The Location of Transition States for the Addition of Singlet Methylene to Substituted Ethylenes

Miguel Moreno, José M. Lluch, Antonio Oliva, and Juan Bertrán *
Departamento de Química Física, Universidad Autónoma de Barcelona, Bellaterra, Barcelona, Spain

The transition states for the addition of singlet methylene to hydroxyethylene and acrolein have been determined by using the MINDO/3 method. It is found that the 'inward' approach of methylene to the unsubstituted carbon atom of the alkene is the most favourable one. The results obtained lead to the conclusions that the simultaneous use of reduced surfaces and of direct location is the best strategy to obtain the true transition state of a reaction.

Methylene is one of the most reactive species in organic chemistry. Although its ground state is a triplet, it is generally admitted that it often reacts in its first singlet state, when it leads to stereospecific additions.[1–3]

Methylene addition to ethylene has been studied in detail from a theoretical point of view by several workers.[4–9] The calculations indicate that the methylene approach to ethylene is off-centre. The hydrogen atoms of methylene are oriented in such a way that they point inwards (approaches I and IV in Figure 2) or outwards (approaches II and III in Figure 2) across the ethylene face. The results of our previous work,[9] which were obtained by a semiempirical MINDO/3 method, show that the mechanism of the singlet methylene addition to ethylene is the 'inward' asynchronous one, compared with the 'outward' reaction path, which does not lead to the addition reaction, but to the insertion of methylene on a C–H bond of the ethylene. In this process two phases can be distinguished in good agreement with Zurawski and Kutzelnigg's results.[8] In the first phase, the two reactants approach each other in approximately parallel planes, the predominant interaction is the one between the HOMO of ethylene and the LUMO if methylene and there is, therefore, an important charge transfer to methylene. In the second phase, methylene rotates in order to get to the position that it has in the final product, in such a way that the above mentioned HOMO–LUMO interaction then disappears and the charge transfer decreases.

The influence of the introduction of substituents in methylene has been investigated by Hoffmann *et al.*[7] and Houk and co-workers.[10] According to Houk and co-workers'[10] results, methylene adds to ethylene without a potential-energy barrier. The introduction of substituents in methylene gives rise to a barrier, which increases as the value of the charge transfer from ethylene to the carbene decreases. In an extreme case, the introduction of two electron-releasing OH groups leads to an inversion of the charge-transfer direction and the magnitude of the potential-energy barrier reaches its maximum value.

However, the effect of the introduction of substituents in ethylene has not been studied very much. To our knowledge, the only theoretical analysis of this problem was by Hoffman *et al.*,[7] who studied the methylene addition to isobutene by means of extended Hückel theory (EHT) calculations. They conclude that methylene always adds to the unsubstituted carbon atom of ethylene, this conclusion being valid for both the inward and outward approaches.

The objective of this work is two-fold. Firstly, from a chemical point of view, we discuss whether the introduction of strongly electron-releasing or electron-withdrawing substituents in ethylene modifies the kind of approach of the reactants, the magnitude and direction of the charge transfer, the energy barrier, and, in short, the reaction mechanism. For this purpose, the OH and CHO groups have been chosen as models of electron-releasing and electron-withdrawing substituents, respectively, thus studying the addition of methylene to hydroxyethylene and acrolein. Secondly, from a methodological point of view, we try to clarify which is the most suitable strategy in order to locate the transition state for this type of reaction.

Procedure

Method of Calculation.—Knowledge of the stationary points of the potential hypersurface is essential in order to study the mechanism of a reaction. Since the whole calculation of the potential hypersurface is impossible for the majority of chemical reactions of interest, two alternative methods can be used. Those of the first type locate the stationary points by examination of the potential surfaces of reduced dimensions. Of these methods the most frequently used is the reaction co-ordinate method.[11–13] One or two degrees of freedom are chosen as independent variables, and the rest of the geometric parameters are optimized for each set of values for the independent variables, the energy being minimized. This method will be correct to the degree to which the true reaction co-ordinate is defined by the independent variables chosen only.

