

# Reaction Pathways for the Triplet Methylene Abstraction $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}^{1a}$

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**Abstract;** A nonempirical quantum mechanical study of the reaction of triplet methylene with molecular hydrogen has been carried out. A contracted Gaussian basis set of double  $\zeta$  quality was employed. Following the determination of each self-consistent-field wave function, configuration interaction was performed including all singly and doubly excited configurations (a total of 649). The potential surface was studied in three dimensions and a total of 780 points computed. From these data, several approximations to the minimum energy path have been computed and compared. The reaction exothermicity is computed to be 5.37 kcal/mol, in good agreement with experiment, 4.5 kcal/mol. The predicted barrier height is 15.5 kcal/mol, a result consistent with the lack of any observed reaction between  $\text{CH}_2(^3\text{B}_1)$  and  $\text{H}_2$  at 300°K. The predicted barrier is 4.2 kcal/mol less than that obtained by Carr using the bond energy bond order (BEBO) method. The saddle point geometry is predicted to be  $\text{H-H} = 0.90 \text{ \AA}$ ,  $\text{H-C} = 1.40 \text{ \AA}$ , and  $\angle \text{HCH} = 126.5^\circ$ .

Methylene reactions have become the topic of an increasing number of experimental<sup>2-16</sup> and theoretical<sup>17-26</sup> studies in recent years. And in fact the experi-

mental studies have already yielded a wealth of valuable information about methylene reactions. For example, it now seems firmly established that triplet methylene abstracts hydrogen atoms from saturated hydrocarbons while the analogous reactions with singlet methylene yield insertion into CH bonds. One should note, however, that the interpretation of these experiments can be somewhat perilous. This is because in most cases the procedure used involves the photolysis of either ketene or diazomethane in the presence of the species with which a methylene reaction is desired. Although the elementary reactions of singlet and triplet methylene with the desired species will certainly occur to some degree, it is equally clear that a number of other chemical reactions may be taking place, e.g., the reaction of methylene with ketene to give ethylene and carbon monoxide. Ideally, one would like to be able to cross a beam of triplet or singlet methylenes with a beam of the other reactant, e.g.,  $\text{H}_2$ . Even though a methylene crossed molecular beam experiment may sound unlikely, there does appear to be a real possibility<sup>27</sup> that such an experiment will be carried out within the next several years. The potential importance of experiments of this kind with respect to the discernment of the dynamics of methylene reactions can hardly be over-emphasized.

In a similar manner, the theoretical studies of methylene reactions, while being something less than the ultimate, have significantly advanced our understanding of the chemistry of this short-lived intermediate. For example, the extended Hückel calculations of Hoffmann<sup>20</sup> and, to a lesser degree, the MINDO work of Dewar<sup>25</sup> have given support to the contested two-step mechanism of Benson<sup>28</sup> for the singlet methylene insertion into methane.

The prototype methylene reaction is  $\text{CH}_2 + \text{H}_2$ , hydrogen being the simplest partner molecule for which both abstraction and insertion reactions might occur.

(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) Department of Chemistry, University of California; (c) Lawrence Livermore Laboratory; (d) M. H. Fellow; (e) Department of Chemistry and Lawrence Berkeley Laboratory; (f) Alfred P. Sloan Fellow.

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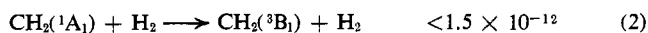
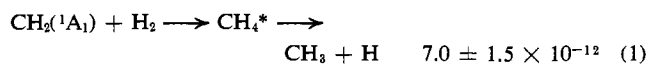
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Among the several experimental studies<sup>29-37</sup> of this reaction, the most recent is that of Braun, Bass, and Pilling.<sup>37</sup> With rate constants at 298°K given in cubic centimeters per molecule second, they summarize their results as follows.



