

Potential Surfaces for the Addition of CH_2 and CF_2 to Ethylene and Isobutene

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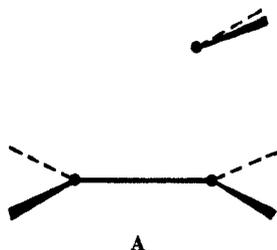
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Molecular orbital calculations favor an attack of singlet CH_2 and CF_2 on ethylene in which the methylene approaches slightly off-center and with its plane approximately parallel to the ethylene plane. The carbene substituents are canted in such a way as to optimally maintain three-center overlap, with corollary symmetry of bond formation and charge transfer. In an approach to an isobutene these pathways are modified for steric reasons, and the possibility of two separated reactive channels arises. A detailed study of the methylene + ethylene surface shows that special care must be taken in the choice of the computational reaction coordinate.

Some fifteen years ago, in the early days of modern carbene chemistry, Skell and coworkers came to the conclusion that the transition state for the addition of methylenes to ethylenes was characterized by the geometrical arrangement shown below as **A**.¹ Methylenes



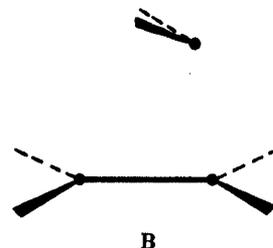
exhibited carbonium or halonium ion type selectivity in their additions to substituted ethylenes. The approach of carbonium ions or other two-electron-deficient species to olefins is likely to begin with an interaction of an unoccupied orbital (*e.g.*, the p orbital in carbonium ion **1a**) with the olefin π system. This line of reasoning led to transition state **A**, whose primary feature is the interaction of the unoccupied methylene p orbital (**1b**), rather than its in-plane "lone pair,"² with the π -system of the ethylene.



The direct experimental probes of transition state geometry are not yet available, and the first test of Skell's conclusion came from a semiempirical molecular orbital calculation of the potential surface for the approach of a methylene to an ethylene.³ Figure 1 shows some superimposed snapshots of a side view of the reaction path thus computed. The calculated reaction path clearly shows the initial approach of the

two molecules in parallel planes, and the concomitant interaction of the methylene p orbital with the ethylene π system.⁴ The insight of the previous workers was thus confirmed.

The transition state for the computed attack, which we may approximate in **B**, differs in a minor but inter-



esting way from transition state **A**. This is in the position of the methylene hydrogens. In **A** they are tilted up and to the right, in **B** up and to the left. Were the methylene carbon directly over the midpoint of the ethylene $\text{C}=\text{C}$ bond then these distortions would be indistinguishable. To the extent that the methylene carbon is off-center they are distinct.

This preference for approach **B** over approach **A** is a detail of the potential surface worthy of further consideration. First we would like to review the procedure utilized for obtaining the computed reaction path.³

(1) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956). See also P. S. Skell and M. S. Cholod, *ibid.*, **91**, 7131 (1969) and W. R. Moore, W. R. Moser and J. E. La Prade, *J. Org. Chem.*, **28**, 22 (1963).

(2) (a) The electronic structure of methylenes is discussed by P. P. Gaspar and G. S. Hammond, in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235; R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); (b) Excellent discussions of the present state of carbene reactivity studies may be found in the papers by G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968); and R. A. Moss in "Carbene Chemistry," L. Friedman, Ed., Wiley-Interscience, New York, N. Y., 1971.

(3) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(4) An alternative approach, involving a symmetrical attack of a linear singlet methylene, has been suggested by A. G. Anastassiou, *Chem. Commun.*, 991 (1968).

