Concerted Non-Least-Motion Pathway for the Singlet Methylene Insertion Reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$

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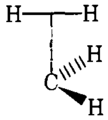
Abstract: The least-motion insertion reaction of singlet methylene into molecular hydrogen is forbidden in the sense of Woodward and Hoffmann and has been predicted to involve a barrier height of ~27 kcal/mol. Here ab initio electronic structure theory has been applied to the non-least-motion features of the same potential energy surface. A double zeta basis set of contracted Gaussian functions was used in conjunction with moderately large (2120 configurations) configuration interaction (CI) techniques. For an initial C_s point group approach of the qualitative type



theory predicts no barrier or activation energy at all. This result is illustrated with the aid of contour maps showing several cuts through the potential energy hypersurface. It is also noted that the single determinant self-consistent field (SCF) method does not properly describe several of the main features of this concerted non-least-motion pathway.

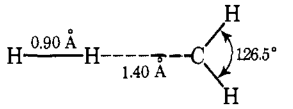
The simplest system allowing the possibility of both carbene triplet abstraction

$$CH_2(^3B_1) + H_2 \rightarrow CH_3 + H \qquad (1)$$

and singlet insertion

$$CH_2(^1A_1) + H_2 \rightarrow CH_4 \qquad (2)$$

reactions is the $CH_2 + H_2$ system.[2] In the anticipation[3] that $CH_2 + H_2$ would serve as a prototype for the reactions of methylene with saturated hydrocarbons, we have made detailed theoretical studies[4,5] of reactions 1 and 2. The triplet insertion reaction is predicted[4] to have the transition-state structure

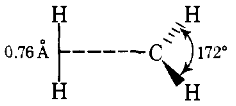


(3)

and a sizable barrier height, 10–15 kcal/mol. The validity of $CH_2 + H_2$ as a prototype has been qualitatively verified[6] for the reaction

$$CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3 \qquad (4)$$

which is predicted to have a transition state analogous to (3) and a barrier height of ~20 kcal. For the singlet insertion reaction 2 only the least-motion pathway has been considered to date[5] and this approach is Woodward–Hoffmann forbidden.[7] As a result, a large barrier (~27 kcal) was predicted, corresponding to the constrained transition state



(5)

Since it seems well established[2] experimentally that at least one of the electronic states of methylene reacts with molecular hydrogen with little or no activation energy, further theoretical work is called for. Actually, the direction seems rather apparent from previous semiempirical studies.[8,9] For the

$$CH_2(^1A_1) + CH_4 \rightarrow C_2H_6 \qquad (6)$$

insertion reaction the groups of Hoffmann and Dewar concur (for the most part) that non-least-motion approaches provide reaction pathways with little or no activation energy. A more recent and more directly relevant semiempirical study is Kollmar's modified CNDO treatment[10] of reaction 2. Allowing consideration of four degrees of freedom, Kollmar predicted a transition state involving small valence angles and a three-center bond, with the activation energy for insertion predicted to be ~5 kcal/mol.

Kollmar's potential surface has taken on special significance since its use by Wang and Karplus[11] in one of the first classical trajectory studies[12] of the dynamics of an organic reaction. However, there is at least one reason to question the quantitative accuracy of the Kollmar surface—namely that it predicts a least-motion barrier height of 13 kcal, compared with the more reliable ab initio result[5] of 27 kcal. In light of the role of reaction 2 as the prototype singlet carbene insertion reaction, it was decided to complete our studies[3-6] of the $CH_2 + H_2$ system by considering the non-least-motion portion of the $CH_2(^1A_1) + H_2$ hypersurface.

Scope of a Theoretical Study

Following the spirit of Kollmar's research,[10] we adopted the coordinate system depicted in Figure 1. Our geometrical parameters R, r, β, and θ are closely related to the four degrees of freedom investigated by Kollmar. Our fifth parameter, α, was constrained by Kollmar to be such that R and r are perpendicular to each other, i.e., $\alpha = 90° - \beta$. Four of the (α, β) values studied most carefully are shown explicitly in Figures 2-5. The $\alpha = 0°$, $\beta = 75°$ combination was also investigated in some detail. Configuration interaction (CI) studies were performed on a total of about 600 points on the five-dimensional potential surface. As will be noted, additional self-consistent field (SCF) studies were carried out to determine the validity of this much simpler theoretical approach.

