Ab Initio SCF Study of the Photochemical Disrotatory Closure of Butadiene to Cyclobutene

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Abstract: An all-electron "ab initio" SCF–CI method is used to calculate the ground and lowest excited states potential energy curves for two reaction paths (linear and quasi-linear) of the photochemically allowed disrotatory cyclization of butadiene to cyclobutene. Three singlet–singlet (allowed or avoided) crossings govern the reaction in the singlet manifold. The absence of triplet reactivity is also explained in terms of two triplet–singlet surface crossings. These results confirm qualitatively and improve quantitatively the van der Lugt and Oosterhoff mechanism which was based on a four-electron four-orbital valence bond model.

The reaction pathway along which *cis*-butadiene in its $\pi\pi^*$ ($^1B_2$) singlet excited state S_1 travels to finally reach cyclobutene in its ground state was first investigated by van der Lugt and Oosterhoff.[2a] They found this antisymmetric S_1 state of butadiene to be scarcely relevant to the mechanism of the photoreaction and, instead, they emphasized the importance of a neighboring symmetric S_2 state. S_2 has a potential well at a nuclear configuration for which the S_0 ground state has a high potential barrier. These necessarily coincide since they arise from an avoided crossing between the two states. Excited molecules are trapped in the S_2 well the bottom of which is below the vertically excited S_1 state. This well is a leakage channel (a funnel[2b]) from S_2 to S_0 since the energy gap between the two states is at its minimum.[3]

From a technical point of view van der Lugt and Oosterhoff consider the reaction butadiene–cyclobutene as a four-electron four-orbital problem. The relevant electrons are obviously the four π electrons of butadiene; the four orbitals are the π MO's of butadiene which correlate with (a) the π and π^* MO's of cyclobutene and (b) the σ and σ^* MO's of the newly formed CC bond. The energies of the four-electron ground and excited states are calculated using (a) a valence bond (VB) method where the approximations introduced by Pariser–Parr[4a] and Pople[4b] in MO theory are applied and (b) a configuration interaction calculation which includes the 20 possible VB structures (ionic and covalent) resulting from the four-electron four-orbital model. The energy changes in the 26 remaining electrons are treated in a nonexplicit empirical fashion. Due to the fact that, in addition, all bond lengths are frozen at their butadiene values and that the terminal C_1 and C_4 atoms retain their trigonal hybridization the model is unrealistic in the cyclobutene region. This probably does not entail any impairment of the proposed mechanism which mainly concerns the butadiene and transition state regions.

In this paper we shall investigate this problem using an all-electron SCF-MO method. The MO treatment of excited states has now reached the stage where the $\pi\pi^*$ singlet state of unsaturated molecules, which, for a long time, had been the villain of the piece, may be fairly well described by (a) the inclusion in the basis set of sufficiently diffuse atomic orbitals and (b) a large but feasible CI. Our aim is then to confirm the qualitative and, possibly, to improve the quantitative descriptions of the mechanism of the photochemical closure of butadiene found by van der Lugt and Oosterhoff. We shall therefore briefly outline our theoretical method and then proceed to discuss in detail the mechanistic implications of our theoretical potential energy surfaces.

Details of the Calculations

The geometries of *cis*-butadiene and cyclobutene are represented in Figure 1. For butadiene we have chosen the experimental geometry as did van der Lugt and Oosterhoff,[2a] but we have not kept the three CC bond lengths constant during the reaction. Instead we use the geometry of cyclobutene resulting from an "ab initio" SCF optimization.[5] Two different reaction paths were investigated. (a) In the first one the major variable, the cyclization angle ϕ, was varied from 120 to 95° by steps of 5°. All the other geometrical quantities, the CC bond lengths, the twisting angle, and the pyramidalization of the terminal CH_2 groups, were allowed to change by small increments (proportional to the changes of ϕ) from their initial values in butadiene to their final cyclobutene values. This first path might be called the *"linear" path.* (b) The second path is the *"quasi-linear" path* which was found by van der Lugt and Oosterhoff to be the probable disrotatory photochemical pathway (Table II of ref 2a). At the very beginning of the reaction ϕ remains constant at its butadiene value (120°) while the two terminal CH_2 groups rotate by 40° (χ varies from 0 to 40°). Then the molecule closes (ϕ changing from 120 to 95°) while the two CH_2 groups terminate their rotation (χ varying from 40 to 90°). At the same time all the other geometrical parameters vary linearly with ϕ from their butadiene to their cyclobutene values.