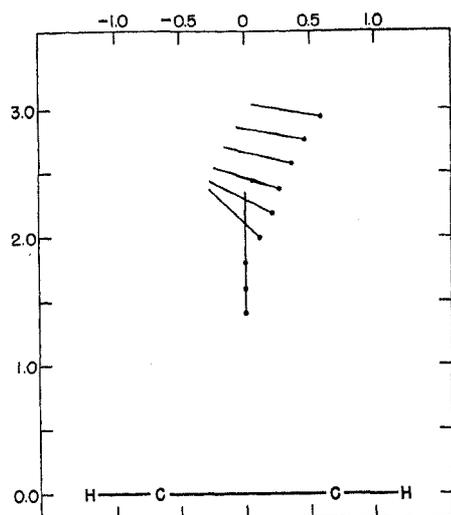


Figure 1. Snapshots of the reaction path for methylene adding to ethylene. The fixed ethylene and the moving methylene are both seen in projection upon the mirror plane of symmetry maintained in the reaction. The tilt of the approaching methylene is that yielding the lowest energy for a given value of R , the distance from the center of the ethylene to the methylene carbon. The scales are in Å. Further details may be found in reference 3.

The full potential surface for the system C₂H₄ + CH₂ spans 21 internal degrees of freedom. Chemically reasonable constraints must be applied to reduce this number to a magnitude which we can reasonably handle. With extended Hückel computation times of 2–3 sec per geometry we are able to deal with an estimated maximum of eight degrees of freedom. In the case at hand, a highly exothermic reaction, we concentrated on the distant approach, in which we could assume that the reactant geometries were not severely affected. The problem reduced to one of the relative motion of two solid bodies, an ethylene and a methylene. A convenient coordinate system for describing this motion could be obtained by freezing the ethylene with the origin at its inversion center, using three spherical coordinates R , θ , φ to locate the methylene carbon and three Euler angles $\epsilon\varphi$, $\epsilon\theta$, $\epsilon\psi$ to specify the orientation of the methylene.

Our computer program automatically searched for those θ , φ , $\epsilon\varphi$, $\epsilon\theta$, $\epsilon\psi$ which gave the minimum energy at a given R .⁵ The result is a computed reaction path. We believe this path approximates the true reaction path, though it must be realized by the reader that in the absence of a view of the whole surface the choice of origin for R remains more or less arbitrary. The final section of this paper will discuss this point further. It was found that the computed reaction path could be described in less than six degrees of freedom. A mirror plane of symmetry was chosen by the molecule along the computed reaction path, thus reducing the number of degrees of freedom to three— R , θ , $\epsilon\theta$. Figure 1 shows the projection of the reactants on the mirror plane which is maintained.

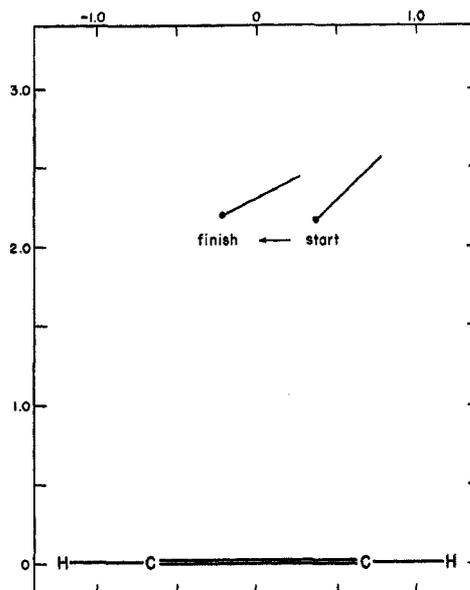


Figure 2. One numerical experiment on the methylene-ethylene potential surface. A methylene with the initial geometry marked "start" moves by an energetically uniformly decreasing path to "finish." The view is the same as in Figure 1.

There is no doubt that the path shown in Figure 1 and symbolized by the snapshot **B** is the favored computed reaction path. In particular if a methylene molecule is placed initially in a geometry resembling **A** and is allowed three to six degrees of freedom in its motion then it moves directly over along a path of uniformly decreasing energy to a mirror image of geometry **B**, designated as **B***. One such numerical experiment, at $R = 2.2$ Å, is shown in Figure 2. At this distance the motion from **A** to **B*** gains 6 kcal in energy. At larger distances the energy gain for a corresponding motion would of course be smaller still.