In the notation of Figure 1, our previous study[5] of the least-motion pathway corresponds to fixing α and β at the (90°, 0°) combination. For that C_{2v} geometry separated $CH_2(^1A_1) + H_2$ is described in the Hartree-Fock or SCF approximation by the single electron configuration

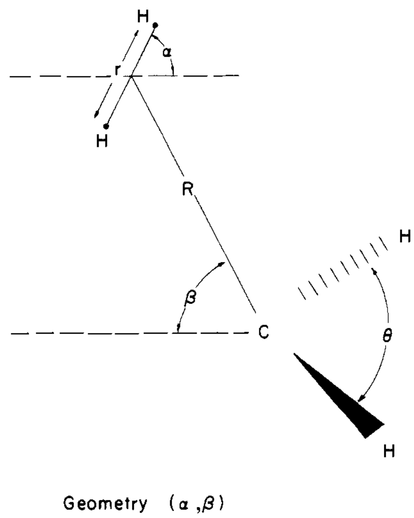


Figure 1. General coordinate system adopted for study of the $CH_2 + H_2$ singlet insertion reaction.

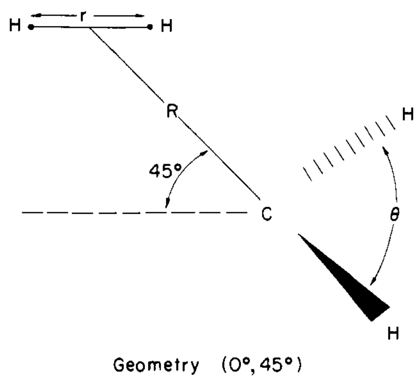


Figure 2. $CH_2(^1A_1) + H_2$ coordinate system for $\alpha = 0°$ and $\beta = 45°$.

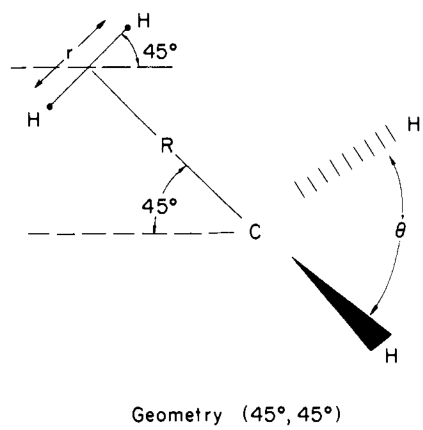


Figure 3. $CH_2(^1A_1) + H_2$ coordinate system for $\alpha = 45°$, $\beta = 45°$.

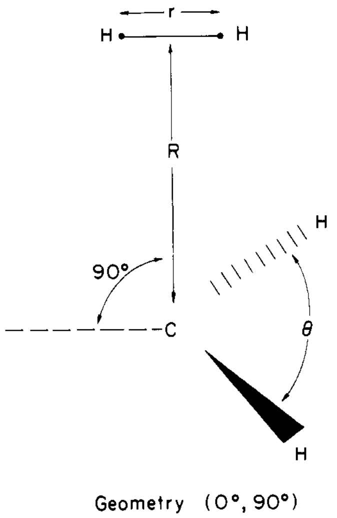


Figure 4. $CH_2(^1A_1) + H_2$ coordinate system for $\alpha = 0°$, $\beta = 90°$.

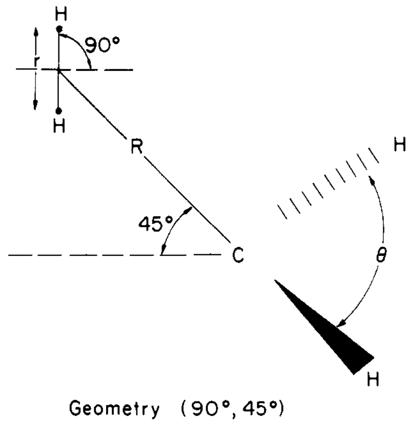


Figure 5. $CH_2(^1A_1) + H_2$ coordinate system for $\alpha = 90°$, $\beta = 45°$.

