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An MO Study of the Photochemical Electrocyclic Isomerization between Vinylketene and Cyclobutenone

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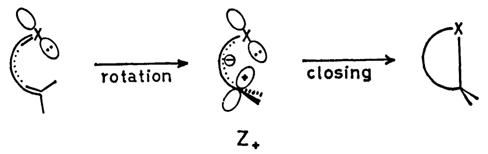
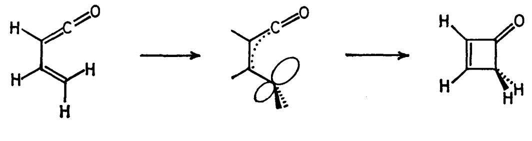
Synopsis. The MINDO/3 CI potential energy surfaces of the vinylketene-cyclobutenone system suggest that the cyclization of vinylketene occurs from the $\pi \rightarrow \pi^*$ state *via* the zwitterion, in which the negative charge is located on the 90°-twisted methylene carbon atom, while the reverse reaction proceeds *via* a diradical structure.

It was shown in previous papers1) that the photochemical electrocyclic reaction mechanism of hetero-atom-conjugated systems is very different from that of the corresponding all-hydrocarbon conjugated systems; there is no distinction between conrotatory and disrotatory modes in the former systems. In the photocyclization of hetero-atom-conjugated systems, the rotation of the terminal methylene group occurs from the $\pi \rightarrow \pi^*$ excited state to give the twisted structure, and the ring closing occurs from the Z_+ zwitterion, in which the positive charge is located on the carbon atom of the twisted methylene group.1) The vinylketene–cyclobutenone isomerization is another example in which the conrotatory/disrotatory dichotomy is meaningless, and its mechanistic examination is of much interest.2)



(1)



(2)

1 2 3

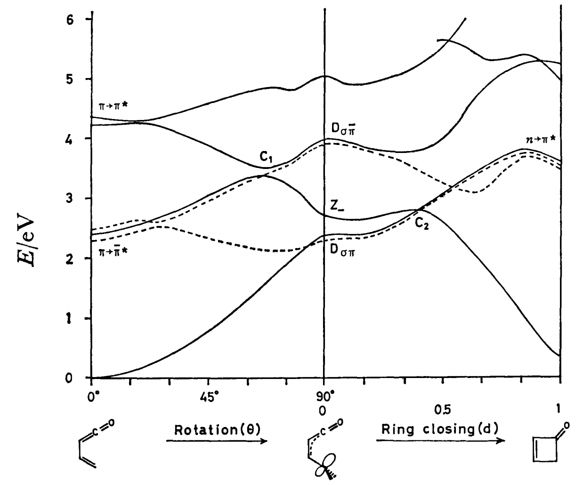
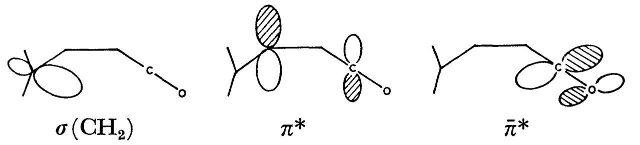
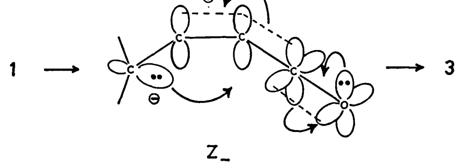


Fig. 1. Potential energy curves of lower four singlet states (solid lines) and two triplet states (broken lines) along the step-by-step path.4)

Figure 1 shows the MINDO/3 3)-CI potential energy curves4) along the step-by-step path of the vinylketene–cyclobutenone system, (2), in which the rotation of the methylene group and the ring closing occur independently. The lower singlet electronic states of the twisted structure, **2**, are the $D_{\sigma\pi}$, Z_-, and $D_{\sigma\bar{\pi}}$ states.5) The lowest singlet state is the diradical one in which the $\sigma(CH_2)$ and π^* orbitals are occupied by unpaired electrons. The Z_- excited state has a pair of electrons in the $\sigma(CH_2)$ orbital, and it is a polarized zwitterion; the negative charge on the terminal carbon atom was calculated to be −0.70. As may be seen from Fig. 1, the excited Z_- state correlates directly with the ground state of cyclobutenone, and it can be generated from the $\pi \rightarrow \pi^*$ excited state of vinylketene. Thus, the following reaction path appears to exist in the **1**→**3** photocyclization: The rotation of the terminal methylene group occurs in the $\pi \rightarrow \pi^*$ excited state of vinylketene to give the Z_- zwitterion, after which this zwitterion undergoes cyclization without any activation energy to form cyclobutenone.



The electrocyclic reaction of vinylketene has been shown to proceed *via* the Z_- zwitterion. This is an interesting contrast with Reaction 1, which proceeds *via* the Z_+ zwitterion. In the hetero-atom-conjugated system, the in-plane lone-pair electrons of the terminal hetero atom are consumed in the new σ bond formation, while in the case of the ketene conjugated system, the anti-bonding $\bar{\pi}^*$ orbital of the carbonyl group receives an electron from the terminal carbon atom to form the new σ bond. This is the reason why the Z_- zwitterion is involved in the **1**→**3** photochemical process.