There are two obvious pathways from **A** to **B** or **B***, and their identification will become important to the sequel. The first pathway, the one chosen in the computed potential surface, is a simple sideways sliding of the CH₂ unit from **A** to **B***.



The second pathway is a pivoting in place of the CH₂ group leading from **A** to **B**.



(5) The optimizing procedure was one due to H. H. Rosenbrock, *Comput. J.*, 3, 175 (1960), and was adapted by K. D. Gibson.

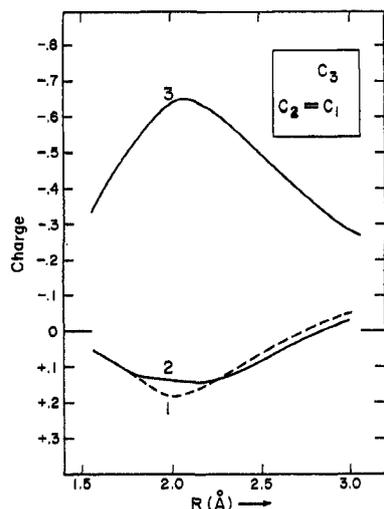


Figure 3. Charge distribution on the carbons along the reaction path of figure 1. C_3 , the methylene carbon, is closer to C_1 at intermediate stages in the reaction.

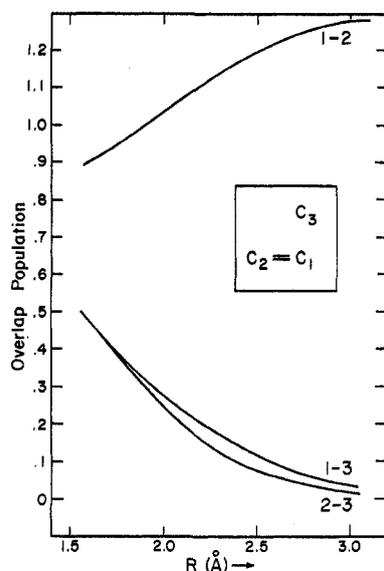


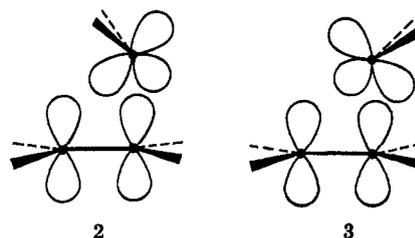
Figure 4. Overlap populations between carbon atoms along the reaction path of Figure 1.

Whereas the sliding over process is energetically downhill, we always find a barrier to the pivoting process. Presumably this is due to the fact that the midpoint in the pivoting motion has the methylene "lone pair" or σ orbital interacting with the π system, approaching the situation for the high energy forbidden reaction.³

What makes transition state **B** better than **A**? Let us first look at the charge distribution on the three carbons as the reaction proceeds (Figure 3). The most striking feature of the charge distribution is the charge transfer from olefin to methylene, consistent with the primary interaction of a filled ethylene molecular orbital with an empty methylene acceptor level. The second remarkable feature of the charge distribution is the extent to which both ethylene carbons are similarly

charged. Examination of the overlap populations (related to bond orders) along the reaction path (Figure 4) shows that while the new CC bonds are forming at unequal rates, with the proximal C_1 - C_3 bond forming first, there is never any great disparity in the rate of bond formation.

Both the charge distribution and the bond orders are consistent with as symmetrical as possible an interaction of the methylene carbon with the ethylene, and yet the methylene carbon is significantly off center most of the reaction path. The symmetry in charge transfer and in bonding is accomplished by tilting the methylene in just the sense required by **B**. That is, given that methylene carbon is off center it can restore approximate symmetry in the p - π interaction by tilting as in **2** (**B**), but makes the electronic interaction still more unsymmetrical if it tilts as in **3** (**A**).



This conclusion is confirmed by examination of charge distributions for geometries like **3**. The occasion for a quantitative comparison will arise below.

