BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(6), 1551—1552 (1974)

Reaction Paths in the Photochemical Isomerization between *cis*-Butadiene and Cyclobutene

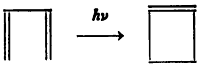
Osamu Kikuchi

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo 112

(Received October 29, 1973)

Synopsis. During the disrotatory process of the photoinduced cycloaddition of *cis*-butadiene, two lower symmetric states play an important role and the ground state of cyclobutene is formed directly through a radiationless transition between these two states.

One of the most important questions in photochemical reactions is the actual path along which the excited molecule travels to the product. van der Lugt and Oosterhoff[1] have proposed an interesting reaction path related to this problem. They have calculated the potential curves of the lowest and excited singlet states in the cyclo-addition of *cis*-butadiene to form cyclobutene:



(I)

and concluded that, for the disrotatory process of (I), the generation of the excited state of cyclobutene derived from the Woodward-Hoffmann rule[2] can not be expected and that the ground state of cyclobutene is formed directly through the excited singlet state, which has a symmetric (not an anti-symmetric) property with respect to the symmetry plane. In their calculations, however, only four electrons, π electrons of butadiene, were included. In this note, the potential curves for (I) will be obtained by an all-valence-electron SCF-CI method, and the reaction processes will be discussed.

The potential curves were calculated for the ideal paths, in which the molecule has C_s and C_2 symmetries for the disrotatory and the conrotatory processes respectively. In the course of doing so, the C-C distances and bond angles were varied from the values of *cis*-butadiene to those of cyclobutene. The rotation angle of the methylene groups, θ, was varied from 0° to 90° in steps of 15°. The energies of the lowest and excited (singlet and triplet) states were calculated by the MINDO/2 method[3], followed by CI calculations in which 38 singly- and doubly-excited configurations were included. One of the deficiencies of the MINDO/2 method is its underestimation of the strain energies of small-membered cyclic compounds. This deficiency was adjusted by adding strain energy to the system which increases with the θ and which is about 1 eV[3] at $\theta=90°$, cyclobutene.

The potential curves are shown in Fig. 1. In the conrotatory process, the potential curve for the ground state has a maximum point which did not appear in the potential curve obtained by van der Lugt and Oosterhoff[1] and was not expected in the qualitative diagram of Longuest-Higgins and Abrahamson.[4] The barrier was 1.8 eV,[5] as compared with an experimental estimation, 1.4 eV,[6] and with a theoretical estimation obtained by Hsu *et al.*, 2.0 eV.[7]

In the disrotatory process, the spectroscopic excited singlet state (A'', $\pi\rightarrow\pi^*$) of *cis*-butadiene[8] crosses an excited state (A') at $\theta\simeq30°$, and two lower singlet states have the same symmetry (A') at $\theta\simeq45°$, in contrast with Longuet-Higgins–Abrahamson's diagram. The approach of the two lower A' states in the intermediate of the disrotatory process is caused by the change in the lowest closed-shell electron-configuration in this area. Thus, an appreciable non-adiabatic transition caused by a finite velocity of the rotational motion of CH_2 groups can be expected from the upper A' state to the lowest A' state. This has been pointed out by van der Lugt and Oosterhoff.[1]

The probability, P, of the non-adiabatic transition between two states can be estimated by Zener's formula:[9]

$$P = \exp\left\{-\frac{4\pi^2}{h}\varepsilon_{12}^2 \Big/ \left|\frac{d}{dt}(\varepsilon_1-\varepsilon_2)\right|\right\}$$

where the ε's are the energies calculated with two configuration functions whose linear combinations describe the two states in question.[10] Zener's formula can be used for the system in which ε_{12} is independent of the time and in which $\varepsilon_1-\varepsilon_2$ is a linear function of time. In the region of $\theta=30°$—60° of the present

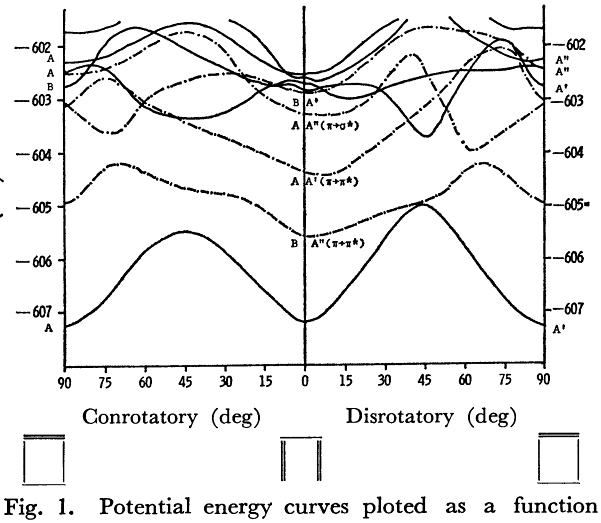


Fig. 1. Potential energy curves ploted as a function of the rotation angle θ of methylene groups.