The GAUSSIAN 70 SCF system of programs[6] was used to carry out the Hartree–Fock calculations. The basis set consists of two parts: the usual localized STO 3G atomic orbitals were completed by a set of diffuse Gaussian p orbitals with an exponent of 0.04 (the three degenerate *x*, *y*, and *z* components were included on each carbon atom). Such diffuse orbitals are necessary to properly describe the $\pi\pi^*$ singlet state of unsaturated molecules.[8] The first step of the calculation, the SCF part, provides us with MO's which will serve to build the various Slater determinants forming the basis for the configuration interaction (CI) calculation. The best set of MO's must be obtained to ensure that the CI procedure which, for practical reasons, has to be limited will nevertheless approach as closely as possible the results of a full CI. In the present case the highest occupied MO of butadiene, A (antisymmetric with respect to the plane of symmetry of the reacting system), correlates with the antibonding π^* MO of cyclobutene and, in the process, crosses the lowest unoccupied π MO of butadiene, S (symmetric), which correlates with the bonding π MO of cyclobutene.[9] In the crossing region the two A and S MO's are nearly degenerate. As a consequence three one-electron configurations become almost equienergetic: A^2 (the "ground state"),

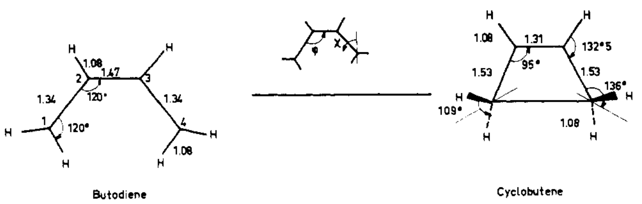

Figure 1. Butadiene and cyclobutene geometries (all bond lengths in Å) and the two important reaction coordinates ϕ (closure) and χ (rotation of the terminal CH_2 groups).

Table I. Energy Difference (ΔE) between Cyclobutene and *cis*-Butadiene ($\Delta E = E_{\mathrm{cycl}} - E_{\mathrm{butad}}$) in Their Ground States (All Values in kcal/mol)

	Present calculations	Other theoretical evaluations	Exptl value
SCF level	−3.0[a]	−5.0[c]	8.9[d]
CI level	+17.4[b]	+7.8[c]	

[a] At the SCF level the absolute energies of cyclobutene and *cis*-butadiene are respectively −153.0864 and −153.0815 au. [b] At the CI level the absolute energies of cyclobutene and *cis*-butadiene are respectively −153.1228 and −153.1508 au. [c] K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, 94, 5639 (1972). [d] Evaluated from the heats of formation of cyclobutene (37.5 kcal/mol) and *trans*-butadiene (26.3 kcal/mol), [N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 50, 1262 (1969)] and the energy difference between *cis*- and *trans*-butadiene (2.3 kcal/mol) [J. G. Aston, G. Ssasz, H. W. Wooley, and F. G. Brickwedde, *ibid.*, 14, 67 (1946)].