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1^2 \qquad (7)$$

while CH_4 (after resolution[13] of the T_d orbitals into those of point group C_{2v}) is written as

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 \qquad (8)$$

The fact that electron configurations 7 and 8 differ by one doubly occupied orbital is another way of saying that the (90°, 0°) or least-motion approach is Woodward-Hoffmann forbidden.[7]

However, for the C_s (only a single plane of symmetry, the plane of the page containing Figure 1) geometries considered here, the a_1 and b_1 orbitals become a' and the b_2 orbital becomes a''. Thus both (7) and (8) under resolution into C_s symmetry become

$$1a'^2 2a'^2 1a''^2 3a'^2 4a'^2 \qquad (9)$$

with the implication that single-configuration Hartree-Fock theory is at least in principle capable of describing the non-least-motion reaction. Of course one must remember that the $4a'$ orbital must be allowed (via the SCF procedure) to gradually transform from the $3a_1$ lone-pair orbital of singlet methylene to the $1b_1$ component of the triply-degenerate methane $1t_2$ orbital as the reaction proceeds. From a qualitative viewpoint, the ability of the $4a'$ orbital to smoothly perform this change of character will determine the magnitude of the insertion reaction activation energy.

The present CI treatment begins with a two-configuration SCF description[14] involving (9) plus

$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 \qquad (10)$$

Then all $^1A'$ configurations arising from orbital occupancies differing by one or two electrons from either (9) or (10) were added to yield a total of 2120 configurations. The latter number is obtained with the standard Huzinaga-Dunning Gaussian double zeta basis[15] used in our previous studies.[4,5,14] As before, our goal was to recover 95% or more of the valence shell correlation energy obtainable with this type of basis. A nearly optimum set of molecular orbitals was guaranteed by use of the iterative natural orbital method.[16] As discussed previously[5]

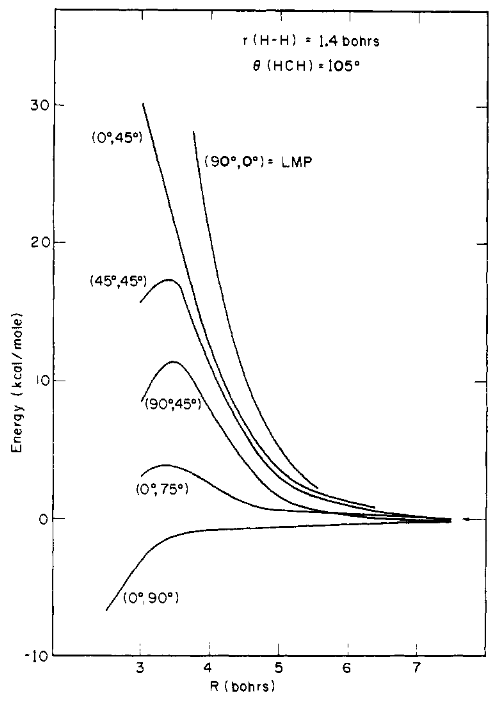


Figure 6. One-dimensional representations of several approaches (α, β) of singlet methylene to H_2. The coordinate system adopted is depicted in Figure 1. These results were obtained using large-scale configuration interaction techniques.