Our calculated potential energy surface for the addition of methylene to ethylene shows no activation energy for the process. In reality there must be an activation energy, but it also must be small,¹ less than 3 kcal/mol. We wanted to confirm our computed reaction path for a carbene addition with a larger activation energy. The species chosen was CF_2 , which is known to possess an activation energy of approximately 11-12 kcal/mol⁶ to addition to ethylene. Our computed reaction path for CF_2 addition is shown in Figure 5. It clearly is very similar to the CH_2 reaction path. Figure 6 shows the energy along the forbidden least motion path^{3,7} as well as the energy along the reaction path of Figure 5. The calculated activation energy of slightly more than 20 kcal/mol is, of course, an upper limit; were we to allow some additional degrees of freedom such as relaxation of the ethylene fragment by bending the hydrogens out of plane we would surely lower the activation energy. Extended Hückel calculations, while qualitatively reliable, typically err by a factor of two on activation energies.

The transition state, marked \ddagger in Figure 5, occurs at a distance of approximately 1.8 Å. Every geometry

(6) See S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, 21, 248 (1970); also R. A. Mitsch and A. S. Rodgers, *Int. J. Chem. Kin.*, 1, 439 (1969).

(7) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969).

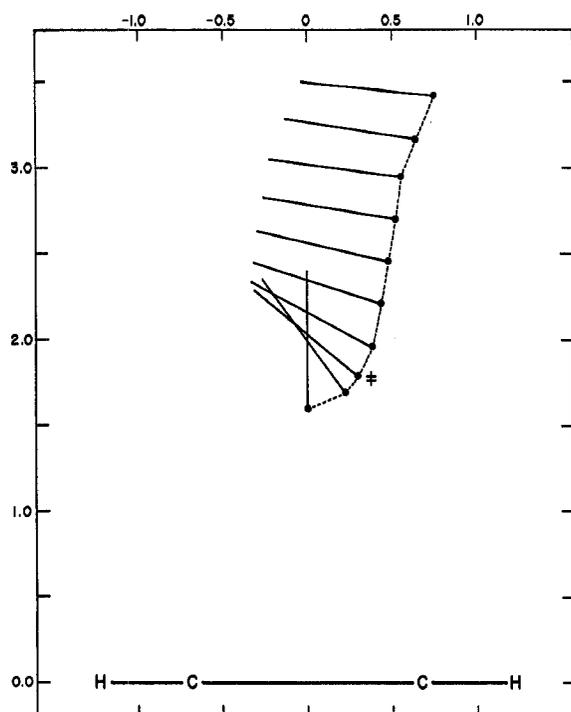


Figure 5. Snapshots of the reaction path for difluoromethylene adding to ethylene. The conventions and view are specified in the caption to Figure 1. The transition state is marked by the symbol ‡.

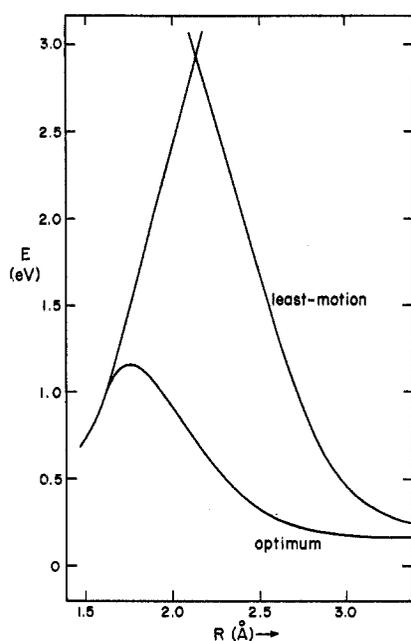
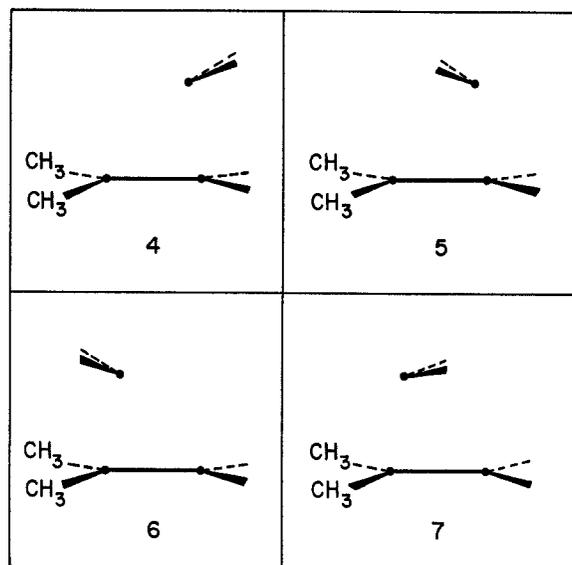