Table II. Tabulation of the Vertical Excitation Energies of the Lower Excited States of *trans*- and *cis*-Butadiene (all Values in eV)[f]

Excited state	Present calculations	Other calculations		Exptl values	
		trans-Butadiene			
^1A_g	7.38	6.67[a]	6.77[b]		
^1B_u	7.69	6.60[a]	7.05[b]	6.05[c]	5.92[e]
^3A_g	6.22	4.95[a]	5.04[b]		4.91[e]
^3B_u	4.28	3.24[a]	3.45[b]	3.32[d]	3.20[e]
		cis-Butadiene			
$^1A_1$	7.40	6.66[a]			
$^1B_2$	7.00	6.35[a]			
$^3A_1$	6.22	4.90[a]			
$^3B_2$	3.93	2.95[a]			

[a] Reference 8b. [b] Reference 12. [c] Optical value: W. C. Pryce and A. D. Walsh, *Proc. R. Soc. London, Ser. A*, 174, 220 (1940). [d] Optical value: D. F. Evans, *J. Chem. Soc.*, 1735 (1960). [e] Electron-impact values: O. A. Mosher, W. M. Flicker, and A. Kuppermann, *Chem. Phys. Lett.* 19, 332 (1973); *J. Chem. Phys.*, 59, 6502 (1973). [f] The SCF and SCF–CI absolute energies of *cis*-butadiene in its ground state have been already given (see Table I). The corresponding values for *trans*-butadiene are respectively −153.09335 (SCF level) and −153.16107 au (CI level).

S^2 the first *doubly* excited state, and S^1A^1 the *singly* excited state. It is unclear as to whether the best MO's result from a closed-shell SCF calculation on the S^2 or A^2 configurations or from an *open-shell SCF* calculation on the S^1A^1 configuration. At each point we have chosen to try both types of calculations and to accept as final result the calculation which, after completion of the CI, yields the lower final energy for the ground state of the system. The closed-shell calculation uses Roothaan formalism.[10] The open-shell calculation was carried out in the Nesbet approximation[11] which involves a unique but approximate Hamiltonian for both the singlet and triplet S^1A^1 configurations and has the virtue of simplicity. It was found that the MO's resulting from the Nesbet open-shell method are the best in the transition region (roughly halfway along the reaction path). On the other hand it is obvious that Roothaan closed-shell formalism should be preferred in the regions of closed-shell reactant (butadiene) and product (cyclobutene).

The second part of the calculation, the CI treatment, was carried out in the following way. The set of important MO's in the description of the lowest excited states of the system results from the union of two smaller groups of MO's: (a) the eight π MO's of butadiene plus those butadiene MO's which correlate with the ten π MO's of cyclobutene and do not already belong to the π system of butadiene, and (b) the ten π MO's of cyclobutene plus those cyclobutene MO's which correlate with the π MO's of butadiene (among these the very important σ and σ^* MO's of the newly formed CC bond). The MO's in the set we have defined were allowed variable occupancy; all singly and doubly excited configurations were constructed and the resulting CI matrix was diagonalized. (For example, the lowest antisymmetric $\pi\pi^*$ singlet state $^1B_2$ requires 176 configurations, the lowest symmetric doubly excited state 186 configurations.) Before going any further let us compare our results with the available experimental and theoretical informations. The energy difference between *cis*-butadiene and cyclobutene in their ground state agrees qualitatively (*cis*-butadiene being more stable than cyclobutene) with the reported values (Table I). Quantitatively, the value ΔE we obtain is in error by ~8 kcal/mol, probably as a result of the low-level basis set used, but this is no way affects the conclusions on the photochemical behavior of the system under study. As shown in Table II, our calculated vertical excitation energies for *cis*- and *trans*-butadiene are roughly 1 eV higher than the results of previous calculations. In order to calculate potential energy curves the sophistication of the method had to be somewhat reduced. As a consequence our results, though reliable, cannot compare with the refined values of Shih et al.[8b] (who use a double ζ basis set to which 3s and 3p diffuse orbitals are added) and Dunning et al.[12] (who introduce *two* 2p diffuse functions on each carbon atom and carry out a very extensive, 2000 × 2000, CI calculation). Still the relative position of the $\pi\pi^*$ singlet state $^1B_2$ and the $(\pi\pi^*)^2$ doubly excited state $^1A_1$ which is, as we shall see, a very important factor in the reaction mechanism, is correctly represented. (We find that the $^1A_1$ state is 0.4 eV above the $^1B_2$ state. A similar gap (0.3 eV) is reported in ref 8b.)