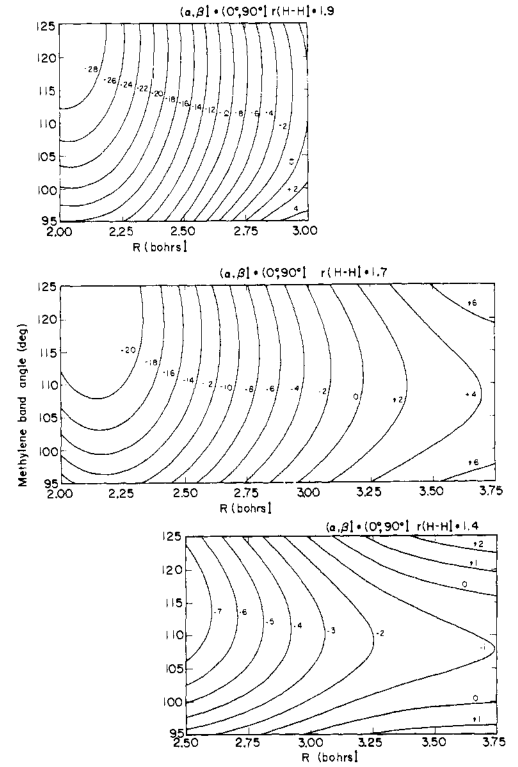


Figure 7. Dependence on R and θ of the $CH_2(^1A_1) + H_2$ hypersurface. Here α, β, and r are constrained to be 0°, 90°, and either 1.4 or 1.7 or 1.9 bohr.

this theoretical procedure gives a good description of the singlet CH_2 and H_2 structures and the reaction exothermicity.

Before proceeding to the potential surface, it is worthwhile to note that the predicted exothermicity of $CH_2(^1A_1) + H_2 \rightarrow CH_2$ is 125.2 kcal/mol. This may be compared with an experimental value of ~120 kcal,[10] which should not necessarily be regarded as ultimate truth due to the uncertainty in CH_2 thermochemical data. In any case, the present result conforms much more closely to experiment than does the value 87 kcal reported by Kollmar.

Each point on the potential energy surface required about 5 min of CDC 7600 computer time. More recently developed CI programs require only about 30 min per point using the Harris Slash Four minicomputer.

Results and Discussion

All four initial approaches sketched in Figures 2-5 are significantly less repulsive than the least-motion pathway (LMP) reported previously.[5] This is shown clearly in Figure 6, which gives potential energy curves for the case r(H-H) = 1.4 bohr and θ(HCH) = 105°. There the LMP, corresponding to (α, β) = (90°, 0°), is compared with the four new approaches and in addition to the (0°, 75°) curve.

Most similar to the LMP is the (0°, 45°) approach (see Figure 2), which is nearly as repulsive. In the range of R values plotted, the other four curves all begin to "turn over", i.e., to feel the attraction inevitable as the deep CH_4 potential well appears. Given the constraints of these curves (α, β, r, and θ fixed) barriers of a certain type are apparent in Figure 6. For the (45°, 45°) approach this "barrier" is ~17 kcal. We were slightly surprised to find that the analogous barrier for the (90°, 45°) case is significantly less (~12 kcal), since the two approaches are in roughly comparable relationships to the highly repulsive LMP. For the (0°, 75°) case there is only a small constrained barrier, ~4 kcal, and for the (0°, 90°) approach the barrier disappears entirely. In addition to the data illustrated in Figure 6, analogous computations were carried out for 95° and 115°. These results are essentially similar to those of Figure 6, although the larger θ value (115°) yields slightly lower energies as R is decreased to 3 bohr. Thus it would appear that although the surface is attractive for the initial (0°, 90°) approach, only (α, β) values quite close to (0°, 90°) allow this pure attraction. This observation should have important dynamic consequences[11,12] and it would certainly be of interest to see a classical trajectory study of $CH_2(^1A_1) + H_2$ using the surface features predicted here. In this regard it is encouraging to note that Kollmar's semiempirical surface also favors β values close to 90° for the initial approach. However, it appears that the present surface favors a somewhat narrower range (about β = 90°) of β values than does the modified CNDO surface. Nevertheless the essential agreement speaks highly of the Kollmar surface. The narrow range of initially attractive β values should be understood in the light of our surface restriction to five degrees of freedom. In particular it seems likely that bringing the H_2 molecule out of the plane of Figure 4 would not raise the energy significantly. Other degrees of freedom (there are a total of $3n - 6 = 9$) may very well allow the initially attractive multidimensional "opening" to be considerably wider than might be imagined solely on the basis of Figure 6.