Figure 6. Energy along the reaction path of Figure 5 (marked optimum), as well as along the least-motion approach of C_{2v} symmetry. The energy zero is arbitrary.

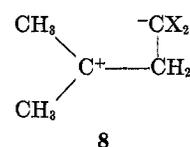
of type A slides over smoothly to one of type B. Electron density is still transferred to the methylene in the course of the reaction, but in accord with the lower electrophilicity of difluorocarbene much less charge transfer occurs than in the methylene case.⁸ Inter-

estingly enough, there is now an imbalance in the source of the electron transfer, most of it originating at C₁, the carbon closest to the CF₂ during the approach.

We next turned to a study of an unsymmetrical olefin substrate, isobutylene. For an unsymmetrical olefin of this type, conformation B is no longer identical with its mirror image B*, nor A with A*. Let us write down the four possible transition state geometries 4 (A), 5 (B), 6 (A*), 7 (B*).



We had noticed that the ethylene carbons were symmetrically participating in the charge transfer to the methylene. However in the case of isobutylene, where there exists the opportunity for very favorable cation stabilization at the methyl substituted end, it seems reasonable that the methylene would take advantage of this fact and accordingly favor conformations 4 and 5. These correspond most closely in geometry to the important valence structure 8.



Moreover there is a possible steric destabilization of conformations 6 and 7.

The interesting case is then conformation 4. This is A type, and in the case of methylene adding to ethylene we have noted that such a conformation slides easily over to B*. However in this case B* is 7, destabilized for the above mentioned reasons. Since in-place pivoting of 4 to attain 5 is also energetically costly, there is here a real possibility that there are two distinct reaction paths, represented by 4 and 5, leading to dimethylcyclopropane.

(8) For some studies on dichlorocarbene related to this point see P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 7131 (1969); I. A. Dyakonov, R. R. Kostikov, and V. S. Aksenov, *Reakts. Sposobnost Org. Soedin.*, **7**, 557 (1970); I. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

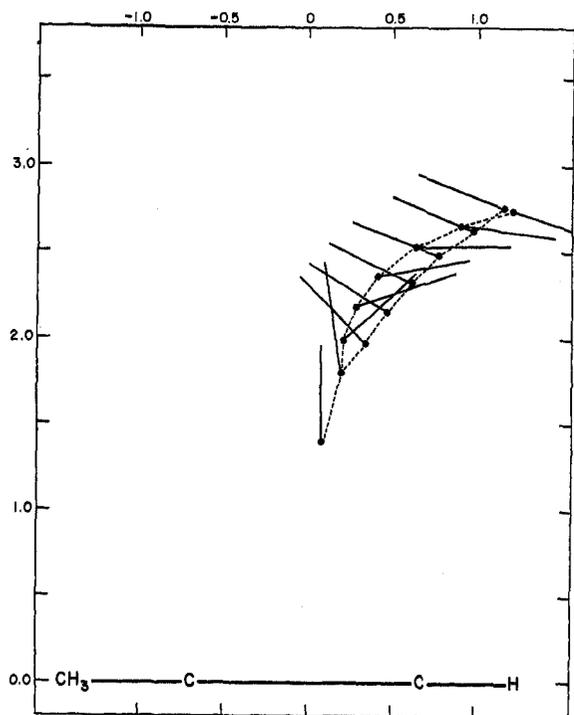


Figure 7. Snapshots of the reaction paths for the addition of methylene to isobutylene. The conventions and view are specified in the caption to Figure 1. The isobutylene methyl groups are at left. Dashed lines connect the independent reaction paths described in the text.

