Methodological Strategy in locating Transition States. Cyclization of the Carbonyl Ylide $CH_2=O^+-CH_2^-$ and its Cycloaddition to Ethylene

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Taking into account the four conditions required by McIver and Komornicki to characterize a transition state, the most convenient technique for locating the transition states of the cyclization of the carbonyl ylide $CH_2=O^+-CH_2^-$ and of its 1,3-dipolar cycloaddition to ethylene is discussed, taken as examples for electrocyclic reactions and for cycloadditions, respectively. The strategy adopted seems to be adequate for studying any reaction.

The main problem in applying the absolute rate theory to a chemical reaction is locating the transition state on the potential hypersurface. McIver and Komornicki [1] define the transition state as the point with the following four conditions: (a) it is a stationary point, that is, 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; (d) it must be the lowest energy point which satisfies the above three conditions.

There are two fundamental ways to find this location. In the first option the potential hypersurface is constructed and the transition state is found by observing the hypersurface. This method has two essential limitations. The potential hypersurface can be visualized only when the energy depends at most on two variables. Since an analytical expression of the potential energy function is not available, the surface must be calculated numerically point by point, which requires an enormous amount of calculation for any reaction of chemical interest. Therefore the practical application of this method requires a reduction in the dimensionality of the surface. One way of doing this consists in permitting only one or two of the geometric parameters of the system to vary, and maintaining the rest constant. An important improvement is attained with methods which require the minimization of the potential energy, as in the reaction co-ordinate method: [2-4] 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 former, the energy being minimized. It is well known that the energy is minimal in any direction perpendicular to the reaction co-ordinate. This method would be correct to the degree to which the true reaction co-ordinates were well defined by only the independent variables chosen. The error made in the location of the transition state depends on the degree in which the rest of the geometric parameters intervene in the reaction co-ordinate.

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. To do this, various procedures have been developed, which can be classified into two groups: those which require energy calculations and those which also require the gradient to be calculated. In the first group the X-method [5] may be cited, which determines the transition state as an intersection point of isoenergy lines adjusted to the hypersurface. Müller and Brown's method [6,7] may also be cited, consisting in minimizing the energy on suitable hyperspheres between initial and final minima so as to generate a series of valley points of increasing energy, which close in on a saddle point from opposite sides. We shall also mention the synchronous transit method. [8] The location of a saddle point is effected by alternately searching for energy maxima along transit paths and energy minima on surfaces of constant path co-ordinates until a point is reached which represents both an energy maximum along a transit path and an energy minimum on a surface of constant path co-ordinate. Liotard's method [9] follows the same idea as the synchronous transit method. Since this requires a calculation of the gradient, it can be considered to be intermediate between the two groups mentioned before. Chains of points are constructed successively in which that with the most energy is substituted by another, the latter generated starting from the former in a shifting vector direction, which initially is perpendicular to the chain of points. McIver and Komornicki's [1] and Poppinger's [10] techniques are typical gradient methods. The first locates the stationary points through the minimization of the square of the gradient norm and determines their nature by calculating the eigenvalues of the force constant matrix. Poppinger's very similar method directs the minimization towards the transition state through the calculation in each point of the eigenvalues of the force constant matrix. These two methods are very efficient but require a great amount 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 point. In general it can be affirmed that none of the direct location methods can insure that the located point will the true transition state of the reaction. In the most favourable cases, only the fulfilment of the first three conditions given by McIver and Komornicki can be guaranteed. Another stationary point that had the same properties and imposed a lesser energy barrier to the reaction could possibly exist.

