

Theoretical Study of Polar 2 + 2 Cycloadditions

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By means of the MINDO/3 method the polar 2 + 2 cycloaddition of hydroxyethylene to 1,1-dicyanoethylene and the dimerization of ethylene have been studied. For the polar reaction the transition state has dipolar character, while for the non-polar reaction it has a tricentric structure. The reaction mechanism and the importance of charge transfer are discussed.

THE mechanism of polar 2 + 2 cycloadditions is the subject of great controversy. We refer to the three mechanisms which seem to us most significant. Huisgen,¹⁻³ taking into account experimental data, proposed a two-step mechanism with a zwitterionic structure (1,4-dipole) as an intermediate. Epiotis^{4,5} also proposed a two-step mechanism from qualitative potential energy surfaces obtained from the linear combination of fragment configurations, but this time the intermediate does not have a zwitterionic but a pericyclic structure; this means that it is not distorted easily. There is evidence to support this structure. Finally, Fukui,⁶ taking into account the third-order perturbation energy terms of a configurational interaction, has suggested that polar 2 + 2 cycloadditions can be initiated by a tricentric interaction among the two carbons of the donor molecule and the most electrophilic carbon of the acceptor molecule. An increase in the charge transfer configuration may facilitate the formation of the final product by means of pseudoexcitation.

To our knowledge, there are no quantitative theoretical studies on polar 2 + 2 cycloaddition energy surfaces that permit us to delve into the mechanism of such reactions. However, there are some theoretical studies in ethylene dimerization by semiempirical⁷⁻¹⁰ as well as by *ab initio* methods.¹¹⁻¹³ Most studies, semiempirical or *ab initio*, favour a two-step process with a biradical intermediate. An exception is by Jug¹⁰ who by means of the SINDO method finds that the concerted process is preferred. The papers of Salem¹¹ and Leroy¹³ only refer to the concerted region of the potential energy hypersurface. Leroy¹³ has also studied the effects of introducing donor and acceptor substituents on ethylene at certain points of the paths previously mentioned.

We have performed a quantitative theoretical study of the potential surface of a polar 2 + 2 reaction. Two geminal cyano-groups have been attached to ethylene as acceptors, and a hydroxy-group has been placed on the other ethylene molecule as a donor, taking hydroxy as a model for the alkoxy-group. In order to compare the mechanisms of polar and non-polar 2 + 2 reactions, the potential surface corresponding to ethylene dimerization was also studied. As the most complete study possible of the two potential surfaces is sought, one must necessarily choose a semiempirical method of energy calcul-

ation in order to keep the volume of calculations within reasonable limits.

METHODS

Due to the impossibility of calculating the total potential energy hypersurface for the majority of chemical reactions, two types of approach are used. The first attempts to reduce the dimensionality of the potential hypersurface by eliminating certain degrees of freedom. However, this involves the introduction of unrealistic restrictions when treating the problem.

An improvement in this approach is made by choosing certain degrees of freedom as independent variables of the potential energy, allowing the system to relax by optimizing all the other geometric parameters for each set of values of the independent variables. Nevertheless one must proceed with great caution when choosing these independent variables, since a bad selection may prevent us from achieving the true transition states and intermediates. The second type of approach takes into account all degrees of freedom of the system, but tries to locate directly certain points of chemical interest in the total potential energy hypersurface.

In our study we explored the potential energy hypersurface, taking as independent variables the lengths of the two new σ bonds being formed, and allowing the system to relax all the other parameters. This preliminary study of the potential energy hypersurface was taken as the starting point for McIver and Komornicki's¹⁴ method of directly locating stationary points. This method, given that the gradient is zero for all the stationary points of the potential energy hypersurface, located them by means of a minimization of the root mean square gradient. By examining the eigenvalues of the force constant matrix, one could discuss whether it is a transition state or another stationary point. Transition states were characterised by the existence of one and only one negative eigenvalue.