The $D_{\sigma\pi}$ twisted diradical correlates with the ground state of vinylketene, and it is derived easily from the $n \rightarrow \pi^*$ excited state of cyclobutenone (Fig. 1). Thus, the ring opening of cyclobutenone is expected to proceed from the singlet (or triplet) $n \rightarrow \pi^*$ excited state of cyclobutenone *via* the $D_{\sigma\pi}$ diradical.6)

Figure 2 shows the two-dimensional potential energy surfaces of three lower singlet states. The symbols W and H indicate the potential minimum and maxi-

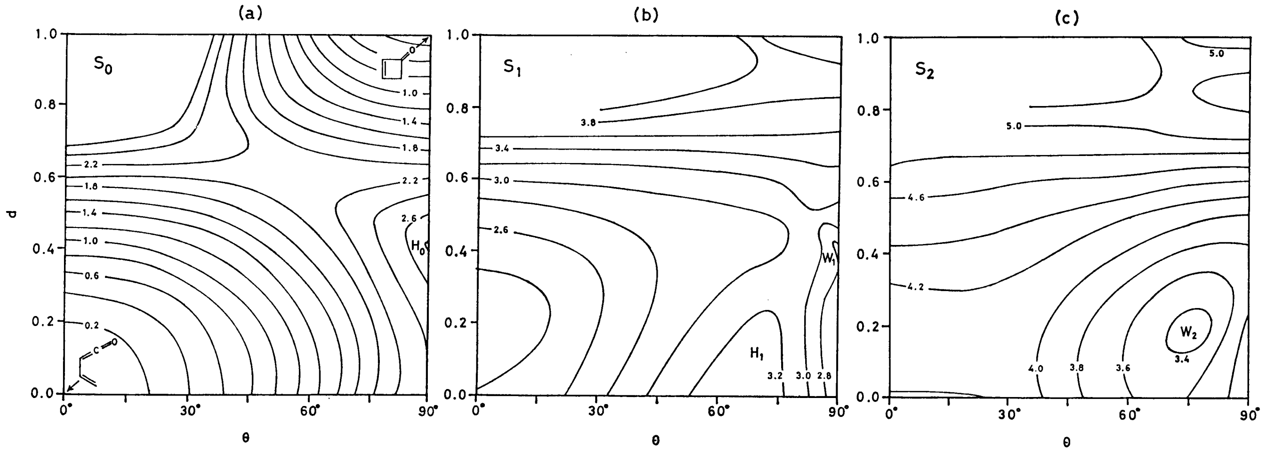
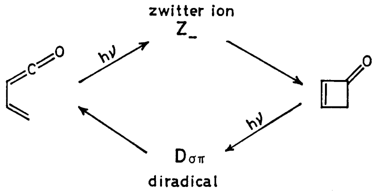


Fig. 2. Two-dimensional potential energy surfaces for three singlet states.[4] The values indicated on the potential curves are energies(eV) relative to the ground state structure of the vinylketene.

mum points respectively. The W_1 and W_2 regions correspond to the C_2 and C_1 crossing regions respectively, shown in Fig. 1. The W_1 well is a pin hole which can be a leakage channel from the S_1 state to the S_0 state. As may be seen from Fig. 2-b, the n→π* state of cyclobutenone undergoes bond-breaking with a small activation energy, forming the S_0 vinylketene *via* the W_1 pin hole. The rotation of the methylene group of the n→π* vinylketene requires an appreciable activation energy (Fig. 2-b), while it occurs very easily on the S_2 surface (Fig. 2-c). The W_2 well on the S_2 surface interacts strongly with the potential height, H_1, on the S_1 surface. Thus, the two dimensional potential energy surfaces also support the reaction paths described above.



References

1) O. Kikuchi, H. Kubota, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **54**, 1126 (1981); O. Kikuchi, *Tetrahedron Lett.*, **22**, 859 (1981).

2) Vinylketenes are very reactive with nucleophiles or with olefins, and their photochemical behavior has not been clarified. The thermal and photochemical isomerization of cyclobutenone derivatives into vinylketenes has, however, been reported: J. E. Baldwin and M. C. McDaniel, *J. Am. Chem. Soc.*, **90**, 6118 (1968); O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968); A. Krantz, *ibid.*, **96**, 4992 (1974); R. Huisgen, and H. Mayr, *J. Chem. Soc., Chem. Commun.*, **1976**, 55; H. Mayr, *Angew. Chem., Int. Ed. Engl.*, **14**, 499 (1975).

3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

4) In the calculation of the potential energy curves, the molecular structures of **1** and **3** were optimized by the use of MINDO/3 (without CI). The structural change involved in the isomerization between **1** and **3** was expressed by two parameters: the rotation angle of the terminal methylene group, θ, which expresses the structure of the CH_2 fragment, and the *d* parameter, which indicates the linear change in the structural parameters, x_i, associated with a substructure other than that of the methylene group; $x_i = x_i^{\text{initial}} + d(x_i^{\text{final}} - x_i^{\text{initial}})$. In the CI calculation, 42 and 41 configuration functions were selected for the singlet and triplet states respectively.

5) The electronic states of the twisted structure were calculated by the closed-shell SCF method, followed by CI; geometry optimization was not performed for any electronic state. The results shown in Fig. 1 are not fit for a quantitative discussion of the relative energy levels of the electronic states of the twisted structure.

6) The photochemical α-cleavage of 2,4-cyclohexadienones from the n→π* manifold *via* the $D_{\sigma\pi}$ diradical has been well explained; W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).