Another critical feature of the surface is its shape after the initially attractive (0°, 90°) approach. In particular, does one encounter a barrier a bit further along the way? Clearly, to reach methane from the (0°, 90°) approach we must decrease R (from ∞ to 0.63 Å), increase r (from 0.74 to 1.78 Å), and decrease β from 90° to 0°. Figure 7 (obtained via two-dimensional spline fits for regularly spaced grids of points) gives the R and θ dependence of the hypersurface for r fixed at 1.4, 1.7, and 1.9 bohr. This figure shows clearly that the most favorable value of r increases steadily as R decreases. In addition there is an initial tendency for θ to increase as the reactants approach each other in the (0°, 90°) manner. The latter tendency is also apparent in Kollmar's work.

Figure 7 makes it quite plain that the $CH_2(^1A_1) + H_2$ surface has *no* barrier height for the reaction to produce methane.

Table I. Minimum Energy Path for the (0°, 90°) Approach of $CH_2(^1A)$ and H_2[a]

R, bohrs	r, bohrs	θ, deg	Energy, kcal
3.6	1.44	107.4	−1.3
3.5	1.45	107.6	−1.5
3.4	1.46	107.9	−1.8
3.3	1.47	108.1	−2.2
3.2	1.48	108.4	−2.9
3.1	1.50	109.3	−3.6
3.0	1.52	110.7	−4.9
2.9	1.54	111.5	−6.4
2.8	1.57	112.1	−7.9
2.7	1.60	112.5	−10.3
2.6	1.65	113.2	−12.8
2.5	1.69	114.1	−15.6
2.4	1.75	115.6	−19.3
2.3	1.81	117.0	−23.1
2.2	1.90	118.1	−27.0

[a] Energies are given relative to infinitely separated $CH_2(^1A_1)$ + H_2.

The r = 1.9 cut shows that the surface has become attractive by 31 kcal at R = 2.0 bohr. The existence of a barrier at smaller R values is completely unreasonable. Actually at R = 2.0 the surface is considerably more attractive, since the (0°, 90°) approach is no longer the most favorable one. The lack of any barrier appears to be one of the most important qualitative differences between the ab initio surface and that of Kollmar.

For the (0°, 90°) approach it is also possible to construct a minimum energy path by performing a three-dimensional spline fit[17] to the surface and following the gradient in the direction of steepest descent.[3,5] Table I gives the result of carrying out this procedure, and it is seen that the three parameters change rather smoothly, in a manner consistent with a concerted pathway. Again we emphasize that the path of Table I is a *constrained* minimum energy path. For the smaller R values, the optimum values of α and β are not 0° and 90°. For example, at R = 2.50, the (15°, 75°) point with r = 1.8 bohr and θ = 115° has a total energy of −40.1297 hartree, or 21.7 kcal below the $CH_2 + H_2$ result of −40.0951.[18] This result is 6.1 kcal lower than the optimum (0°, 90°) energy reported in Table I. An even lower energy (−22.3 kcal) is obtained for the same r and θ values and the (45°, 45°) approach. Before leaving Table I, it is well to note that the grid used is considerably more sparse than those used in constructing our previous pathways.[3,5] However, the general trends (if not the precise values of any single entry) should be correct to ±0.5°, ±0.5 kcal, and ±0.05 bohr. In light of the sparsity of our grid we have not bothered to construct a coordinate independent path.[3,5]

From the tabulated list of ~600 points (available in punched form upon request from C.W.B.), one can estimate the point at which the (15°, 75°) approach becomes more favorable than the initial (0°, 90°) approach. From the previous paragraph we know that this occurs for $R > 2.5$ bohr. At R = 2.75, r = 1.6 bohr, and θ = 115°, the (15°, 75°) and (0°, 90°) points are attractive by 10.5 and 9.1 kcal. At R = 3.00, r = 1.5, and θ = 115°, the analogous two results are −3.7 and −4.6 kcal. Thus it appears that the crossover from (0°, 90°) to (15°, 75°) as the optimum orientation of approach occurs at about R = 2.9 bohr. A comparable analysis suggests that the (45°, 45°) approach becomes more favorable than (15°, 75°) at $R \sim 2.55$ bohr. Presumably an intermediate approach, say (30°, 60°), would be optimum in the range R = 2.7–2.8. Although these conclusions are very qualitative, they should be helpful in visualizing the shape of the $CH_2(^1A_1) + H_2$ hypersurface.