The preliminary calculations were carried out using the MINDO/3 program of Dewar *et al.*¹⁵ and the GEOMO program of Rinaldi.¹⁶ The first one used the Davidson-Fletcher-Powell¹⁷⁻¹⁹ algorithm for energy minimization, while the second had three options, known as the Murtagh,²⁰ Fletcher,¹⁸ or Rinaldi²¹ algorithms. Another difference between the two resided in the way the calculations of the energies were done. In MINDO/3¹⁵ they were calculated by the finite difference method, while in GEOMO¹⁶ this was accomplished in an analytical way. All the energy calculations were carried out using Dewar's semiempirical method, MINDO/3,²² which has been proved to be satisfactory in

most cases. McIver and Kormornicki's method¹⁴ was implemented by the SIGMA and FORCE programs which also use the MINDO/3²² method of energy calculation.

RESULTS AND DISCUSSION

We present first the results obtained for ethylene dimerization, and secondly those for the reaction of hydroxyethylene and 1,1-dicyanoethylene, in order to examine the change in mechanism in going from a non-polar towards a polar 2 + 2 reaction.

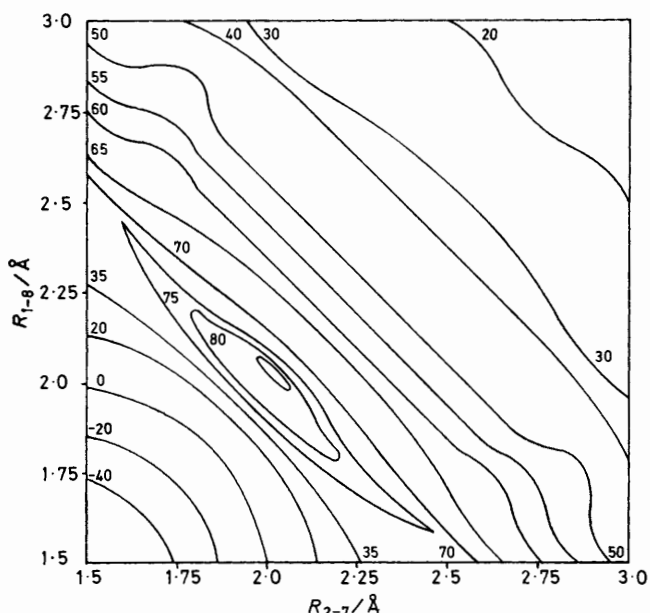


FIGURE 1 Potential energy surface for ethylene dimerization

In Figure 1 the potential surface obtained for ethylene dimerization is presented, choosing as independent variables the two new σ bonds being formed, and optimizing the remainder of the geometric parameters. One can see that the synchronous path is clearly disfavoured with respect to one where the two new bonds are formed at different rates. The potential barrier for a synchronous path is 85.6 kcal mol⁻¹, and this maximum appears at a distance of 2.0 Å for the two new bonds. Soon after surpassing the energy maximum crossing of the frontier orbitals takes place, according to Woodward-Hoffmann correlation diagrams.²³ In the potential surface of Figure 1 the transition state can be located with one bond almost completely formed (1.5 Å) and the other with a length of *ca.* 2.5 Å, with a potential barrier >70 kcal mol⁻¹. Nevertheless, the transition state located on the surface obtained by choosing two independent variables does not necessarily correspond to the true transition state, if the selected independent variables do not coincide exactly with the true reaction co-ordinate. In order to clarify this aspect we directly located the stationary points in the total potential energy hypersurface by means of McIver and Komornicki's¹⁴ method. This method requires taking as a starting point a geometry

close to that of the stationary point. As starting points we took two energy minima which appear on cutting the surface of Figure 1, and imposed the restriction that the sum of the lengths of the two new bonds is the same as the one they have at the point of maximum energy on the synchronous path. Two points were found, one at 72.1 kcal mol⁻¹ with R_{2-7} 1.61 and R_{1-8} 2.42 Å, and the other at 58.8 kcal mol⁻¹, with R_{2-7} 1.72 and R_{1-8} 2.20 Å. In order to clarify the nature of such stationary points, we calculated by means of the FORCE program the force constant matrix. The point at 72.1 kcal mol⁻¹ had two negative eigenvalues of this matrix, which means, according to the theorem of Murrell and Laidler,²⁴ that it was not a transition state, and that a transition state lower in energy must exist. The second stationary point at 58.8 kcal mol⁻¹ did have a single negative eigenvalue, so it was the true transition state. The transition state, whose structure is presented in Figure 2,

