Quantum-chemical Interpretation of Photo-induced Electrocyclic Reactions

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ELECTROCYCLIZATIONS and many related stereospecific reactions have found a common interpretation in the form of the Woodward-Hoffmann rules. The essential feature of the interpretation is the symmetry of the molecular orbitals involved in the reaction process. The importance of symmetry was first suggested in a paper by Havinga and Schlatmann,[1] but the general nature of the principle was formulated by Woodward and Hoffmann.[2]

In spite of this interpretation many aspects of reaction mechanisms remain unexplained of which the photochemical cyclization of butadiene to cyclobutene is an example. Dauben[3] has pointed out that since the ground state of cyclobutene is *ca.* 20 kcal./mole less stable than butadiene, the spectroscopic singlet of cyclobutene is *ca.* 50—60 kcal./mole higher than that for butadiene, and he concluded that the formation of the former singlet from the latter is improbable. The question is: what is the driving force of the reaction

$$S^1_{\text{butadiene}} \rightarrow [?] \rightarrow S^0_{\text{cyclobutene}}$$

and what is the actual path along which the final state is reached?

Energy levels have been calculated for the ground state and excited states of butadiene, of cyclobutene, and of a large number of intermediate configurations resulting in potential surfaces essential for a detailed discussion of the course of the reaction.

The energies of ground and excited states are calculated as a function of the three angles ϕ, χ, and θ.† ϕ is the angle between C(2)–C(3), C(1)–C(2), and C(3)–C(4); it is directly related to the ring closure and has been varied from 125° to 90°. χ describes the rotation of the *p*-orbitals on C(1) and C(4); it has been varied from 0 to 90°. In the conrotatory process the *p* orbitals are rotated in the same direction, in the disrotatory process in the opposite direction. θ is a measure for the rotation about C(2)–C(3); it has been varied from -90 to $+90°$.

The distances C(1)–C(2), C(2)–C(3), and C(3)–C(4) have been kept constant and C(1) and C(4) were supposed to retain their trigonal hybridization in all the configurations. These simplifications of the model make it somewhat unrealistic in the neighbourhood of the cyclobutene. By use of this simplified model the total number of nuclear configurations for which the energies have been calculated still amounts to 4408.

Calculations were performed with a valence-bond method by use of the modifications introduced by Pariser and Parr,[4] and Pople.[5] Since it is a four-electron–four-orbital problem, complete calculations involve twenty singlet valence-bond structures (covalent and ionic structures), all of which were essential for good agreement with the first absorption band of *trans*-butadiene; details of this method have been published.[6]

To the energy of the four electrons, two energy terms were added: the interaction between non-bonded hydrogen atoms and the angle strain on C(2) and C(3) caused by the change of ϕ from equilibrium. The parameters for these two terms were taken from Gleicher and Schleyer.[7]

For each combination of ϕ and χ the value of θ which gives the lowest energy for that combination has been selected for the ground state as well as for the excited states and thus θ can be eliminated as an independent variable. Then for each state two-dimensional graphs can be made of the energy as a function of ϕ and χ. From these potential surfaces[6] probable paths of the thermal and photo-induced reaction are determined.

The first two excited states of butadiene differ little in energy, since there is an antisymmetric excited state at 5·4 ev and a symmetric one at 6·1 ev. The transition to the antisymmetric level has a calculated oscillator strength of 0·31 whereas the transition to the symmetrical level is forbidden. The energies of these two states along the probable reaction paths are shown in the Figure together with the energy of the ground state as a function of the angle ϕ.

Although in the ground state the disrotatory process of ring closure is impossible since an activation energy of *ca.* 100 kcal./mole is required, in the conrotatory process there is no activation energy at all. As described already the simplification makes the results of the calculations rather inaccurate for low values of ϕ when the cyclobutene is nearly formed.

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† All calculations were performed on the computer of the University of Leiden, an IBM 360–50.

U.v. irradiation of *cis*-butadiene gives the antisymmetric excited state. At $\phi \sim 116°$ the antisymmetric and symmetric energy levels intersect, but in nuclear configurations which deviate from twofold symmetry the degeneracy is lifted and the levels no longer cross. In this manner the molecule proceeds into the symmetric excited state initiating a disrotatory ring closure. From this state the molecule is supposed to reach the lower potential surface of the ground state. The mechanism of this transition is unknown but is connected with radiationless processes in molecules. It may well be that collisions with other molecules are essential for the completion of the ring closure.‡

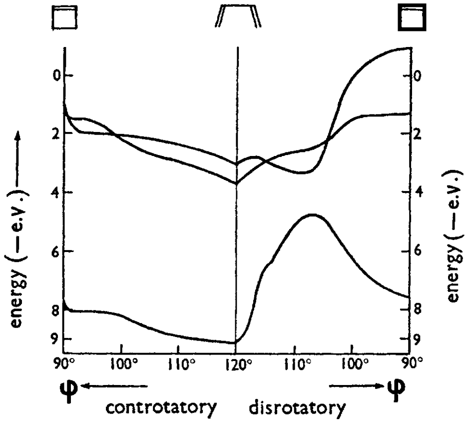

FIGURE. *The energies for the ground state and two excited states during the reactions.*

Thus, it is insufficient to restrict the considerations to the antisymmetric excited state, as has been done by many authors,[2,8,9] since this state is scarcely relevant to the course of the photoinduced reaction.

A comparison of the potential surfaces from our calculations with those of Longuet-Higgins and Abrahamson[10] shows that their correlation diagram pertaining to the disrotatory mode for the interconversion of butadiene and cyclobutene is similar to our potential surfaces since it also reveals a potential well in a symmetric excited state situated above a high potential barrier in the ground state. We stress, however, a dissimilarity to the present results. Our calculations show, in contrast with the qualitative diagram of Longuet-Higgins, that the energy of the symmetric excited state during the photoinduced reaction reaches a lower value than the energy of the antisymmetric excited state. The importance of this well in providing the driving force to the photochemical reaction cannot be derived from a qualitative description.

An interpretation in terms of valence-bond structures is surprisingly simple[6] as the occurrence of a high potential barrier in the ground state and a potential well in the symmetric excited state in the disrotatory process is a result of the noncrossing rule. Similar results have been obtained from calculations on the ring closure of allylic systems.

The results suggest a statement which could be generally applicable.

If a conrotatory (disrotatory) process is unfavourable in the ground state it implies the presence of a high potential barrier. From general principles it follows that there will be another potential surface of the same symmetry *which has a well not far above this barrier. The photoinduced reaction may profit from this energy well to bring about ring closure or opening by a conrotatory (disrotatory) process opposite to the reaction in the ground state.*

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‡ The transition into the symmetric excited state provides an explanation for the absence of fluorescence and phosphorescence in dienes.

[1] E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, 1961, **16**, 146.
[2] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395, 2046, 4388.
[3] W. G. Dauben, "13th Chemistry Conference of the Solvay Institute, Reactivity of the Photoexcited Organic Molecule", Interscience, New York, 1967, p. 171.
[4] R. Pariser and R. Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.
[5] J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.
[6] Details described in the dissertation of W. Th. A. M. van der Lugt, Leiden, 1968.
[7] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582.
[8] K. Fukui, *Bull. Chem. Soc., Japan*, 1966, **39**, 498.
[9] H. E. Zimmermann, *J. Amer. Chem. Soc.*, 1966, **88**, 1564.
[10] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 1965, **87**, 2045.