In fact, Braun, *et al.*, were unable to observe any reaction of triplet methylene with hydrogen at 300°K, and the figure given is an upper limit to the true rate constant. Recently, Carr<sup>22</sup> has been able to rationalize this <sup>3</sup>B<sub>1</sub> nonreactivity using Johnston and Parr's empirical bond energy bond order method<sup>38</sup> for the calculation of activation energies. Carr predicts the activation energy for CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) + H<sub>2</sub> → CH<sub>3</sub> + H to be quite high, 19.7 kcal/mol. Other computed abstraction activation energies ranged from 7.9 kcal/mol for C<sub>3</sub>H<sub>6</sub> to 44.2 kcal/mol for HCN. It is worth noting that Dewar's predicted activation energy<sup>25</sup> of 3.8 kcal/mol for CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) + CH<sub>4</sub> → 2CH<sub>3</sub> is qualitatively different from that of Carr, 25.6 kcal/mol.

Our *ab initio* theoretical study concerns the apparently slow CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) + H<sub>2</sub> abstraction reaction. The method used, which explicitly considers electron correlation, is analogous to that adopted in our previous study<sup>39</sup> of isolated CH<sub>2</sub>. That study unequivocally predicted the nonlinearity of methylene at a time when a linear structure had been almost universally accepted. The two primary goals of the present study were (a) to obtain a reliable (±5 kcal/mol) prediction of the activation energy and (b) to map out the minimum-energy path for this simple reaction.

### Theoretical Approach

A double ζ basis set of contracted Gaussian functions<sup>40</sup> was used in the present work. For the carbon atom, Huzinaga's (9s 5p) primitive Gaussian basis<sup>41</sup> was contracted to (4s 2p) following Dunning.<sup>42</sup> In analogous fashion a (4s/2s) basis was chosen for each H atom. The hydrogen basis functions were scaled by a factor of 1.2; *i.e.*, each Gaussian exponent α was multiplied by 1.44.

For C<sub>2v</sub> approaches of the hydrogen molecule to <sup>3</sup>B<sub>1</sub>

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methylene, the self-consistent-field (SCF) wave function is of the form

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1 1b_1 \quad (4)$$

The SCF wave functions were obtained using a method recently developed by Davidson.<sup>43</sup> In addition we have computed configuration interaction wave functions which include all (except that the 1a<sub>1</sub> orbital is always doubly occupied) singly and doubly excited configurations with respect to this SCF reference state. However, we have deleted those doubly excited configurations which do not retain the open-shell spin coupling of the reference configuration. The deleted configurations *i* have identically zero Hamiltonian matrix elements *H*<sub>1*i*</sub> with the SCF configuration.<sup>44,45</sup> A total of 649 configurations were included in the calculations.

Fortunately, the same SCF wave function (eq 4) dissociates properly to SCF wave functions for the products CH<sub>3</sub> + H. Hence, the true wave function should be reasonably well described by a single configuration along the entire minimum energy path. This being the case, our single and double excitation CI should be nearly comparable (~95-98% of the correlation energy attainable from the chosen basis) to a full CI within the valence shell.<sup>40</sup> Three natural orbital iterations<sup>46</sup> were used in each calculation. Although in general such iterations tend to accelerate (lower total energy with fewer configurations) convergence of the CI expansion, the total energy was lowered relatively little (typically 0.003 hartree) in the present cases, since the CI was initially nearly complete in a practical sense.

The accuracy of the potential surface should fall somewhere between that of our two surfaces<sup>47,48</sup> for F + H<sub>2</sub> → FH + H. Although the basis set here is analogous to that used in our preliminary study,<sup>47</sup> a more thorough level of CI was used in the present study. Both the F + H<sub>2</sub> studies indicated the necessity of describing correlation effects in order to reliably predict the barrier height and exothermicity. Finally, we note that the level of theory used in the present study seems<sup>49</sup> to predict equilibrium bond distances with a reliability of 0.03 Å and bond angles to 2°.