The presence of two such distinct paths is confirmed by the molecular orbital calculations. Figure 7 shows a superposition of snapshots of the reaction paths. For large R there are two conformations, each of them a local minimum in the five angular dimensions. At $R \sim 1.9$ Å these merge, close to the product cyclopropane. At each R the minimum corresponding to **4** is at higher energy than that corresponding to **5**, as we would have expected from our experience with methylene plus ethylene. The destabilization of **4** is not great, amounting to a maximum of 2 kcal/mol. Potential curves for **4** or **5** show no activation energy for the reaction. One might also note the increasing parallelism of the **4** and **5** methylene planes at large R , terminating in a geometry for **4** in which the hydrogens come below the carbon. Clearly at these long distances all that seems to matter is that the methylene p orbital be directed toward the center of the ethylene π bond. Starting geometries corresponding to **6** and **7** are not local minima, but slide over to **5** and **4**, respectively.⁹

The theoretical presence of two computed reaction paths allowed us to compare the electron density changes along approaches **A** and **B** (**4** and **5**) more precisely. This is accomplished in Figure 8. It will be noted that the lower energy **B** approach necessitates somewhat less charge transfer, as well as less charge imbalance among the ethylene carbons.

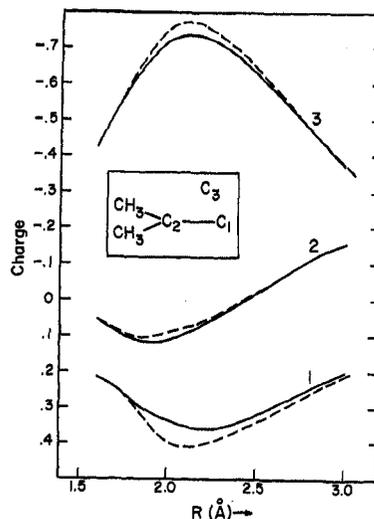


Figure 8. Charge distribution along the two reaction paths of Figure 7. The solid line is for the reaction path of type **B**, the dashed line for that of type **A**.

We have also calculated a potential surface for CF_2 and isobutylene. This shows the combined features of the $\text{CF}_2 + \text{C}_2\text{H}_4$ and $\text{CH}_2 + (\text{CH}_3)_2\text{C}=\text{CH}_2$ surfaces. There are two distinct reaction paths of type **4** and **5**. There is also present a sizable activation energy.

Importance of Proper Choice of Computational Reaction Coordinate. In the process of studying the methylene-ethylene surface we came across a problem of some significance in the general computation of potential surfaces. The reaction path of Figure 1 was calculated by optimizing θ , φ , $\epsilon\varphi$, $\epsilon\theta$, $\epsilon\psi$ for a given value of the computational reaction coordinate R . R was chosen as the distance between the ethylene center and the methylene carbon.

Suppose the computed reaction coordinate R is chosen in a different way, for instance as the distance between the methylene carbon and *one* of the ethylene carbon atoms. The computed reaction path is shown in Figure 9. The distance R is here measured from the *right-hand* ethylene carbon. This second calculated reaction path is primarily of type **A**, and the optimum approach brings the methylene closer to the *left-hand* carbon. If bond formation is to be a consequence of reaction then this seems to be a poor choice for a reaction coordinate, since bonding is first established with a carbon other than the one from which the reaction coordinate is measured.

What is needed here is a view not only of the reaction path but a substantial section of the entire potential surface. Without such an examination the true reaction path cannot really be said to have been established.

(9) Some interesting stereochemical consequences of the favored paths of approach of alkylidenecarbenes to unsymmetrical olefins are given by M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969); **92**, 4312 (1970).