All the strategies described for locating the transition state are incomplete, since none of the methods taken separately can guarantee that the four conditions McIver and Komornicki require are fulfilled. A more convenient technique for locating the transition states of two types of representative reactions, with a minimum volume of calculation compatible with reasonable certainty, seemed of interest to study: they are electrocyclic reactions and cycloadditions. In conclusion, as an example of both types, the two competitive reactions which the carbonyl ylide can undergo when it is formed *in situ* in the presence of a dipolarophile [11] have been chosen, its cyclization and its 1,3-dipolar cycloaddition to ethylene, respectively.
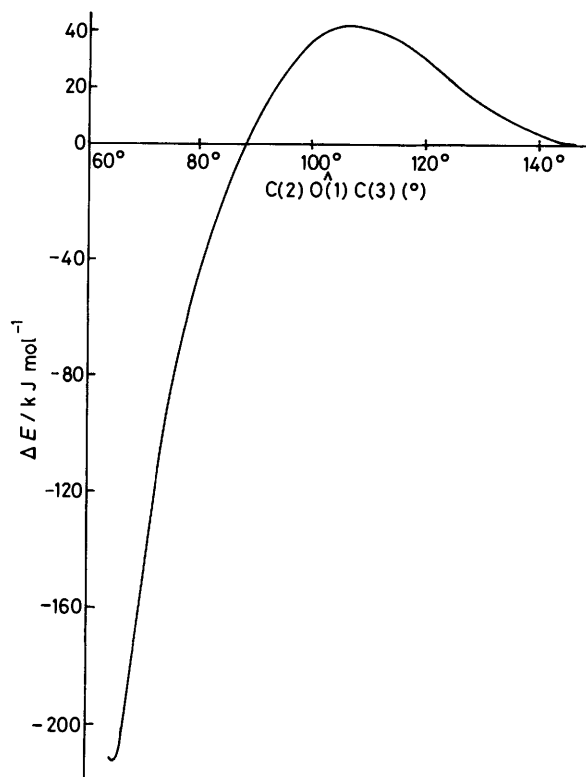
Figure 1. Energy profile of the cyclization of the carbonyl ylide $CH_2=O^+-CH_2^-$

Figure 2. Transition state of the cyclization of the carbonyl ylide $CH_2=O^+-CH_2^-$, with the components of the transition vector for each atom

Method

In this paper the advantages of the reaction co-ordinate methods,[2-4] the synchronous transit one,[8] and McIver and Komornicki's direct location method,[1] have been combined. An initial exploration of the potential surface has been carried out in each case with the first two methods, which allowed good starting points to be obtained for the application of the third. Given the volume of calculation required to carry out a sufficiently extensive exploration of the potential surfaces, the energy calculation was performed with the semi-empirical MINDO/3 method. The DFP (Davidon–Fletcher–Powell) method [12-14] has been used for the minimization of the energy as a mathematical procedure, based on the Fletcher–Powell algorithm and implemented in Dewar's MINDO/3 program.[15,16] The direct location of the stationary points has been performed with the SIGMA program. The eigenvalues of the force constant matrix have been calculated with the FORCE program.* The SIGMA as well as the FORCE program provide the gradient and the second derivatives by finite differences.

Discussion

In the first instance we shall study the cyclization of the carbonyl ylide $CH_2=O^+-CH_2^-$ and afterwards its cycloaddition to ethylene.

In an electrocyclic reaction a new σ bond is formed, at the expense of a reduction of the delocalized π-system. According to Woodward and Hoffmann's rules, the thermal reaction
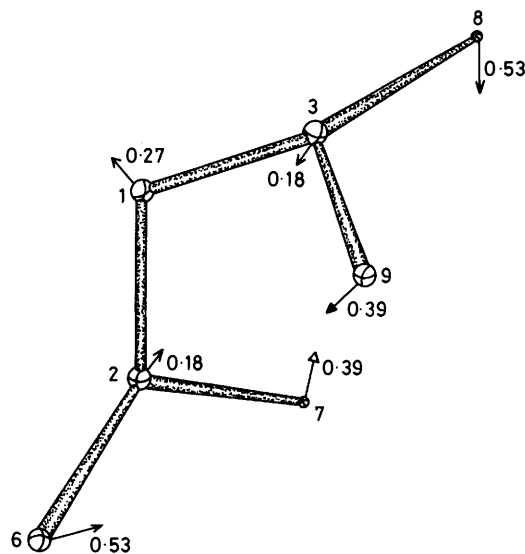
will be conrotatory or disrotatory, depending on the number of electrons associated with the π-system. With four π-electrons the process should be conrotatory for the carbonyl ylide. This completely optimized molecule, using the MINDO/3 method, shows a non-planar structure with a conrotatory rotation in the carbon atoms, demonstrating in this way its tendency towards cyclization to ethylene oxide. The potential energy of the ylide throughout the process will depend on the fifteen internal degrees of freedom of the system. To operate a reduction of the dimensionality of the hypersurface, let us pay attention to the geometric parameters whose variation is greatest in the course of the reaction. The most striking structural differences between the carbonyl ylide and ethylene oxide are seen in the differences of the CC and CO bonds, and in the dihedral angles of the hydrogens joined to the carbons. It is expected that the reaction co-ordinate should depend essentially on the degree of advancement of the σ bond formation. For that reason the COC angle, which decreases continually from 147° in the ylide to 63° in ethylene oxide, has been chosen as an independent variable. The energy profile shown in Figure 1 was obtained by optimizing the rest of the geometric parameters. A maximum for the COC angle of 105° appears, which should give a good estimate of the true transition state if the selection of the independent variable has been adequate. In effect, in taking this structure as a starting point for the application of McIver and Komornicki's method, a stationary point was located with a COC angle of 107.7°, but whose remaining geometric parameters and energy were practically identical to the maximum of Figure 1. The calculation of the eigenvalues of the force constant matrix at this stationary point, using the FORCE program, gives a single negative eigenvalue, as must happen in a true transition state. The eigenvector corresponding to the negative eigenvalue of the force constant matrix is the transition vector that gives the reaction co-ordinate of the stationary point. In Figure 2 the structure of the stationary point located with the SIGMA program is presented, indicating the components of the transition vector for each atom. The movement of the O(1), C(2), and C(3) atoms corresponds precisely to the formation of the C(2)C(3) σ-bond and to the lengthening of the O(1)C(2) and O(1)C(3) bonds. At the same time a conrotatory rotation of the hydrogen atoms is brought