### Geometries Considered

Intuition suggests that the minimum energy path for CH<sub>2</sub> + H<sub>2</sub> should occur for a planar configuration in which the H-H molecule falls on the line bisecting the HCH methylene bond angle. However, Hoffmann has noted<sup>50</sup> that the surface may be rather flat with respect to a bending of the H<sub>2</sub> out of this plane. Such a C<sub>2v</sub> reaction path is also the only path fully consistent with the MINDO results of Bodor, Dewar, and Wasson<sup>25</sup> for the analogous reaction CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) + CH<sub>4</sub> → 2CH<sub>3</sub>.

Therefore, we have restricted our study to the C<sub>2v</sub> coordinate system shown in Figure 1. In addition, the two methylene CH distances have been frozen at 2.06

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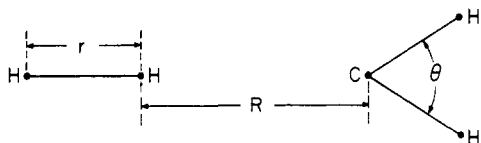
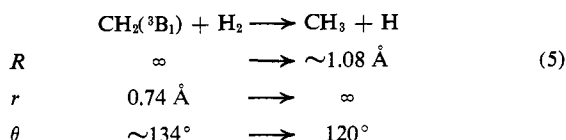


Figure 1. Coordinate system for  $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ .

bohrs = 1.090 Å. The remaining geometrical parameters are (a)  $R$ , the distance between the carbon atom and the closer of the two H atoms in  $\text{H}_2$ , (b)  $r$ , the H-H separation in  $\text{H}_2$ , and (c)  $\theta$ , the methylene bond angle. As we go from reactants to products, these variables should change as follows.



This three-dimensional potential surface has been determined at 780 points. The  $R$  values considered were 100.0, 10.0, 6.0, 5.0, 4.0, 3.0, 2.8, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.06, and 2.0 bohrs. The H-H separation  $r$  took the values 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 5.0, 6.0, 10.0, and 100.0 bohrs. Bond angles  $\theta$  considered were 110, 120, 130, and  $140^\circ$ . It is apparent that not all points on this  $15 \times 19 \times 4 = 1140$  point grid were computed. Many points which were clearly far from the minimum energy path were omitted. However, near the saddle point, a number of additional  $R$  values were used. The 780 computed total energies, in hartrees and kilocalories per mole relative to separated  $\text{CH}_2 + \text{H}_2$ , are given in the appendix to our complete report<sup>51</sup> of this research.

Table I summarizes our results for the reactants

Table I. Geometries and Total Energies of Reactants and Products

$\text{CH}_2(^3\text{B}_1) + \text{H}_2$
$E = -40.12866$ hartrees
$r(\text{CH}) = 1.090 \text{ \AA}$ (assumed)
$\theta(\text{HCH}) = 134.1^\circ$
$r(\text{HH}) = 0.748 \text{ \AA}$
$\text{CH}_3 + \text{H}$
$E = -40.13722$ hartrees
$r(\text{CH}) = 1.094 \text{ \AA}$
$\theta(\text{HCH}) = 120.2^\circ$

(separated  $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ ) and products (separated  $\text{CH}_3 + \text{H}$ ). The former results were obtained at  $R = 100.0$  bohrs and the latter at  $r = 100.0$  bohrs.

The methylene bond angle is predicted to be  $134.1^\circ$ , which is nearly identical with the  $134^\circ$  value obtained from the best available theoretical calculation<sup>52</sup> and consistent with experiment<sup>53</sup>  $136 \pm 5^\circ$ . The predicted  $\text{H}_2$  equilibrium separation is  $0.007 \text{ \AA}$  longer than the exact result,<sup>54</sup>  $0.7414 \text{ \AA}$ .

