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Reaction Paths of the Photochemical Electrocyclic Reaction of Acrylaldehyde. A Possible Path *via* a Zwitterion

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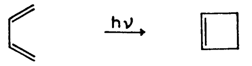
The photochemical electrocyclic reaction paths of *s-cis*-acrylaldehyde to oxetene were examined on the basis of the potential surfaces obtained by the MINDO/3 CI calculation, and compared with those of the corresponding conjugated hydrocarbon system. The strong S_0-S_2 interaction, which appears in the disrotatory mode of the cyclization of butadiene, was not observed in the acrylaldehyde–oxetene system. There appears to be a step-by-step path, in which the $\pi\to\pi^*$ induced rotation of the methylene group is followed by the ring-closing step. The zwitterion in which the positive charge is localized on the terminal carbon atom is involved in this step. Since the σ lone-pair electrons of the oxygen atom play a key role in the ring-closing step, this path is characteristic of the hetero-atom conjugated system and cannot be deduced by analogy or by a simple extension of the concepts established for the photoreactions of all-hydrocarbon conjugated systems. The possible decay paths from acrylaldehyde in the excited states were also discussed.

Orbital symmetry arguments[1)] and calculated reaction paths[2)] have well elucidated the thermal and photochemical electrocyclic reactions of the all-hydrocarbon conjugated system, **1**→**2**. Little attention, however, has been paid to the electrocyclic processes of the hetero-atom conjugated system, in which one of the terminal methylene groups is replaced by a hetero atom. The formal photochemical electrocyclic reaction of *s-cis*-acrylaldehyde **3**→**4**, for example, has been considered to proceed by means of a mechanism similar to that of *s-cis*-butadiene, **1**→**2**, if the $\pi\to\pi^*$ excited state is involved.[3)] However, there are two essential differences between the **1**→**2** and **3**→**4** reactions. The first is the mode of rotation of the methylene groups. In the conjugated hydrocarbon system, the disrotatory and conrotatory modes give very different shapes of the potential cuves, while there is no distinction between these two modes in the **3**→**4** reaction, since only one methylene group is involved in the acrylaldehyde–oxetene system. It is thus impossible to consider the photochemical reaction mechanism of the **3**→**4** reaction by simple analogy with the disrotatory cyclization of the **1**→**2** reaction.



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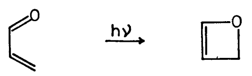

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The second difference is the existence of the lone-pair electrons of the terminal hetero atom. Since the lone-pair electrons are distributed on the σ framework where the new σ bond is being formed, the lone-pair electrons should participate in the electrocyclic reaction mechanism of the hetero-atom conjugated system, even if the photochemical reaction proceeds from the $\pi\to\pi^*$ excited state. Because of these essential differences, the electron behavior during the **3**→**4** reaction cannot be understood sufficiently well by analogy with the **1**→**2** reaction; therefore, it is worthwhile to investigate the reaction processes of the **3**→**4** reaction and to compare the reaction mechanism with that of the all-hydrocarbon system, **1**→**2**.

The experimental evidence applicable to the **3**→**4** reaction has been reported by Friedrich and Schuster.[4)] The irradiation of 3,4-dimethyl-3-penten-2-one in a hexane solution through a Pyrex filter gave no observable reaction, while the irradiation with Vicor-filtered UV light gave cyclic compound, the oxetene. They also investigated the thermal ring-opening reaction of the methyl-substituted oxetene and compared it with that of the cyclobutene derivatives.[4b)]

In the present study, the potential curves for the ground and several excited states of the **3**→**4** reaction were obtained by means of the semi-empirical MINDO/3[5)] CI calculations. On the basis of these potential surfaces, the possible photochemical paths of the **3**→**4** reaction are discussed. Attention is mostly paid to the clarification of the differences between the reaction mechanisms of the **1**→**2** and **3**→**4** reactions, and also to the comparison between the theoretical and experimental results.