A second option consists in directly locating the transition states, without having to construct a potential hypersurface, permitting free and simultaneous variation of all the degrees of freedom of the system. According to McIver and Komornicki[14] the transition state is a point that fulfils the following four conditions: (*a*) it is a stationary point, *i.e.*, of zero gradient; (*b*) the force constant matrix at the point must have only one negative eigenvalue; (*c*) it must be the highest energy point on a continuous line connecting reactants and products; and (*d*) it must be the lowest energy point that satisfies the previous three conditions.

The direct location methods only fulfil the requirements of the first two conditions, and not the last two. In addition, although these methods are very efficient, they require a great deal of calculation time and are only operative in the area of the stationary points to be located, for which it is necessary to start from a point very near to the final product.

In this work, we have tried to combine the advantages of both the reaction co-ordinate and the direct location methods. So far, in the calculations carried out for the addition of carbenes to alkenes with the reaction co-ordinate method, only one independent variable has been chosen. Given that two new bonds are formed, we believe that it is necessary to take these two C–C bond lengths as independent variables. Since methylene can approach the alkene in inward or outward ways and in this work it has been added to asymmetric alkenes, it becomes necessary to build up two bidimensional potential-energy surfaces for each reaction. Given the large amount of calculation that is required in order to carry out a sufficiently

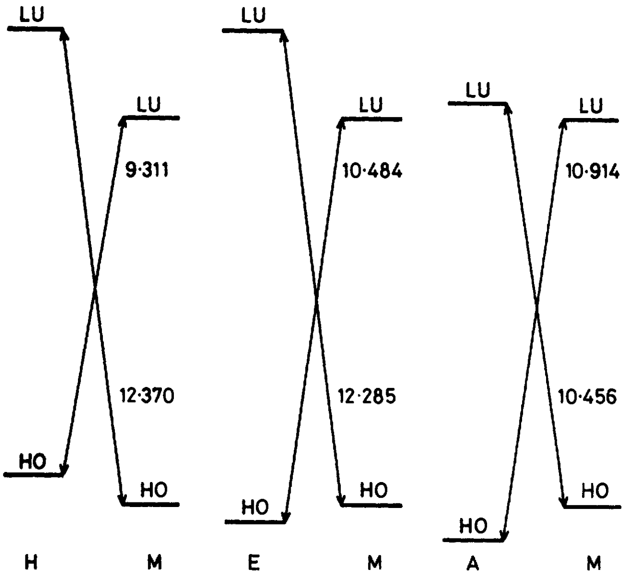

Figure 1. HOMO—LUMO energy differences (eV) for the reactants of the reaction under study. H, E, A, and M are hydroxyethylene, ethylene, acrolein, and methylene, respectively.

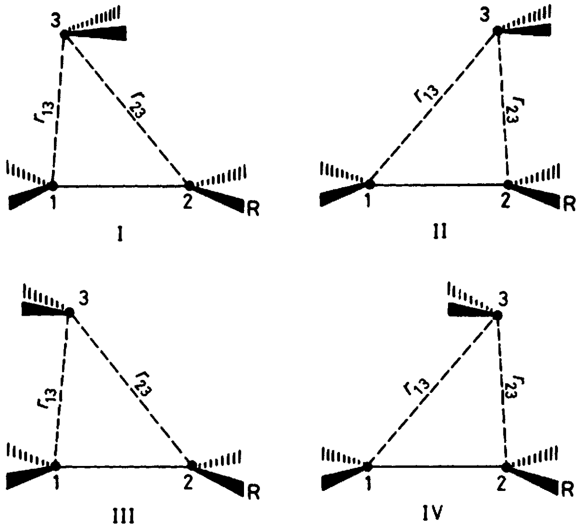

Figure 2. Types of approach of methylene to substituted ethylene: inward to the unsubstituted carbon atom (I); outward to the substituted carbon atom (II); outward to the unsubstituted carbon atom (III); and inward to the substituted carbon atom (IV)

extensive exploration of each surface, the energy calculation has been performed with the semiempirical MINDO/3 method,[15a] which is implemented in the GEOMO program.[16]

The MINDO/3 calculations gave satisfactory results for a wide variety of cycloaddition reactions.[15b] The mathematical procedure used was Rinaldi's method[16] in order to minimize the energy.