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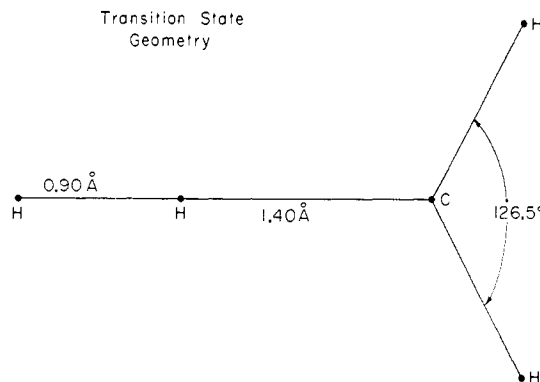


Figure 2. Transition state geometry for  $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ .

Although the two methylene CH distances were everywhere constrained to be  $2.060$  bohrs =  $1.090 \text{ \AA}$ , the third CH bond distance of the methyl radical is a variable, determined to be  $1.094 \text{ \AA}$ . In addition, our calculations predict the methylene bond angle to be  $120.2^\circ$ . However, this bond angle is uncertain by perhaps  $0.2^\circ$ , since the calculations were carried out at  $10^\circ$  intervals. Hence, although slightly unsymmetrical, our methyl radical structure is essentially the same as the planar experimental  $\text{CD}_3$  structure of Herzberg<sup>55</sup> with  $r_0(\text{CD}) = 1.079 \text{ \AA}$ .

The reaction exothermicity is  $0.00855$  hartree =  $5.37$  kcal/mol, in very good absolute agreement with the experimental value given by Carr,<sup>22</sup>  $4.5$  kcal/mol. The latter value is obtained from  $D_e(\text{H-H}) = 109.5$  kcal/mol and  $D_e(\text{CH}_2\text{-H}) = 114.0$  kcal/mol.

The saddle point or transition state<sup>56</sup> is the energetically highest point on a continuous path connecting  $\text{CH}_2 + \text{H}_2$  with  $\text{CH}_3 + \text{H}$ . If several such points and paths occur, the true saddle point for the reaction is that which is energetically lowest. The saddle point for our three-dimensional potential energy surface was located by using the stationary property

$$\partial E / \partial R = \partial E / \partial r = \partial E / \partial \theta = 0 \quad (6)$$

With the obvious exception of the reactants, products, and long-range attractions, the predicted saddle point appears to be the only point on the *ab initio* surface which satisfies eq 6.

The predicted saddle point, seen in Figure 2, occurs at  $R = 2.640$  bohrs =  $1.397 \text{ \AA}$ ,  $r = 1.702$  bohrs =  $0.900 \text{ \AA}$ , and  $\theta = 126.5^\circ$ . This geometry is intermediate between that of the products and reactants; the H-H separation is  $0.152 \text{ \AA}$  or  $20\%$  longer than in  $\text{H}_2$ , while the H-C separation is  $0.303 \text{ \AA}$  or  $28\%$  longer than in the isolated methyl radical. The fact that the transition state geometry is somewhat closer to the reactants than the products is consistent with Hammond's idea<sup>57</sup> that, in a highly exothermic reaction, the transition state should resemble the reactants.

The *ab initio* total energy at the saddle point is  $-40.10400$  hartrees, which lies  $15.5$  kcal/mol above  $\text{CH}_2(^3\text{B}_1) + \text{H}_2$ . This  $15.5$  kcal/mol barrier does not, of course, reflect the zero-point vibrational energies of the re-

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actants and transition state. The barrier height defined in this way is sometimes called the classical activation energy.<sup>58</sup> The Arrhenius activation energy for  $\text{CH}_2(^3\text{B}_1) + \text{H}_2$  has not been measured, and the only related experimental information is the finding of Braun, Bass, and Pilling<sup>37</sup> that no reaction was observed at 300°K. Our 15.5-kcal/mol barrier is sufficiently large to be consistent with their negative finding. As noted earlier, Carr<sup>22</sup> has used the empirical BEBO method to predict a barrier height of 19.7 kcal/mol. Although it is impossible to place error bars on our theoretical barrier height, based on earlier work,<sup>46,47</sup> we intuitively feel that the 15.5-kcal/mol result should be within 5 kcal/mol of the exact result. Thus our study gives further<sup>59</sup> evidence of the usefulness of the BEBO method. The only example we are familiar with in which BEBO fails seriously is the  $\text{F} + \text{HF} \rightarrow \text{FH} + \text{F}$  reaction. There BEBO predicts a barrier of 6 kcal/mol,<sup>60</sup> while the best *ab initio* calculations<sup>61</sup> imply a barrier  $\geq 18$  kcal/mol.