Analysis of the Potential Energy Curves

The potential energy curves for the low-lying states of the reacting system are presented in Figure 2 (*linear* reaction path) and 3 (*quasi-linear* path). The two sets of curves are clearly similar, at least qualitatively, and, for that reason, will be discussed simultaneously. In the butadiene and transition state regions, our potential energy curves have the same aspect as those of van der Lugt and Oosterhoff (cf. Figure 6, ref 2a) but the cyclobutene region is greatly improved. The prominent feature of the *singlet* states curves is the existence of three regions of allowed (C_1, C_3) or avoided (C_2) crossings. Let us then analyze these three regions successively.

(1) The closed-shell SCF calculation on butadiene gives six virtual π MO's. Most of them are purely diffuse but the lowest and the highest ones retain a clearly localized covalent character (though they also contain a nonnegligible diffuse contribution) and can still be recognized as the familiar π_3 and π_4 MO's obtained in the simple minimal basis set study of butadiene. The lowest excited singlet state $^1B_2(S_1)$ (antisymmetric with respect to the plane of symmetry which is conserved during the disrotatory motion) results from the promotion of one electron from π_2 to π_3. The second excited singlet state is the (symmetric) $^1A_1$ state. Its

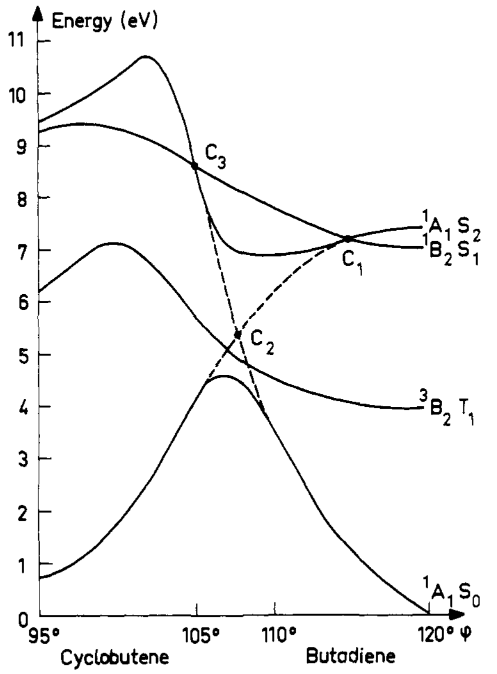

Figure 2. Potential energy curves for the lowest states of the butadiene–cyclobutene system in the *linear* reaction path for the disrotatory closure of butadiene.

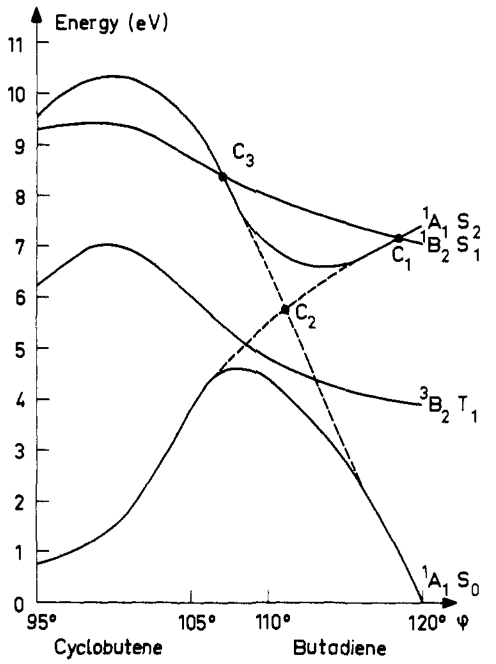

Figure 3. Potential energy curves for the lowest states of the butadiene–cyclobutene system in the *quasi-linear* reaction path for the disrotatory closure of butadiene.