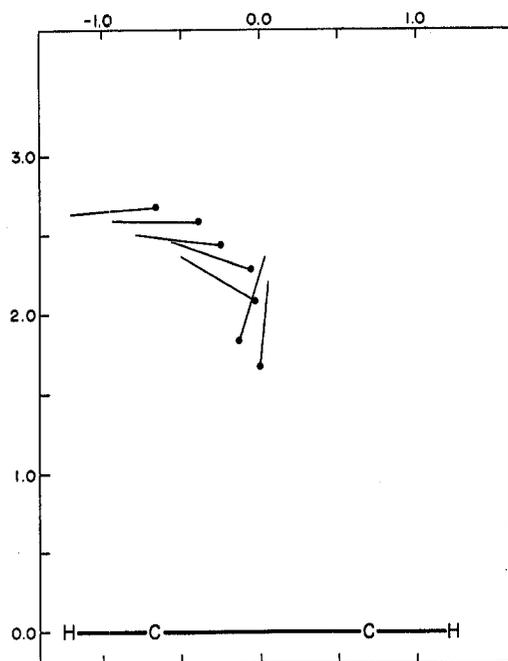


Figure 9. Snapshots of reaction path for the addition of methylene to ethylene when the reaction coordinate R is chosen as the distance from the *right-hand* carbon of ethylene.

In Figure 10 we show an enlarged section of the area covered by Figure 1. The methylene carbon is fixed at the indicated y and z coordinates (the horizontal and vertical coordinates of Figure 1) and the optimum tilt of the methylene group is computed. This tilt is indicated by a slant line and its energy is specified below this line.¹⁰

The figure illustrates clearly why if motion is constrained to be along an arc of equal distance from the center of the ethylene the **B** geometry is preferred, while if the motion is along an arc measured from an ethylene carbon, an **A** geometry is favored. More energy is gained from moving down to the ethylene than from moving sideways. The general features of the potential surface revealed in Figure 10 confirm our original choice of reaction coordinate and provide

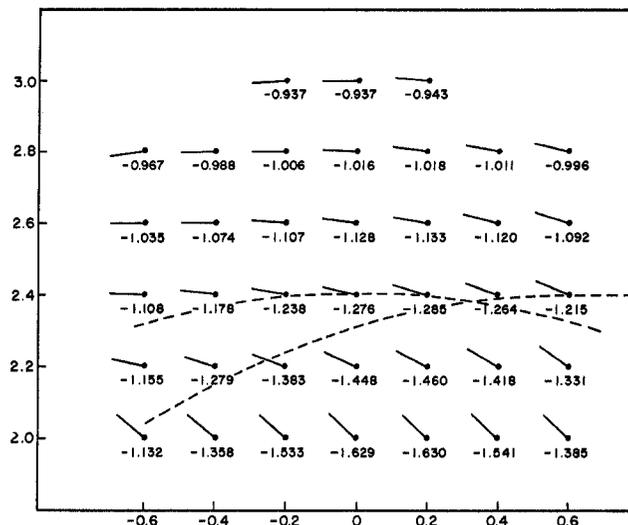


Figure 10. A section of the area of Figure 1, for altitudes 2 to 3 Å above the ethylene. The methylene carbon is fixed at the indicated point and the optimum tilt of the methylene is computed. The tilt is indicated by the slope of the line—which is not of sufficient length to be a true projection of the methylene. Associated energies are in electron volts relative to an arbitrary zero. The dashed curves are loci of points 2.4 Å from the center of the ethylene and from the right-hand ethylene carbon.

a better picture of the energy attached to various impact geometries. Finally we would like to emphasize that we have included the numerical experiments in this section not because they yield any chemical insight but because they are instructive in demonstrating the dangers of arbitrary choice of computational reaction coordinate in limited searches of a complex potential surface.

Acknowledgment. This work was supported at Cornell by the Petroleum Research Fund and the National Science Foundation. P. S. S. acknowledges the support of the Air Force Office of Scientific Research.

(10) Only nonequivalent geometries are specified. For each point there are **A** and **B** type minima, if methylene tilt is the only degree of freedom allowed.