On the basis of our earlier work on the radical plus diatom reactions<sup>47,48,61,62</sup>  $\text{F} + \text{H}_2$ ,  $\text{H} + \text{F}_2$  and  $\text{F} + \text{HF}$ , we were skeptical of the ability of single configuration SCF wave functions to describe the  $\text{CH}_2(^3\text{B}_1) + \text{H}_2$  potential surface. However, from a theoretical point of view, any information on the suitability of the Hartree-Fock approximation with respect to such reactions is extremely valuable. Therefore, the relative energies and geometries of the reactants, saddle point, and products were obtained from the SCF potential surface. The calculated exothermicity for  $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$  was found to be 4.84 kcal/mol, which is actually in somewhat better agreement with experiment,<sup>21</sup>  $\sim 4.5$  kcal/mol, than the CI result, 5.37 kcal/mol. However, the barrier height is computed to be 25.1 kcal/mol, or 9.6 kcal/mol higher than the CI result. Although the barrier height is not known experimentally, our previous experience<sup>47,48,61,62</sup> would suggest that it may be close to or slightly lower than the CI result and hence that the SCF barrier may be much too high. The SCF saddle point geometry is  $R = 2.53$  bohrs,  $r = 1.69$  bohrs, and  $\theta = 124.8^\circ$ . Thus the SCF and CI transition state geometries are quite similar, much more so than was the case<sup>46,47,61</sup> for  $\text{F} + \text{H}_2$  and  $\text{H} + \text{F}_2$ .

### Reaction Pathways

In both textbooks and the literature, one frequently finds terms such as "reaction coordinate," "reaction path," "path of least energy," and "minimum energy path" used interchangeably. We find this situation unfortunate, since there are at least two distinct procedures by which such a path might be obtained.

The most frequently used procedure is to choose a "reaction coordinate," some geometrical parameter that varies significantly during the course of reaction. For the  $\text{CH}_2(^3\text{B}_1) + \text{H}_2$  reaction, either  $R$  (which goes from  $\infty$  to 1.094 Å) or  $r$  (which goes from 0.748 Å to  $\infty$ ) would be reasonable choices.  $\theta$ , which goes from

134 to 120°, would probably not be a very good choice, since it does not undergo a large change during the reaction. Given a value of the "reaction coordinate," one finds a point on the "reaction path" by minimizing the total energy with respect to all other geometrical parameters.<sup>63</sup> Hereafter, our use of the terms "reaction coordinate" and "reaction path" will be strictly as defined above.

Under favorable conditions, a reaction coordinate will vary monotonically along the reaction path, and the energetically highest point on the reaction path will occur near the true saddle point. However, there are many exceptions to this favorable behavior, an especially interesting example being the MINDO treatment of the interconversion of cyclobutene and butadiene.<sup>64</sup> Even if a reaction path does pass close by the saddle point, there are situations in which the reaction path will appear unrealistic. These situations generally occur when a small change in the chosen reaction coordinate is accompanied by large changes in other geometrical parameters. One example of such behavior is noted by Dobson, Hayes, and Hoffmann<sup>20</sup> in their study of  $\text{CH}_2(^1\text{A}_1) + \text{CH}_4$ .

There is at least one procedure<sup>47,56</sup> which defines the reaction pathway (an intentionally vague term) in a far more satisfactory manner. Rather than starting from either reactants or products, this procedure begins with the saddle point. From the saddle point, one follows the gradient  $\vec{\nabla} V$  of the potential energy in the direction of most negative curvature. Following the gradient leads in one direction to reactants and in the other direction to products, and we refer to the resulting path between products and reactants as the "minimum energy path." Note that although this definition is dependent on choice of coordinate system one expects such dependence to be in general unimportant.

