kcal/mol. Thus the potential energy surface is very flat in this region, a result predicted intuitively by Hoffmann[10] 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/mol), 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.

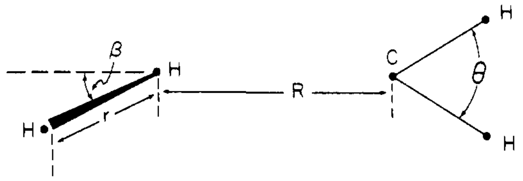

Figure 3. Illustration of the angle β used in constrained saddle point studies of $CH_2(^3B_1) + H_2$.

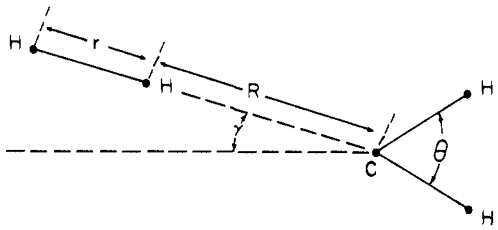

Figure 4. Illustration of the angle γ used in constrained saddle point studies of $CH_2(^3B_1) + H_2$. Note that if γ were constrained to be, e.g., 20° along the entire path from reactants to products, the resulting CH_3 radical would be vibrationally excited.

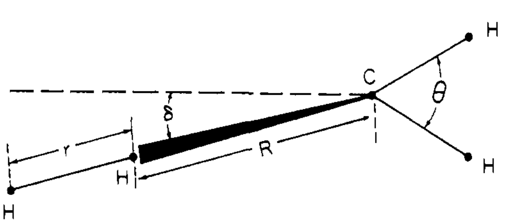

Figure 5. Illustration of the angle δ used in constrained saddle point studies of $CH_2(^3B_1) + H_2$.

$CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3$

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.

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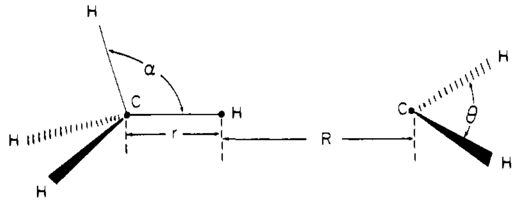

Figure 6. Coordinate system used to study the abstraction reaction $CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3$.

The same double ζ basis set[2a] used for $CH_2 + H_2$ was used for $CH_2 + CH_4$. Based on the present confirmation of the C_{2v} transition state (Figure 1) for $CH_2(^3B_1) + H_2$, the present geometry search was limited to four variables, depicted in Figure 6. Of these, the methylene angle θ is identical with that used for $CH_2 + H_2$. R plays an analogous role, but is now the methylene carbon-leaving hydrogen separation. Also playing an analogous role to the $CH_2 + H_2$ 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 $CH_2(^3B_1) + CH_4$, 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

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

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

$$\frac{\theta_M{}^{SP}}{\theta_M{}^{RX}} = \frac{\theta_H{}^{SP}}{\theta_H{}^{RX}}$$

or

$$\frac{\theta_M{}^{SP}}{\theta_M{}^{PR}} = \frac{\theta_H{}^{SP}}{\theta_H{}^{PR}}$$

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 $\theta = 124.8°$. As will be seen, these simple predictions are quite accurate.

Our principal result is an SCF prediction of 33.3 kcal/mol for the barrier height. If we allow, analogous to our findings for $CH_2 + H_2$, a correlation energy lowering of 10-15 kcal/mol, the final prediction is $E_a \approx 18\text{-}23$ 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 $CH_2(^3B_1) + H_2$, the SCF and CI saddle point structures were quite similar.[2a] This, combined with the large body[12] of ab initio structure predictions for stable molecules, suggests that the present transition state prediction (see Table III) should be quite reliable. Carr[5] and Dewar[6] do not report transition state geometries from the BEBO and MINDO studies. As expected[15] for a nearly thermoneutral reaction, the transition state lies about halfway between reactants and products. The reaction is actually exothermic by 5 ± 1 kcal/mol,[16] while the present calculations predict −0.5 kcal/mol for this quantity.

Table III. Geometry Predictions for $CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3$, and the Transition State Connecting Them

	$CH_2(^3B_1) + CH_4$	Saddle point	$CH_3 + CH_3$
R, bohrs	∞	2.50	2.06
r, bohrs	2.06	2.50	∞
θ, deg	130.3	122.1	120
ϕ, deg	109.4	105.2	90

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 $CH_3NC \rightarrow CH_3CN$ isomerization, where MINDO/2 predicts[13] a spurious[14] 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 semiempirical methods.

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References and Notes

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