nature is more complex. The *doubly* excited one-electron configuration $(\pi_2 \rightarrow \pi_3)^2$ of butadiene is nearly degenerate with the $(\pi_1 \rightarrow \pi_3)$-$(\pi_2 \rightarrow \pi_4)$ combination of the two *singly* excited one-electron configurations $\pi_1 \rightarrow \pi_3$ and $\pi_2 \rightarrow \pi_4$. These two configurations $(\pi_2 \rightarrow \pi_3)^2$ and $(\pi_1 \rightarrow \pi_3)$-$(\pi_2 \rightarrow \pi_4)$ have the same A_1 symmetry and therefore interact when the electron correlation is included. As a consequence their out-of-phase combination S_2 is strongly stabilized. It may be noted that this $^1A_1$, S_2 state may also be described, in the exciton model, as two ethylene molecules individually excited to their $\pi\pi^*$ triplet state and coupled to yield an overall singlet.[13] The very important point is that S_1 and S_2 are in a *near-touching* situation,[14] the gap between them being, as we have already said, of the order of 0.4 eV. Now when the reaction proceeds the S_1 state (and also the corresponding B_2 triplet state T_1) is slowly destabilized. This is because the gap, and therefore the excitation energy, between the highest occupied and the lowest empty MO's of a $2k$ π electron system (here, for butadiene, $k = 2$) is smaller than that of the $2(k - 1)$ π electron system (here, cyclobutene) which results from the cyclization. On the other hand S_2 is strongly stabilized since, at the end, it correlates with the ground state of cyclobutene.[9,15] The resulting crossing occurs at the very beginning of the reaction (C_1) and is strictly *allowed* when there is a true plane of symmetry (in that case the two states have different symmetry). This crossing becomes avoided if the displacement of one or several nuclei destroys the plane of symmetry. C_1 is a geometry-dependent avoided crossing.[16]

(2) On the cyclobutene side of Figures 2 and 3 the point C_3 also corresponds to a truly *allowed* crossing between the potential energy curves of the two lowest, antisymmetric and symmetric, singlet states of cyclobutene.

(3) The third crossing is the familiar *avoided* crossing between the S_0 ground state and the S_2 doubly excited state potential energy curves of the butadiene–cyclobutene system.[9,15] This model-dependent avoided crossing[16] is a direct consequence of the allowed crossing between the highest occupied A (antisymmetric) MO and the lowest vacant S (symmetric) MO of butadiene during the cyclization process. Physically this avoided crossing corresponds to the gradual movement of two electrons from the A to the S MO (or conversely) in the crossing region.

These three crossing regions are fundamental and we shall now discuss their mechanistic implications. The first crossing C_1 is only slightly higher than the vertically excited $^1B_2$ state (s_1) of butadiene (5 kcal/mol in the linear path, 8 kcal/mol in the quasi-linear path). This means that excited molecules with a small vibrational energy will be able to populate the neighboring well in the S_2 potential energy surface in a time compatible with the lifetime of the excited S_1 state. (This switch from a S_1- to a S_2-governed system seems, at least according to our results, easier in the linear than in the quasi-linear reaction path.) Let us recall here that van der Lugt and Oosterhoff reported for this switch an activation energy of 14 kcal/mol,[2a] a value which is too high for excited molecules to pass through the C_1 region in a photochemically reasonable period of time. If, on the other hand, cyclobutene is excited in its lowest singlet state an energy barrier of 6 kcal/mol (in both pathways) must be overcome if the system is to reach the (allowed) crossing C_3 where it may switch from the singly excited to the doubly excited surface. Whether we start with butadiene or cyclobutene the potential well in the S_2 surface may therefore be populated. As was noted by van der Lugt and Oosterhoff[2a] the bottom of this well is below the vertically excited S_1 state of butadiene (4 and 8 kcal/mol in the linear and quasi-linear reaction paths, respectively). In this avoided crossing region the S_2 surface is approximately 45 kcal/mol above the maximum of the S_0 surface. The gap between the two states is $2K_{SA}$, i.e., twice the exchange integral between the crossing S and A MO's. Such an exchange integral is usually small unless the two S and A MO's are located over the same set of atoms, as in antiaromatic transition states.[17] The present transition state is antiaromatic but nevertheless the gap is largely overestimated. The ground state S_0 is fully correlated via a configuration interaction which includes all the important doubly excited states whereas the S_2 "doubly" excited state is only partly so since the CI did not include the triple and quadruple excitations which would be necessary to reach a full correlation of the S_2