Table II gives the reaction path for reaction coordinate  $R$ , the reaction path for reaction coordinate  $r$ , and the minimum energy path. Let us first describe the "minimum energy path," since this is the mathematical embodiment of what the chemist visualizes as the reaction pathway. Along the minimum energy path, all three variables  $R$ ,  $r$ , and  $\theta$  vary smoothly. On the reactants side, prior to  $R = 3.0$ ,  $R$  is changing rapidly relative to the rather small changes in  $r$  and  $\theta$ . Around the saddle point, say between  $R = 3.0$  and  $r = 2.0$ , all three geometrical parameters are changing significantly. Finally, from  $r = 2.0$  to 100, small changes in  $R$  and  $\theta$  accompany large changes in  $r$ .

Inspection of Table II makes it quite apparent that the choice of  $R$  as a reaction coordinate is appropriate for the reactant side of the minimum energy path, but not for the product side. The problem is that the value of  $r$  lurches from 1.756 to 6.0 as  $R$  changes from 2.6 to 2.5. As the minimum energy path shows, the "correct" value of  $r$  for  $R = 2.5$  is  $\sim 1.81$  bohrs.

An opposite, but even more serious, breakdown occurs with respect to the choice of  $r$  as reaction coordinate. That is, on the product side ( $r > 2.0$  bohrs), the reaction path obtained using  $r$  as reaction coordinate is quite similar to the minimum energy path. However, this reaction path also lurches, between  $r = 1.9$

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**Table II.** Reaction Paths for  $\text{CH}_2(^3\text{B}_1) + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}^a$ 

Minimum energy path				$R$ reaction coordinate				$r$ reaction coordinate			
$R$	$r$	$\theta$	$E$	$R$	$r$	$\theta$	$E$	$R$	$r$	$\theta$	$E$
100.0	1.414	134.1	0.00	100.0	1.414	134.1	0.00	6.0	1.4	134.1	-0.02
6.0	1.412	134.1	-0.04	6.0	1.412	134.1	-0.04				
5.0	1.412	133.9	0.50	5.0	1.412	133.9	0.50				
4.5	1.412	133.8	1.35	4.5	1.412	133.8	1.35				
4.0	1.420	133.3	3.39	4.0	1.420	133.3	3.39				
3.8	1.428	132.9	4.66	3.8	1.428	132.9	4.66				
3.6	1.440	132.4	6.22	3.6	1.440	132.4	6.22				
3.4	1.452	131.9	8.05	3.4	1.452	131.9	8.05				
3.2	1.468	131.2	10.27	3.2	1.468	131.2	10.27				
3.0	1.524	130.0	12.72	3.0	1.504	130.0	12.63	6.0	1.5	134.1	0.81
2.8	1.612	128.1	14.82	2.8	1.572	128.2	14.70				
2.7	1.660	127.2	15.35	2.7	1.640	127.2	15.35	6.0	1.6	134.1	3.40
2.640	1.702	126.5	15.48	2.65	1.692	126.6	15.48	6.0	1.7	134.1	7.13
2.514	1.80	125.2	14.92	2.6	1.756	126.0	15.41	6.0	1.8	134.1	11.64
2.394	1.90	123.5	13.23	2.5	6.0	123.6	8.52	2.268	1.9	122.6	12.57
2.301	2.0	122.4	11.28	2.4	6.0	122.6	3.64	2.175	2.0	122.0	10.87
2.198	2.2	121.6	7.89	2.3	6.0	122.0	-0.54	2.155	2.2	121.3	7.68
2.140	2.4	120.9	4.82	2.2	6.0	121.3	-3.66	2.125	2.4	120.9	4.87
2.110	2.6	120.6	2.52	2.1	6.0	120.5	-5.29	2.103	2.6	120.6	2.54
2.095	2.8	120.4	0.63					2.090	2.8	120.3	0.63
2.085	3.0	120.3	-0.89					2.083	3.0	120.3	-0.89
2.073	3.5	120.2	-3.37					2.073	3.5	120.2	-3.37
2.068	4.0	120.2	-4.58					2.068	4.0	120.2	-4.58
2.068	5.0	120.2	-5.33					2.068	5.0	120.2	-5.33
2.068	6.0	120.2	-5.41	2.06	6.0	120.2	-5.40	2.068	6.0	120.2	-5.41
2.068	100.0	120.2	-5.37					2.068	100.0	120.2	-5.37