The direct location of the stationary points has been carried out through the minimization of the square of the gradient norm[14] by means of the SIGMA program. The characterization of these points has been carried out by calculating the eigenvalues and eigenvectors of the force constant matrix with the aid of the FORCE program.

Results and Discussion

According to Schoeller,[17] singlet methylene additions to olefins can be classified into two groups [(I) and (II)], depending on the relative energy of the frontier orbitals. Figure 1 presents the HOMO—LUMO energy differences (eV), for the reactants of the reactions under study. It can be seen that the addition of methylene to ethylene and hydroxyethylene are both of type (I), since the dominant interaction is that between the HOMO of the alkene and the LUMO of methylene. It is therefore to be expected that in these two cases the charge transfer will be from the alkene to methylene, this charge transfer being more important in the addition to hydroxyethylene. However, the addition to acrolein is of type (II), as the interaction between the HOMO of methylene and the LUMO of the alkene is now slightly dominant. Therefore, an inversion in the charge transfer might be expected in this case.

Figure 2 shows the four possible ways methylene can approach hydroxyethylene and acrolein. The study of these four types of approach for the addition to hydroxyethylene, using r_{13} and r_{23} as independent variables, leads to the potential surfaces that are presented in Figure 3. The upper triangle (zone I) of Figure 3(*a*), with r_{13} smaller than r_{23}, corresponds to the inward approach to the unsubstituted carbon atom of hydroxyethylene (approach I in Figure 2). The lower triangle (zone II), with r_{13} greater than r_{23}, corresponds to the outward approach to the substituted carbon atom of hydroxyethylene (approach II in Figure 2). Similarly, zones III and IV in Figure 3(*b*) correspond, respectively, to approaches III and IV in Figure 2.

We will discuss the two types of outward approach first. A clear discontinuity, represented by dotted isoenergetic lines, appears in zone II of Figure 3(*a*), which corresponds to the outward approach to the substituted carbon atom of hydroxyethylene. This is due to the fact that nuclear configurations of the hypersurface zone leading to the addition reaction have suddenly changed, on building up the reduced surface, to nuclear configurations of the hypersurface zone leading to the insertion reaction. As a consequence, a valley that leads to vinyl alcohol can be observed in the dotted zone of Figure 3(*a*).

In contrast, in the outward approach to the non-substituted carbon atom [zone III of Figure 3(*b*)] there are no discontinuities. In this zone we have drawn a dotted–dashed reaction path, whose maximum energy point, A, shows the apparent features of a transition state. However, when A is taken as the starting point in the direct location method, the stationary point that is obtained has a force constant matrix with two negative eigenvalues. The most negative root is associated with the displacement of methylene towards the alkene. The other negative eigenvalue is more difficult to explain. The fundamental components seem to indicate a rotation from the outward to the inward approach and a displacement of methylene towards the plan of the alkene. According to the theory of Murrell and Laidler,[18] a lower energy stationary point must exist, whose force constant matrix will only have one negative eigenvalue. However, if we apply small displacements to the stationary point already found in the direction of the vector associated with the second negative root, we again obtain the starting point. If we carry out large displacements in the two directions that correspond to the fundamental components of this vector, two stationary points with only one negative eigenvalue are actually obtained, but they are situated in the hypersurface zones leading, respectively, to the inward addition reaction and to the insertion reaction. From this analysis it seems possible to conclude that a true transition state for the outward addition of methylene to hydroxyethylene does not exist.