Method of Calculation

The structures of Compounds **1**—**4** were optimized by the SCF (without CI) calculation; Fletcher's variable metric method[6)] was employed. They are shown in Fig. 1. The potential surfaces for the **1**→**2** and **3**→**4** reactions are the functions of many geometrical variables. In the present study, the potential surfaces were calculated with respect to two independent parameters. One of these is the rotation algle, θ, of the methylene group(s). All the other geometrical variables were allowed to vary simultaneously from their inital to final values. This variation is expressed by the second parameter, d, which varies from 0.0(initial) to 1.0(final). In the CI calculation, 47 and 43 configuration functions were selected from the singly- and doubly-excited configurations for the singlet and triplet states respectively. MINDO/3 underestimates the strain energy of small cyclic compounds, while it overestimates the heats of formation of acrylaldehyde and butadiene.[5)] The

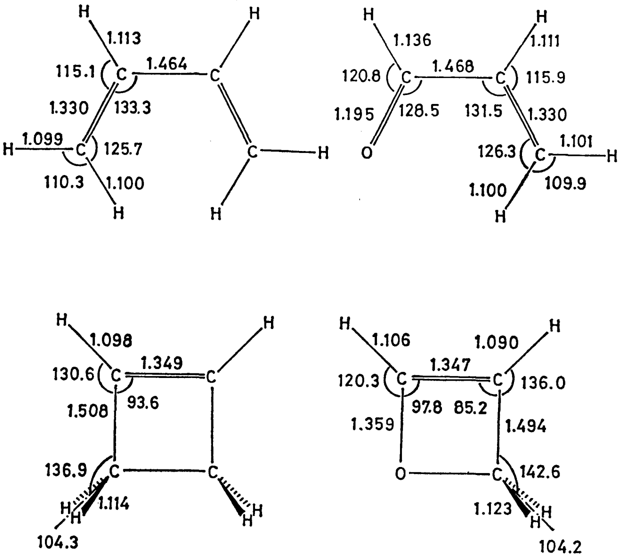


Fig. 1. Molecular structures of *s-cis*-butadiene, cyclobutene, *s-cis*-acrylaldehyde, and oxetene optimized by the MINDO/3 method. Bond lenghts are in Å, bond angles are in degrees.

Table 1. Excitation energies (eV) of *s-trans*-butadiene and *s-trans*-acrylaldehyde as calculated by the MINDO/3 CI method

State	MINDO/3	*ab initio*[2c]	Obsd
Butadiene			
^1B_u	5.11	7.69	5.92[7a] 6.05[7b]
^3A_g	3.35	6.22	4.91[7a]
^3A_u	3.11	4.28	3.20[7a] 3.32[7c]
Acrylaldehyde			
$^1n\rightarrow\pi^*$	3.48		3.21[7d]
$^1\pi\rightarrow\pi^*$	5.70		6.41[7d]
$^3\pi\rightarrow\pi^*$	3.27		3.01[7d]

excitation energies as calculated by MINDO/3 CI were compared with the experimental values (Table 1). Although the MINDO/3 and MINDO/3 CI calculations do not give sufficiently good results for the energetics of the present systems, we feel that the present objectives can be achieved satisfactorily on the basis of the MINDO/3 calculations.

Results and Discussion

Linear Variation of Geometrical Variables. First let us consider the concerted path in which the θ and d parameters are changed simultaneously. Figure 2 shows the potential curves of several electronic states for the disrotatory mode of the butadiene–cyclobutene system. Their shapes are very similar to those obtained previously by semi-empirical[2b] and *ab initio*[2c] methods. Notice two important features which appear in Fig. 2. The first is a true crossing at C_1 which takes place at the beginning of the cyclization and which involves the $\pi\rightarrow\pi^*$ singly-excited B_2 state and its doubly-excited counterpart. The second is an avoiding crossing at C_2 involving the ground state and the $\pi\rightarrow\pi^*$ doubly-excited state. The cyclobutene formation from the $\pi\rightarrow\pi^*$ state of butadiene can be understood in terms of these two crossings; the $\pi\rightarrow\pi^*$ state of butadiene populates the W_b well through the C_1 crossing, and this well is a leakage channel[8] from the excited state to the ground state.

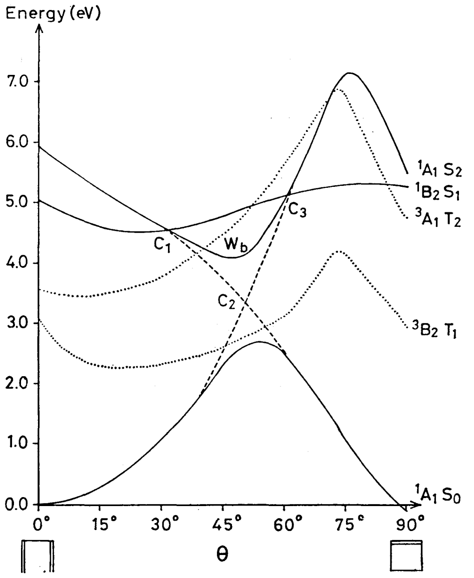


Fig. 2. Potential energy curves for the disrotatory mode of the butadiene–cyclobutene system. All the geometrical variables are varied simultaneously between the optimized structures of butadiene and cyclobutene.