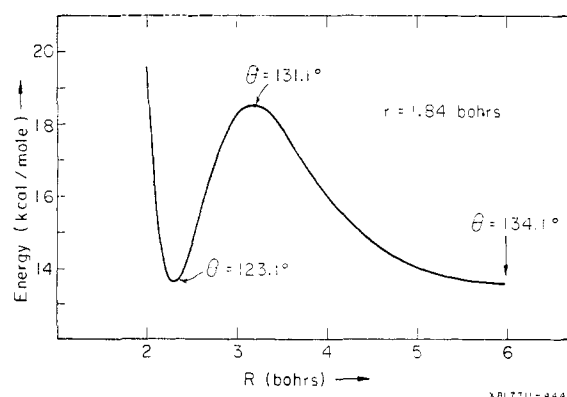
<sup>a</sup> Bond distances are in bohr radii, bond angles in degrees, and energies in kilocalories per mole.

and 1.8, and is inapplicable on the reactants side of the saddle point. Hence the saddle point position is not correctly predicted. In fact, inspection of Table II would suggest that we have found a lower energy ( $\sim 13$  kcal barrier) route from  $\text{CH}_2 + \text{H}_2$  to  $\text{CH}_3 + \text{H}$ . The problem lies with the discontinuous change of  $R$  and  $\theta$  along this reaction path.

Recall that a point on the above reaction path is obtained, for a particular value of  $r$ , by minimizing the total energy with respect to  $R$  and  $\theta$ . Unfortunately, when  $r$  is in the range 1.6–1.9 bohrs, there are two distinct relative minima. The first occurs for  $R \approx 2.3$  bohrs and  $\theta \approx 123^\circ$  and the second for  $R \approx 6.0$  bohrs and  $\theta \approx 134^\circ$ . When  $r$  is greater than 1.84 bohrs, the first minimum is the lower, but for  $r < 1.84$ , the second minimum is lower. At  $r = 1.84$ , the two minima both have depth 13.59 kcal/mol, as illustrated in Figure 3. Hence the reaction path based on  $r$  as reaction coordinate has a discontinuity at  $r = 1.84$ . This gives the mistaken impression that the barrier height is 13.59 kcal/mol. In fact, as Figure 3 shows, a continuous reaction path between  $r = 1.841$  and 1.839 would have to pass over a barrier of 18.50 kcal/mol.

If one must choose a reaction coordinate, a reasonable choice is  $(r - R)$ , which changes in a fairly smooth manner all along the minimum energy path. Although this conclusion is by no means unanticipated, the quantitative analysis made possible by Table II seems to be of considerable value.

Finally, we must point out that there is no necessary relationship between the minimum energy path and the dynamics of a chemical reaction. That is, for any par-



**Figure 3.** Illustration of the discontinuity of the reaction path obtained by choosing  $r$  as reaction coordinate. Each point on the curve corresponds to the value of  $R$  shown on the  $x$  axis,  $r = 1.84$  bohrs, and the value of  $\theta$  for which the potential energy is minimized.

ticular classical trajectory, the probability of following the minimum energy path is zero. Nevertheless, such a minimum energy path may be as close as one can come in a theoretical sense to the chemist's notion of a reaction mechanism. A reasonable alternative to this definition would be an "average" or "most probable" classical trajectory for the conditions of interest.

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