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* The SIGMA and FORCE programs were written originally by J. W. McIver and A. Komornicki, and implemented by S. Olivella and R. Caballol.

about. In view of all these results, it can be reasonably affirmed that the point found is the true transition state of the reaction. Strictly speaking, the calculations done up to now only guarantee that the structure in Figure 2 fulfills the first two conditions required for a transition state. The stationary point located with the SIGMA program practically coincides with the maximum of the energy profile of Figure 1, which goes from the reactive species to the product. Therefore the reaction path traced by means of the reaction co-ordinate method insures that the third condition is fulfilled. To be absolutely certain that the fourth condition is verified, the whole potential surface would have to be constructed. However, based on chemical intuition, it does not seem very likely that another reaction path that implies a lower energy barrier can exist. In this case then, it can be practically affirmed that the stationary point located on the potential hypersurface is the true transition state of the carbonyl ylide cyclization.

Cycloadditions which form two new σ-bonds at the expense of a reduction of the π-systems of both reactives present a much more complex problem. In the example adopted in this paper, the cycloaddition of the carbonyl ylide $CH_2=O^{+-}CH_2^-$ to ethylene, the potential hypersurface will depend on 33 internal degrees of freedom. As in the preceding case, the geometric parameters whose variation is more and more intense as the process goes on are chosen to reduce the dimensionality of the potential surface. The essential differences between the reactants and the final product lie in both the lengths of the σ bonds in formation and the bonds that intervene in the π-systems of both reactants, and in the deviation of the heavy atoms of the supermolecule from coplanarity. It is expected, as in the preceding case, that the reaction co-ordinate will depend essentially on the lengths of the two new σ bonds in formation. So, in this case it is absolutely necessary to take two independent variables. This implies the construction of a two-dimensional surface at least which, even for the example chosen, turns out to be costly. We initiated our research on this reduced surface, adopting a strategy analogous to that used in the synchronous transit or in Liotard's method. In the first place a sequence of points corresponding to the synchronous reaction path is constructed. To do this the two σ bond lengths are maintained the same, and the rest of the the parameters are optimized. A maximum for a value of 2.45 Å for both bond lengths appears. To carry out an initial exploration of the asynchronous zone of the reduced surface, a section orthogonal to the preceding one at its maximum point is made, following the strategy of the two methods cited above. To do this the two independent parameters are allowed to vary, maintaining their sum as a constant. In this way a series of points is generated until one of minimum energy is reached for values of 1.6 and 3.3 Å of the two independent variables. The resulting energy profile is symmetrical with a central maximum corresponding to the synchronous path, and two lateral minimums in the asynchronous zones of the surface. Each minimum point turns out to be the maximum in the orthogonal direction. It is a saddle point of the reduced surface. This structure is taken as a starting point for McIver and Komornicki's direct location method. A stationary point for the σ bond lengths of 1.59 and 3.12 Å, with an energy of 33.1 kJ mol⁻¹ with respect to the reactant and slightly more stable than the saddle point of the reduced surface, is obtained. The force constant matrix has a single negative eigenvalue at this point. This means that it is a saddle point of the whole potential hypersurface. It therefore fulfils the first two conditions required by McIver for a transition state. In Figure 3 the structure of this stationary point is shown, indicating the components of the transition vector for each atom. It can be seen that the C(2)C(4) bond hardly evolves, while the C(3)C(4) one closes rapidly. As a
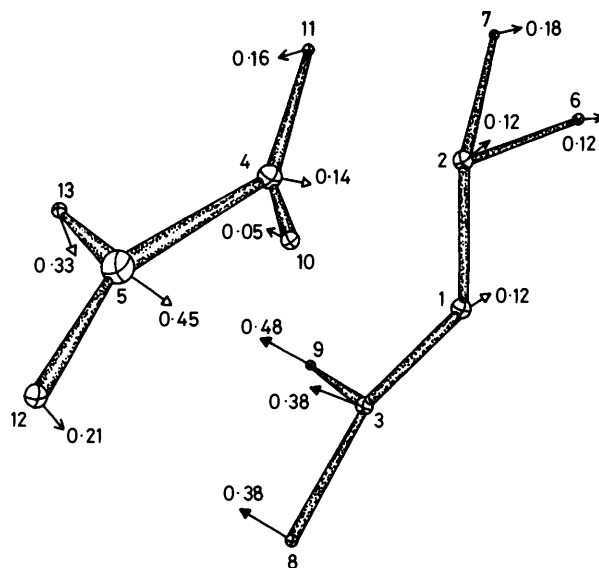