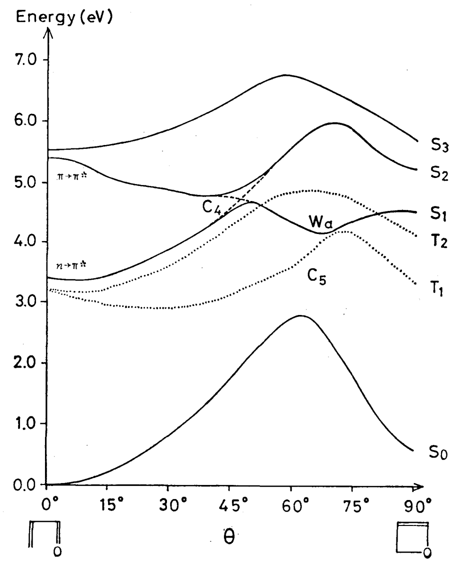


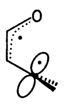
Fig. 3. Potential energy curves for the acryladehyde–oxetene system. All the geometrical variables are varied simultaneously between the optimized structures of acryladehyde and the oxetene.

Figure 3 shows the corresponding potential curves for the *s-cis*-acrylaldehyde–oxetene system. In this system, there is no distinction between the disrotatory and conrotatory modes of the methylene rotation,[9] and both the thermal and photochemical processes can be considered on the basis of these potential curves. The thermal ring-opening reaction of the substituted oxetene has been studied by Friedrich and Schuster.[4b)] The activation enthalpy of 1,2,3,3-tetramethyloxetene was found to be 100—105 kJ mol^{-1} (solvent dependent),[4b)] while that of 1,2,3,4-tetramethylcyclobutene is 152 kJ mol^{-1}.[4b)] The calculated values 213 kJ mol^{-1} for the oxetene and 242 kJ mol^{-1} for cyclobutene,[10)] are somewhat larger than the observed values for the substituted compounds. This discrepancy comes partially from a deficiency in the MINDO/3 approximation, which overestimates the heats of formation of butadiene and acrylaldehyde, while underestimating the strain energy of the cyclic compounds. However, the faster thermal ring opening of the oxetene in comparison with that of cyclobutene is reflected in the calculated values.

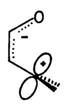
The S_1 and T_1 states of acrylaldehyde are the singlet and triplet $n \rightarrow \pi^*$ states which are missing in butadiene. The S_2 and T_2 states are the $\pi \rightarrow \pi^*$ states which correspond to the B_2 singlet and triplet states of butadiene respectively. The most important feature observed in the potential curves of the acrylaldehyde–oxetene system is the absence of the crossings related to the doubly-excited configuration; they appear at C_1 and C_2 in the case of the butadiene–cyclobutene system. This is due to the non-symmetric property of acrylaldehyde with respect to the vertical plane; no crossing occurs between the π_2 and π_3 orbitals. Two new types of crossings are observed in the acrylaldehyde–oxetene system. They are the C_4 crossing between the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states, and the C_5 crossing between S_0 and S_1 states at the later part of cyclization. The concerted cyclization path of *s-cis*-acrylaldehyde may be elucidated as follows: the reaction proceeds from the $\pi \rightarrow \pi^*$ excited state of acrylaldehyde, this state reaches the W_a well through the C_4 crossing, and the non-adiabatic transition from W_a to the ground state gives the oxetene. As will be described later, the W_a well is not a clear well on the two-dimensional S_1 surface, and the transition from the W_a well to the ground state is expected to be much more inefficient than that from the W_b well to the ground state in the butadiene–cyclobutene system.