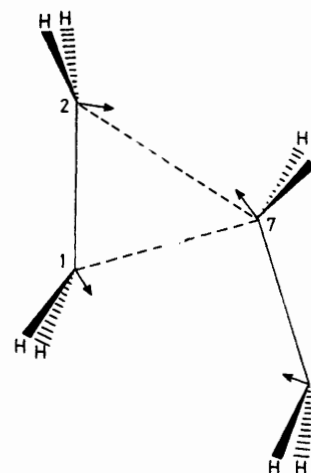


FIGURE 2 Structure of the transition state for ethylene dimerization, with the vectors of displacement of carbon atoms

is found somewhat further away from the point where one would expect to find it on analysing the surface of Figure 1. It also has a lower energy than would correspond to it on the same surface. This is due to the formation of a structure involving tricentric interaction among C-1, -2, and -7, in agreement with the prediction by Fukui.⁶ This tricentric structure has a charge transfer of 0.11 electrons from the ethylene whose two carbons belong to the ring towards the other ethylene; this involves a noteworthy stabilization of this structure. In Figure 2 the displacement vectors of the atoms that define the reaction co-ordinate are also presented. Such vectors correspond to the eigenvector associated with the one negative eigenvalue of the force constant matrix. From these displacement vectors it can be observed that the reaction co-ordinate makes the starting structure evolve towards cyclobutane.

Before concluding this study on ethylene dimerization we make two remarks. First, only the *supra-supra*-surface has been studied, since all our attempts at building a *supra-antara*-surface with the same indepen-

dent variables have spontaneously led to the former surface. Secondly, no intermediate appears on the surface explored, even in other sectors far from Figure 1. However, one must point out that our study has been done using the Restricted Hartree-Fock method²⁵ with a single Slater determinant which makes the appearance of biradical-type intermediates difficult. An Unrestricted Hartree-Fock²⁶ (UHF) study has permitted us to locate a biradical-type intermediate which exists outside the studied zone. It must be remarked that the MINDO/3 parametrization is done for the Restricted Hartree-Fock method,²² so the Unrestricted Hartree-Fock method overestimates the energy stabilization as a function of biradical character. Given that polar 2 + 2 reactions have little biradical character, it seems to us that the whole study must be done with the Restricted Hartree-Fock method in order to obtain comparative results.

The reaction of hydroxyethylene with 1,1-dicyanoethylene can give rise to two different adducts, 1-hydroxy-3,3- and the 1-hydroxy-2,2-dicyanocyclobutane. We have made a preliminary study of the reactions which lead to both adducts, with the restriction that the formation of the two new σ bonds is synchronous. That study allowed us to find two potential barriers, one of 92 kcal mol⁻¹ for the formation of 1-hydroxy-3,3-dicyanocyclobutane and another of 67 kcal mol⁻¹ for the formation of 1-hydroxy-2,2-dicyanocyclobutane, so that it can be expected that the formation of the latter adduct is much more favourable. For this reason we have carried out only a partial study of the potential surface for the former adduct, whereas for the latter the study has been more complete.

The transition state drawn in Figure 3 has been located by means of the SIGMA program starting from a partial study of the potential surface leading to 1-hydroxy-3,3-dicyanocyclobutane. This structure shows a barrier of 59.7 kcal mol⁻¹, the distances being R_{2-9} 1.77

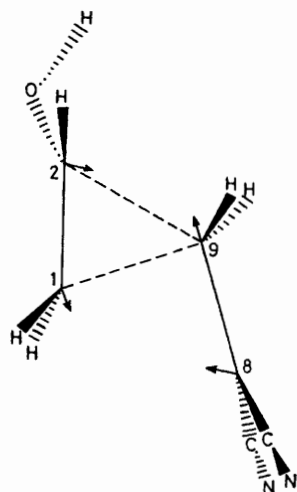


FIGURE 3 Structure of the transition state for the addition of hydroxyethylene to 1,1-dicyanoethylene leading to 1-hydroxy-3,3-dicyanocyclobutane, with the vectors of displacement