The results obtained for the outward approach clearly show that the building up of a reduced potential surface is not

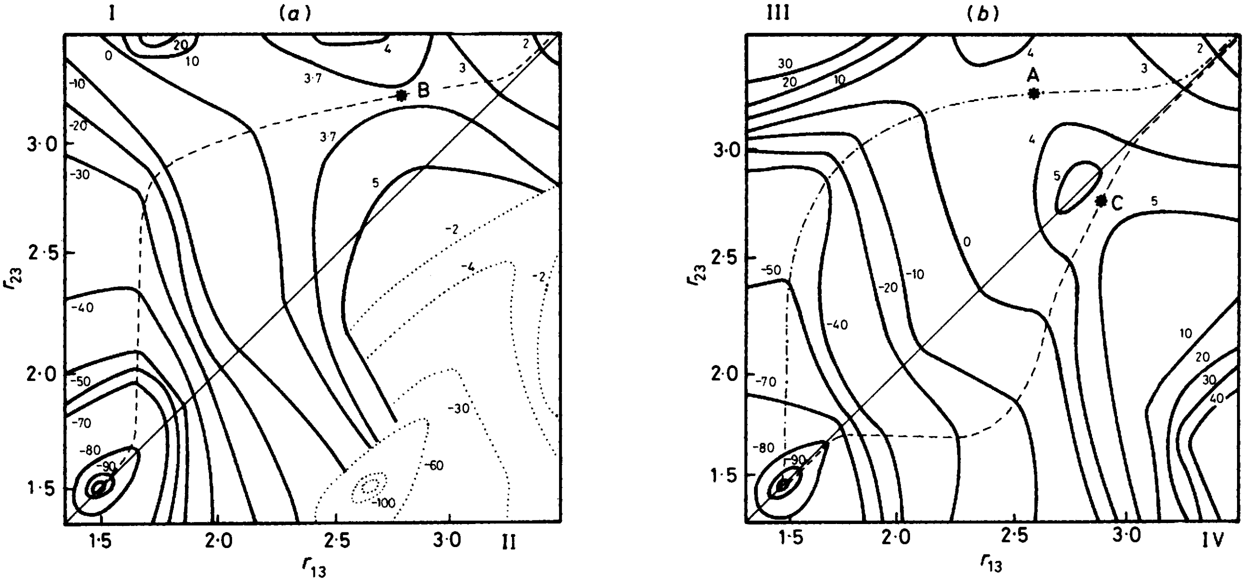

Figure 3. Reduced potential surfaces for the addition of methylene to hydroxyethylene. Energy in kcal mol^{-1} and bond lengths in Å

sufficient to carry out a correct interpretation of the reaction mechanism. A sudden jump can be produced from the hypersurface area under study to a very different one, this fact implying the existence of important discontinuities in the reduced surface. However, points may exist that seem to fulfil the requirements of a true transition state in the reduced surface, but they do not do so in the complete hypersurface. So, the correct characterization of a true transition state requires the direct location on the potential hypersurface and the subsequent diagonalization of the force constant matrix.

The results obtained for the inward approaches of methylene to the non-substituted [zone I of Figure 3(*a*)] and to the substituted [zone IV of Figure 3(*b*)] carbon atoms of hydroxyethylene will now be discussed. In both cases, a reaction path can be drawn, whose points of maximum energy are indicated by letters B and C, respectively. Taking B and C as starting points and minimizing the square of the gradient norm, two stationary points whose force constant matrix has only one negative eigenvalue have been directly located in the complete hypersurface. It is interesting to note that the stationary points located in this way are, geometrically and energetically, very close to points B and C, thus indicating that the reaction coordinate is well defined by the chosen independent variables. Once the fulfilment of McIver's two first conditions is guaranteed, the fulfilment of the third condition can be investigated through complete optimization of the structures obtained by displacing both stationary points in the direction of their respective transition vectors. The third condition is also satisfied since optimization leads either to the reactants or to cyclopropanol, the final product of the addition reaction, depending on the method of displacement.

From the above analysis, it might be thought that two transition states exist for the addition of methylene to hydroxyethylene, corresponding, respectively, to both inward approaches. However, McIver's fourth condition implies the existence of only one transition state. As can be expected from the examination of Figure 3, the true transition state is the stationary point corresponding to the inward approach to the unsubstituted carbon atom of hydroxyethylene. The necessity of fulfilling this fourth condition implies that any direct location method on the complete hypersurface has to be complemented with the building up of reduced potential surfaces, for two reasons. Firstly, the search of a stationary point in the complete hypersurface turns out to be impossible unless one starts from a close enough geometry. Secondly, it is very difficult to know whether all the possible saddle-points for a given reaction have been located. Only reduced surfaces allow us to guarantee, with some confidence, that all the hypersurface zones that could possibly contain stationary points have been investigated.