Figure 3. Second transition state of the cycloaddition of the carbonyl ylide $CH_2=O^+-CH_2^-$ to ethylene, with the components of the transition vector for each atom

result, the reaction co-ordinate of this saddle point consists essentially in the closing of the C(3)C(5) bond. This reaction co-ordinate clearly leads in one direction towards the final product. But it is clear that it does not take us to the reactant in the opposite direction and, hence, that McIver's third condition is not fulfilled. In effect, in choosing the C(3)C(5) distance as an independent variable, it is found that the saddle point is a maximum of an energy profile that has two minima. One corresponds to the final product and the other to an intermediate which, completely optimized, has an energy of 27.6 kJ mol⁻¹ with respect to the reactant, and bond lengths of 1.62 and 3.90 Å. In view of these results one must consider it a two-step process, with a first transition state between the reactant and the intermediate. Just as the reaction co-ordinate in the second step is essentially the formation of the C(3)C(5) bond, the first step must be the closing of the C(2)-C(4) bond, which is practically formed in the intermediate. Choosing the C(2)C(4) bond length as an independent variable, an energy profile is generated, which leads from the intermediate to the reactant through a maximum. Taking this as a starting point for McIver's direct location method, a stationary point is found which corresponds to a saddle point. This point has an energy of 51.1 kJ mol⁻¹ with respect to the reactant, for bond distances of 2.10 and 4.30 Å. In effect, the transition vector shows that the reaction co-ordinate corresponds mainly to the closing of the C(2)C(4) bond.

So far, combining the reaction co-ordinate, the synchronous transit, and McIver and Komornicki's methods, we have been able to find three stationary points on the potential hypersurface. They are an intermediate and two saddle points, which by means of a two-step mechanism forms part of a reaction path that leads from the reactant to the products. However, given the complexity of the process, it is not so evident that the reaction path found is the only possible one among those which leads from reactant to products, and if others do exist, that it is the most favourable. For that reason it seems absolutely necessary, to guarantee the fulfilment of McIver's fourth condition, to at least construct a reduced surface regarding the two new σ bonds. In Figure 4 such a two-dimensional surface is shown, obtained by taking the σ bond lengths being formed as independent variables. For each pair

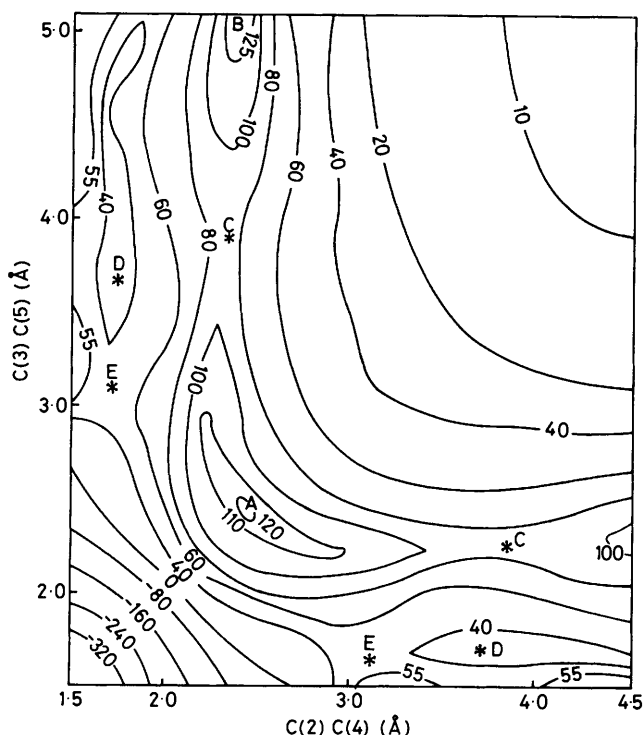**Figure 4.** Two-dimensional potential surface of the cycloaddition of the carbonyl ylide $CH_2=O^+-CH_2^-$ to ethylene (energy in kJ mol^{-1} and bond lengths in Å)