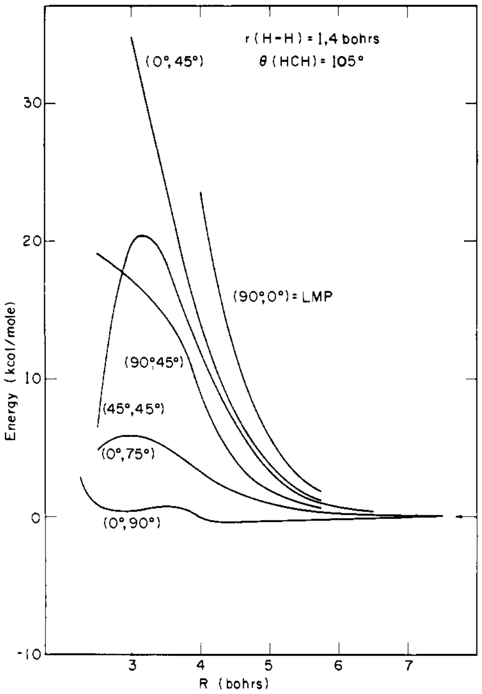


Figure 8. Single-configuration SCF results analogous to Figure 6, which is based on large-scale CI.

A final topic worthy of discussion is the degree to which the single-configuration SCF approximation reproduces the more reliable CI results. We have noted previously[5] that for the least motion (90°, 0°) approach, CI lowers the SCF barrier by ~30 kcal. For a direct comparison of several non-least-motion approaches, in Figure 8 are illustrated computations completely analogous to Figure 6, except at the SCF level of theory. Our general conclusion is that the SCF calculations are not only quantitatively but as well qualitatively different from the CI results. This is most apparent for the (0°, 90°) approach, which shows no sizable well at all for r = 1.4 bohr. In contrast the CI predictions of Figure 6 suggest a considerable well. It can also be noted that SCF calculations for $R < 2.5$ bohr show a continuing repulsive potential curve. The (0°, 75°) curve of Figure 8 is in much better agreement with the CI results but again too repulsive, a barrier of 6 kcal being evident. Another major discrepancy occurs for the (90°, 45°) curve, which "turns over" (i.e., begins to become attractive) at $R \sim 3.5$ in the CI treatment, but only at ~2.5 from the SCF curve of Figure 8. The three most repulsive curves, the (45°, 45°), (0°, 45°), and (90°, 0°), have the same general shape in both SCF and CI descriptions.

Concluding Remarks

The non-least-motion hypersurface for the $CH_2(^1A_1) + H_2 \rightarrow CH_2$ insertion reaction has been studied in detail. There is a range of pathways leading from reactants to products with no barrier at all. In general there is good qualitative agreement between the present ab initio results and the modified CNDO surface of Kollmar.[10] The two most serious discrepancies appear to be the prediction of a 5-kcal barrier by Kollmar and his smaller (13 vs. 27 kcal here) barrier for the least-motion approach. Thus the differences between the least-motion and non-least-motion pathways appear much greater than indicated by the modified CNDO surface.

Acknowledgments. We thank Professors Don Bunker, Roald Hoffmann, and Martin Karplus for encouragement and Dr. David Hayes for illuminating discussions. Computations were carried out primarily on the Lawrence Livermore Laboratory

CDC 7600, with work in the final stages on the Berkeley Harris minicomputer, supported by NSF Grants GP-41509X and GP-39317.

References and Notes

(1) This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory, or the United States Energy Research and Development Administration.