and R_{1-9} 1.62 Å. So a tricentric-type structure also appears among C-1, -2, and -9, the distance R_{1-9} being shorter than R_{2-9} corresponding to the bond being formed. This tricentric structure among the two carbons of the electron-donating molecule and the most electrophilic atom on the electron-withdrawing molecule appears as Fukui⁶ had anticipated. In the stabilization of that structure there is an important contribution from the charge transfer configuration, which is revealed by the transfer from hydroxyethylene to 1,1-dicyanoethylene of 0.34 electrons. In Figure 3 the atomic displacement vectors corresponding to the reaction coordinate, obtained with the FORCE program, are also presented. From them, it can be observed that the system evolves towards closure of bonds 1-8 and 2-9, leading to a final product.

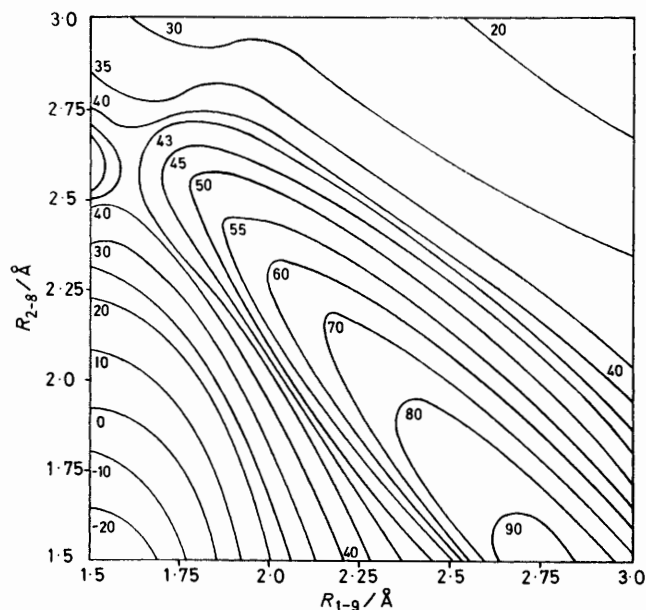


FIGURE 4 Potential energy surface for the addition of hydroxyethylene to 1,1-dicyanoethylene leading to 1-hydroxy-2,2-dicyanocyclobutane

In Figure 4 the potential surface of formation of 1-hydroxy-2,2-dicyanocyclobutane is presented, choosing as independent variables the two new bonds being formed. The reaction path is clearly asynchronous, the bond between the non-substituted carbons being closed first. The transition state can be located at R_{1-9} 1.60 and R_{2-8} 2.63 Å, which means that the 1-9 bond is almost formed whereas the 2-8 bond is in the first stages of formation. The potential barrier of this transition state is *ca.* 42 kcal mol⁻¹. Due to the structure of the surface, the appearance of an intermediate in a region outside the one explored in Figure 4 can be expected. It has been located by full geometric optimization, and found at R_{1-9} 1.74 and R_{2-8} 3.32 Å, which means that 2-8 bond has not yet begun to form whereas 1-9 bond is in the process of formation. The energy of this intermediate is 25.6 kcal mol⁻¹ above the reactants, the charge transfer from the hydroxyethylene to 1,1-dicyanoethylene

being 0.20 electrons. In order to find the transition state previous to the intermediate, the 1-9 bond in formation has been taken as the independent variable, and optimization carried out for the remainder of the geometric parameters. So a transition state for R_{1-9} 1.79 and R_{2-8} 3.43 Å has been obtained, the energy being only 0.02 kcal mol⁻¹ greater than that of the intermediate, with a charge transfer of 0.18 electrons.