Potential surfaces corresponding to the addition of methylene to acrolein are presented in Figure 4, the different zones of these surfaces being defined in the same way as those corresponding to the addition to hydroxyethylene. It can be observed that the surfaces of both reactions are very similar. Hence, all the points considered so far are also valid for the addition to acrolein.

From the potential surfaces obtained for both reactions it can be observed that the approach of methylene to the non-substituted carbon atom of the alkene is always more favourable than that to the substituted one. These results agree with those obtained by Hoffmann *et al.*[7] for the addition of methylene to isobutene. However, while Hoffmann considers that both the inward and the outward approaches give rise to addition, our results have shown that only the inward approach leads to the addition product.

In order to carry out a quantitative study of the results obtained, we compared the stationary points with only one negative eigenvalue, the points being directly located for the inward approaches of methylene to ethylene, hydroxyethylene and acrolein. The Table presents the energy barriers, the bond distances r_{13} and r_{23}, and the charge transfer towards methylene for all these stationary points. It can be observed that the energy barriers for the approach to the unsubstituted carbon atom of hydroxyethylene and acrolein are approximately 1 kcal mol^{-1} lower than those corresponding to the approach to the substituted carbon atom, these lower energy barriers being associated with a greater asynchronism of the process.

The effect of the introduction of substituents in ethylene on the reaction mechanism can be analysed by comparing the three central columns of the Table. The introduction of an electron-releasing group, such as OH, increases the charge transfer towards methylene and diminishes the energy barrier. However, the introduction of an electron-withdrawing group, such as

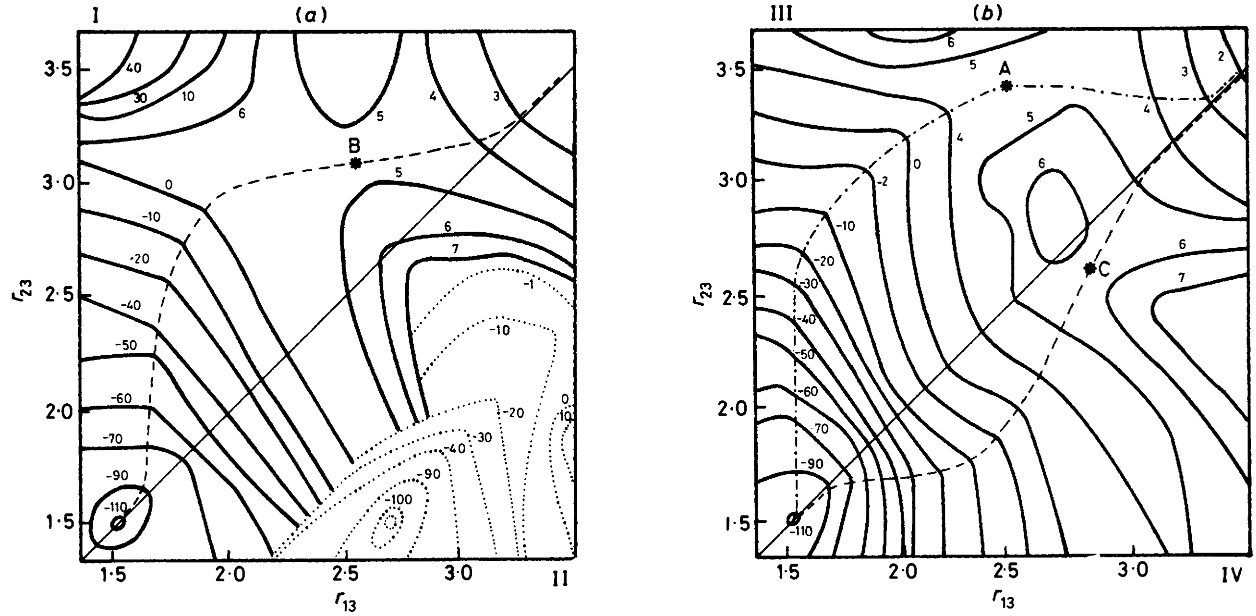

Figure 4. Reduced potential surfaces for the addition of methylene to acrolein. Energy in kcal mol^{-1} and bond lengths in Å