state. As we have already mentioned the two S_1 and S_2 states are equally biased and about 1 eV too high in energy. We may therefore expect the real gap to be of the order of 20–25 kcal/mol. The well in the S_2 surface is a *leakage channel* from S_2 toward the ground state S_0 surface. (In the two-state model for avoided crossings the probability for such a jump to occur would be given by the Landau–Zener formula.[3,16]) The intimate mechanism of the "jump" is not known at the present time though it certainly involves the coupling of the discrete vibrational levels of S_2 with the quasi-continuum of the S_0 vibrational levels. When the system has reached the ground state manifold it may end up in the butadiene or/and cyclobutene ground states.

Let us now turn our attention toward the lowest B_2 triplet state T_1 of butadiene. Halfway along the reaction coordinate the T_1 surface is in a near-touching situation with the maximum of the S_0 surface. If again we take into account the 1 eV overestimate of the excited state energies we should instead obtain two true crossings of the two curves. At such points intersystem crossing might bring the triplet excited species back to the ground state surface. Starting with triplet butadiene the first (hypothetical) crossing point (on the right-hand side of the ground state potential barrier) might possibly be reached (the necessary activation energy is about 9 kcal/mol) but intersystem crossing would bring the system back to the starting material. The second crossing point (on the left-hand side of the barrier) necessitates an activation energy of 35 kcal/mol and appears unreachable. If, on the other hand, we excite cyclobutene in its lowest triplet state the activation energy which is needed to overcome the neighboring barrier in the triplet surface appears again too high (17 kcal/mol) for a photochemical process. The triplet states of butadiene and cyclobutene do not react. Indeed, Srinivasan has shown that the photolysis of 2,3-dimethyl-1,3-butadiene in the vapor phase cannot be quenched by oxygen or nitric oxide.[18]

Conclusion

The destabilization of S_1 when the reaction starts and the concomitant stabilization of S_2 on one hand and the avoided crossing between S_0 and S_2 on the other hand are already known to be general characteristics of these cyclization reactions. The third remaining factor, the near degeneracy of S_1 and S_2, need be confirmed by "ab initio" SCF–CI calculations on other systems. Still we may reasonably hope that it is also a general property of conjugated systems. The pattern of potential energy surfaces we have described then goes certainly beyond the scope of the particular butadiene–cyclobutene reaction. For this reason let us briefly summarize the main physical features of this photochemically allowed reaction. (1) The first singlet excited state S_1 is slowly *destabilized* when the reaction proceeds. S_1 acts as a reservoir of excited species. (2) The second singlet excited state S_2 is in a *near-touching* situation with S_1 and is *stabilized* during the reaction. (3) The resulting allowed crossing between S_1 and S_2 (C_1) is a *valve* which allows excited species which have a small (5 kcal/mol) vibrational energy to populate the well in the S_2 surface. (4) The well in S_2 and the maximum in the ground state S_0 surface both result from an avoided crossing between the ground and doubly excited states of the system (C_2). The role of the pair well in S_2 maximum in S_0 is to allow the excited species to decay from S_2 to S_0. This region is therefore an *exit or leakage channel* (*funnel*) from the excited state back to the ground state of the system.

In this paper we have limited our attention to two cuts through the full 25-dimensional potential energy hypersurfaces. A complete understanding of the reaction path would require, of course, the study of a much larger portion of the hypersurfaces. Nevertheless, it is our belief that the essential features of the reaction conform to the results presented here.

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