Solid lines: Singlet states whose electronic symmetry properties are shown at both sides of the figure. The characters of excited states are given in the Ref. 8.

Broken lines: Triplet states whose electronic symmetry properties are shown at the center of the figure. The characters of excited states are given in parentheses.

disrotatory process, $\varepsilon_1-\varepsilon_2$ is approximately a linear function of θ and ε_{12} is almost constant. The probability of the non-adiabatic transition from the upper A′ singlet state to the lowest A′ one within the half-period of the oscillation was estimated as $P \simeq \exp\{-25\}$, a value which corresponds to the mean lifetime, $\simeq 10^{-3}$ s, of the upper A′ state. Between the two corresponding A states of the conrotatory process, no appreciable non-adiabatic transition can be expected because of the lack of interaction between the two A states, as in the two A′ states of the disrotatory process. We feel that the path proposed by van der Lugt and Oosterhoff is reasonable: *cis*-butadiene excited into the A″ singlet state changes its electronic symmetry property near $\theta = 30°$,[12] and then the ground state of cyclobutene is formed directly through a radiationless transition at $\theta \simeq 45°$ from the upper A′ state to the lowest A′ state.

The potential curves of the triplet states indicate that the excited triplet states of *cis*-butadiene have no driving force for Reaction (I). This agrees with the experimental facts.[13] A photochemical ring opening of cyclobutene occurs from the upper excited triplet state (not the excited singlet states or the lowest triplet state) of cyclobutene.[13–14] The potential curves of the triplet states in Fig. 1 indicate that the photoinduced ring opening of cyclobutene is possible if cyclobutene is excited into the upper triplet state, T_2, and if the non-adiabatic transition from T_2 to T_1 is appreciable near $\theta = 70°$. This path, however, involves the generation of the excited triplet state (A″) of *cis*-butadiene, which may be inconsistent with the experimental facts.[13] Moreover, the absence of the ring-opening path *via* the excited A″ singlet state of cyclobutene[13] can not be understood from the potential curves in Fig. 1.

The calculations were carried out on a HITAC 8700 computer at the Computer Center, The University of Tokyo. The author wishes to thank Professor K. Suzuki for his useful suggestions.

References and Notes

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5) This value may be reduced by including the flexibility of the rotation about the C_2-C_3 bond.

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8) The four lower excited singlet states of *cis*-butadiene are $\sigma\to\pi^*$(B,A′), $\sigma\to\pi^*$(A,A″), $\pi\to\pi^*$(B,A″), and $\pi\to\pi^*$(A,A′), lying in this order within the range of 4.4—4.6 eV above the ground state. At $\theta = 15°$ for the disrotatory process, the lowest excited stinglet state (A″) has the $\pi\to\pi^*$ character. At $\theta = 15°$ for the conrotatory process, the second excited singlet state has the $\pi\to\pi^*$ character.

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10) The electron configuration functions, $\Psi_1 = |\cdots(7a')^2(5a'')^0|$ and $\Psi_2 = |\cdots(7a')^0(5a'')^2|$, contribute effectively to the two A′ states in $\theta = 30°$—$60°$ of the disrotatory process. In this region, $d|\varepsilon_1-\varepsilon_2|/d\theta = 0.5$ eV/degree and $\varepsilon_{12} = 1.5$ eV.

11) $\varepsilon_1-\varepsilon_2$ is not a linear function of the time but of the θ in $\theta = 30°$—$60°$, and the value of $d|\varepsilon_1-\varepsilon_2|/dt$ was estimated from the value of $d|\varepsilon_1-\varepsilon_2|/d\theta$.

12) Two states, A′ and A″, will mix with only a small distortion of the molecular symmetry property, and the non-crossing curves enable the symmetry property of the system to change from A″ to A′.

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