Table. Energy barriers (kcal mol^{-1}), bond lengths (Å), and charge transfer (a.u., towards methylene) for the inward approach of methylene to hydroxyethylene, ethylene, and acrolein

	Hydroxyethylene			Acrolein	
	Substituted C atom	Unsubstituted C atom	Ethylene	Unsubstituted C atom	Substituted C atom
ΔE	4.8	3.6	3.9	4.9	5.9
r_{13}	2.8	2.6	2.7	2.6	2.9
r_{23}	2.6	3.3	3.1	3.2	2.5
t	0.043	0.051	0.022	0.022	0.041

CHO, increases the energy barrier but leaves the charge transfer practically unchanged. It has to be pointed out that although the addition of methylene to acrolein is of type (II) (see Figure 1), the charge transfer is always directed towards methylene. This is due to the fact that both reactants initially approach in almost parallel planes and, therefore, the most important overlap takes place between the HOMO of acrolein and the LUMO of methylene.

It is also interesting to note that for all the reactions studied we found a two-phase mechanism, which is similar to that proposed by Zurawski and Kutzelnigg[8] for the addition of methylene to ethylene. Therefore, the charge transfer towards methylene increases just up to the moment when methylene rotates in order to get the orientation that it has in the final product of the addition reaction.

Conclusions

Two main conclusions can be reached from this work. Firstly, the introduction of substituents in ethylene slightly changes the potential-energy barrier but the mechanism of the addition reaction remains nearly the same, methylene approaching the unsubstituted carbon atom of the alkene in an inward way. Secondly, it has been clearly shown that the best strategy in order to obtain the true transition state of a reaction is the simultaneous utilization of reduced surfaces and of direct location, since both methods complement each other.

References

1 F. J. Duncan and R. J. Cvetanovic, *J. Am. Chem. Soc.*, 1962, **84**, 3593.
2 P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, 1959, **81**, 3383.
3 K. R. Kopecky, *J. Am. Chem. Soc.*, 1961, **83**, 2397.
4 R. Hoffmann, *J. Am. Chem. Soc.*, 1968, **90**, 1475.
5 H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc., Jpn.*, 1972, **45**, 2424.
6 N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, 1972, **94**, 9095.
7 R. Hoffmann, O. M. Hayes, and P. S. Skell, *J. Phys. Chem.*, 1972, **76**, 664.
8 B. Zurawski and W. Kutzelnigg, *J. Am. Chem. Soc.*, 1978, **100**, 2654.
9 M. Moreno, J. M. Lluch, A. Oliva, and J. Bertrán, *J. Mol. Struct., THEOCHEM*, 1984, **107**, 227.
10 N. G. Rondan, K. N. Houk, and R. A. Moss, *J. Am. Chem. Soc.*, 1980, **102**, 1770.
11 P. Empedocles, *Int. J. Quantum. Chem.*, 1969, **35**, 47.
12 M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, 1971, **93**, 4290, 4291, 4292.
13 O. Ermer, *Struct. Bonding (Berlin)*, 1976, **27**, 161, 202.
14 J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, 1972, **94**, 2625.
15 (*a*) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285; (*b*) M. J. S. Dewar, *J. Am. Chem. Soc.*, 1984, **106**, 209; S.-W. Chiu and W.-K. Li, *J. Mol. Struct.*, 1980, **66**, 221; H.-T. Tsang and W.-K. Li, *Croat. Chem. Acta*, 1983, **56**, 103.
16 D. Rinaldi, *Comput. Chem.*, 1976, **1**, 108; *QCPE*, 1975, **11**, 290.
17 W. W. Schoeller, *Tetrahedron Lett.*, 1980, **21**, 1505.
18 J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 371.

Received 16*th April* 1984; *Paper* 4/622