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(18) The comparable energy of the isolated CH_2 molecule is -38.9472 hartree and that of H_2 is -1.1510. The sum of these is -40.0992, or 2 kcal lower than the result reported in the text. The latter result was obtained in a calculation on the CH_4 "supermolecule", with the CH_2 and H_2 separated by 100 bohr radii. This small difference is due to the fact that the separate CH_2 and H_2 calculations implicitly include triple and quadruple excitations (unlinked clusters) not accounted for in the supermolecule treatment. For a discussion of these effects, see W. Meyer, *J. Chem. Phys.*, **58**, 1017 (1973).

Potential Energy Barriers for Halogen Six-Center Reactions: Semiempirical Valence-Bond Predictions[1a]

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Received November 8, 1976

Abstract: An approximate, semiempirical valence-bond formulation is employed to compute potential energy surface reaction barriers for six-center reactions involving the halogens (F_6, Cl_6, Br_6, I_6) and hydrogen (H_6). The method is based on approximations comparable to those in the London-Eyring-Polanyi-Sato (LEPS) formulation. The surfaces are not adjusted using data for the systems treated, but are computed using parameter values that have been used in studies of other systems. The predicted energy barriers are in qualitative accord with existing experimental results for related systems.

The London-Eyring-Polanyi-Sato[2] (LEPS) semiempirical potential energy surfaces in many variations have been widely used in quasiclassical trajectory calculations. While the theoretical basis for these surfaces is rather weak, it seems to be a well-established fact that given reasonable adjustments of parameters the surfaces are realistic and accurate descriptions of the forces in at least certain types of chemical reactions.[3]

We have made many applications of one particular semiempirical valence-bond formulation to describe three- and four-atom systems.[4] In this method, first used by Raff, Stivers, Porter, Thompson, and Sims[5] to describe the H_2I_2 reaction system, the empirical adjustments are made using parameters that are specific to the types of atoms, rather than atom pairs. A well-studied reaction is used to adjust these parameters; for example, the measured activation energy for $H_2 + Cl \rightarrow HCl + H$ was used to obtain a value for the chlorine atom parameter.[6] In applications, we assume that the value of this parameter is independent of the environment of the particular atom; that is, the surface parameters are assumed to be transferable. The qualitative validity of this assumption is supported by the close accord between computed and experimental results for a number of systems. Here we make the assumption again and apply the method to six-center reactions.

Wright,[7] in 1970, suggested that a six-center transition state might offer a lower energy pathway for H_2, D_2 exchange than the four-center transition state. Recently, Dixon, Stevens, and Herschbach[8] have carried out SCF-CI calculations and obtained a barrier height of ~68 kcal/mol for H_6.

Shock tube[9] and stimulated Raman[11] experiments on the $H_2 + D_2$ exchange reaction have been interpreted in terms of a four-center process with an activation energy of 42 kcal/mol. Quantum-mechanical calculations[12-17] suggest an even higher barrier (as much as three times) than has been determined from these experiments. Quasiclassical trajectory studies[18,19] on various potential energy surfaces have failed to resolve the controversy surrounding the $H_2 + D_2$ reaction. Nevertheless, it seems to be a fact that the energy barrier to exchange is relatively high.

Other aspects of four-center reactions, in some respects related to the high energy barriers, are the collisional constraints, dynamic and steric, that affect the crossing from reactants to products. The trajectory results of Brown and Silver[19] illustrate the molecular orientational constraints on reaction in $H_2 + D_2 \rightarrow 2HD$. The trajectory studies of $H_2 + 2I$ by Raff, Thompson, Sims, and Porter[20] show the dynamics restrictions on four-center, termolecular processes. Thompson and McLaughlin[21] have investigated the severe constraints present in $H_2 + F_2 \rightarrow H + HF + F$ for reaction path geometries and reactant energy partitioning.

The inference from all these studies, and others not mentioned here, is that severe energy and dynamic constraints exist for four-center, atom exchange reactions. In 1974, King, Dixon, and Herschbach[22] reported results of crossed molecular beam experiments that suggest a new and exciting mechanism