By means of the SIGMA program we have located more accurately the transition state corresponding to the closure of the 2-8 bond. In Figure 5 we show the structure obtained, the distances of the two new bonds being R_{1-9} 1.59 and R_{2-8} 2.48 Å. This transition state

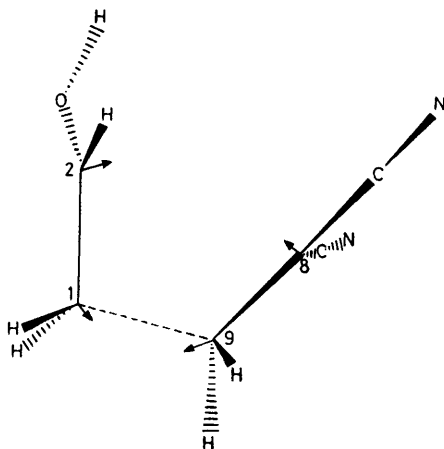


FIGURE 5 Structure of the transition state for the addition of hydroxyethylene to 1,1-dicyanoethylene leading to 1-hydroxy-2,2-dicyanocyclobutane, with the vectors of displacement

does not have tricentric character, as R_{2-9} (2.29 Å) and R_{1-8} (2.56 Å) are noticeably larger than R_{1-9} . The potential barrier for this transition state is 44.1 kcal mol⁻¹, leading to a charge transfer of 0.53 electrons. In Figure 5 the atomic displacement vectors of the reaction co-ordinate over the four-carbon ring are also shown. In the remaining atoms of the complex the displacement vectors are almost zero except for oxygen where it has a measurable value. One can easily see that the reaction co-ordinate corresponds to simultaneous closure of the 2-8 and 1-9 bonds. All our tests of directly locating the first transition state by means of the SIGMA program have been unsuccessful, as the program leads to an intermediate, very close to the potential surface.

From an experimental point of view of the three reactions studied, only the addition of 1,1-dicyanoethylene to isobutenyl methyl ether is observed to lead to an adduct of the same type as 1-hydroxy-2,2-dicyanocyclobutane.¹ As already mentioned in our theoretical study, in order to reduce the volume of calculations, the methyl groups have been substituted by hydrogens. The theoretical results obtained for the potential barriers 58.0, 59.7, and 44.1 kcal mol⁻¹ agree with the experimental data.¹ The barrier obtained for this polar 2 + 2 cycloaddition is of the same order as those obtained for a series of Diels-Alder²⁷ reactions, also in good agreement

with experimental data. The decrease of potential barrier in the three reactions studied is directly related to the increase of charge transfer in the transition state.

The most significant result of the present study of ethylene dimerization using the semiempirical method MINDO/3²² is the location of a transition state with a tricentric structure in agreement with that anticipated by Fukui.⁶ This result cannot be compared with *ab initio* studies¹¹⁻¹³ previously carried out on ethylene dimerization, as they have not explored this region of the potential hypersurface. Nevertheless, this study agrees with the *ab initio* calculations in that the formation of cyclobutane takes place predominantly in an asynchronous path.

Passing to the polar 2 + 2 reactions, from which we have selected as the prototype an ethylene with a strong donor group and another with strong acceptor groups, two different mechanisms have appeared, the first similar to that of non-polar 2 + 2 reactions with low charge transfer, and a second radically different one when the charge transfer is much greater. Fukui⁶ had already pointed out that the formation of tricentric structures was not favoured when charge transfer was very high. In the polar 2 + 2 reaction leading to the most favourable adduct, a two-step mechanism appeared, with an intermediate which has a certain amount of 1,4-dipole character, with a charge transfer of 0.20 electrons and a potential barrier leading to reactants close to zero. The transition state of the reaction corresponds to the transformation of this intermediate into final products, the transition state having a dipolar structure with a charge transfer of 0.53 electrons, and with the 1-9 bond almost formed whereas the 2-8 bond is just beginning its formation. The intermediate which has appeared in this theoretical study presents little zwitterionic character, not in full agreement with Huisgen's¹⁻³ postulate. On the contrary, the second transition state, decisive in this reaction, has greater charge transfer and a pericyclic structure in good agreement with that proposed by Epiotis.^{4,5} Nevertheless, one must remark that all theoretical calculations have been carried out for gas-phase reactions whereas experimental data correspond to processes in the liquid phase with different solvents.^{1,3} Early results from such theoretical calculations introducing the effect of the solvent by means of the cavity model, besides decreasing the barrier, have increased the well depth of the intermediate and its dipolar character in the direction proposed by Huisgen.¹⁻³

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