starting from very extended structures led spontaneously to the zone of the first transition state C. The fact is, the true first transition state, located by the SIGMA program, shows quite an extended conformation and undergoes a significant rotation to reach the intermediate. In view of this two-dimensional surface it does not seem possible that any other reaction path could exist. Therefore, the directly located saddle points seem to fulfill McIver's fourth condition and can be characterized as true transition states.

It must be taken into account that the study carried out in this paper refers exclusively to the potential surfaces of the reactions analysed here. Each reaction, with its own surface, will present a particular problem. But we believe that the strategy we propose, combining the reaction co-ordinate and synchronous transit methods, is adequate in general for finding good starting points for the application of the direct location method. Once the saddle points of the potential hypersurface are found, the fulfillment of McIver's first two requirements is guaranteed. The analysis of the transition vector of the saddle point is a first indication of whether the reaction co-ordinate really leads to reactant and to products. But, the surest technique for guaranteeing the third condition consists in generating two steepest descent paths in the two directions of the transition vector on the potential hyper-surface. The most difficult problem is fulfilling the fourth condition. Its verification requires at least the construction of a reduced surface. However, a complete hypersurface would have to be constructed to be absolutely sure. Since this is impossible, chemical intuition must frequently be resorted to, combining it with the knowledge of the reduced surface. Any strategy that ignores any of the four conditions given by McIver and Komornicki can be subject to a wide margin of error.

Finally, it should be clear that the potential hypersurfaces and therefore the transition states, depend on the energy calculation method. Our experience has shown that the structures of the stationary points located on the hyper-surface calculated with a given method are not acceptable for recalculating the energy of the stationary points on the hyper-surface calculated with another method. On the other hand, the methodological strategy proposed is independent of the method used to calculate the energy and requires an enormous volume of calculation. In practice, when trying to elucidate theoretically the mechanism of a chemical reaction, one is faced with the dilemma of using a perfect energy calculation method, but performing a rather incomplete exploration of the potential hypersurface, or using a quicker energy calcul-ation method which allows for a significant exploration of the hypersurface. In general, a compromise solution which questions the physical significance of the results obtained must be adopted.

of values for these independent variables the rest of the geometric parameters are optimized. The investigation of the surface has been confined to the bond distance of 5.20 Å because at a greater distance the supermolecule easily breaks into fragments that are different from the carbonyl ylide and from ethylene. It can be observed that there is a symmetrical surface, with a central hill A, which corresponds to the maxi-mum point of the synchronous path. The minimum of the energy profile, which comes about by performing a section orthogonal to the synchronous path at point A, is very near to E. From a global observation of the surface it is deduced that cycloaddition really occurs along the asynchronous path. The C(2)C(4) σ bond starts forming until the process gets to the first transition state C, placed between the energy hills A and B. From here on the C(2)C(4) bond continues closing until it gets to intermediate D. The second σ bond immediately begins to form, increasing as a consequence the energy until it reaches the transition state E. Until the process reaches D the reaction co-ordinate is essentially defined by C(2)C(4), whereas starting from D the reaction path is practically parallel to C(3)C(5). That is, the cycloaddition takes place in two successive steps, each being associated with the formation of the two new σ bonds.

The fact that a very elongated well potential around inter-mediate D can be observed when going in the direction of C(3)C(5) is interesting. This corresponds to an internal rotation of the supermolecule around the C(2)C(4) bond, which is almost completely formed. By increasing the C(3)C(5) distance the intermediate goes, with hardly any energy barrier, from a conformation of a cyclic type to an extended type. Another possible reaction path can be imagined, which goes around the other side of the hill, forming a first transition state with a completely extended conformation, and after-wards reaches intermediate D by means of the internal rotation mentioned above. All attempts to find this path,

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