The $n \rightarrow \pi^*$ excited acrylaldehyde cannot reach the W_a well because of the high activation energy, and no appreciable formation of the oxetene is expected from the $n \rightarrow \pi^*$ state of acrylaldehyde. This agrees well with the experimental evidences.[4b)]

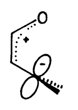
Step-by-step Path via a Zwitterion. The rotation of methylene occurs easily in the $\pi \rightarrow \pi^*$ excited state of acrylaldehyde to give the twisted acrylaldehyde. The lower electronic states of the twisted acrylaldehyde involve the diradical,[11)] $D_{\sigma\pi}$, and two zwitterions, Z_+ and Z_-.[12)]



$D_{\sigma\pi}$



Z_+



Z_-

The energies of several states of the twisted acrylaldehyde are shown in Fig. 4.

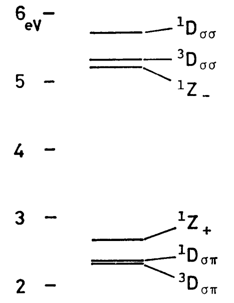
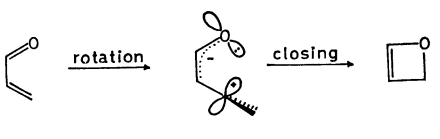


Fig. 4. Energy levels for several lower states of the twisted acrylaldehyde.

The Z_+ zwitterion, in which the positive charge is located at the terminal carbon atom, can undergo ring closing very easily, since a strong attraction is expected between the positive charge and the lone-pair electrons of the oxygen atom.



Z_+

The step-by-step path in which the rotation of the methylene group is followed by the ring-closing is expected to exist. The state correlation diagram for this path is shown in Fig. 5.[13)] As may be seen from Fig. 5, the excited Z_+ state correlates with the ground state of the oxetene. It can thus be expected that, if the Z_+ state of the twisted acrylaldehyde is formed from the $\pi \rightarrow \pi^*$ excited state of acrylaldehyde, the oxetene formation proceeds without any activation energy or with only a small activation energy.

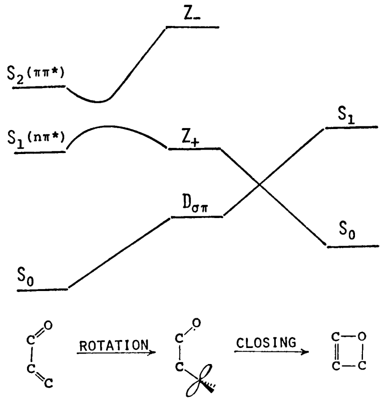


Fig. 5. State correlation diagram for the acrylaldehyde–twisted acrylaldehyde–oxetene system.

The potential curves along the suggested path are shown in Fig. 6. The molecule has a distinctive zwitterionic character between A and C on the Z_+ potential curve.[15)] Figure 6 indicates that the internal conversion from the Z_+ state to the $D_{\sigma\pi}$ state occurs efficiently at the twisted acrylaldehyde; this results in the reproduction of the ground state of acrylaldehyde, and no formation of oxetene is expected. However, if the Z_+ zwitterion is formed from the $\pi \rightarrow \pi^*$ excited state[16)] and has a high

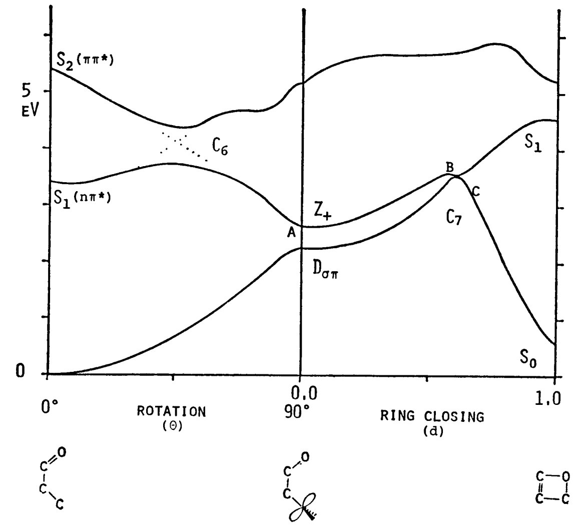
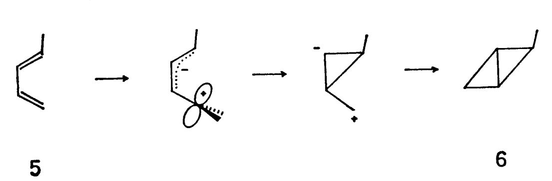


Fig. 6. Potential curves for the step-wise path of the acrylaldehyde–oxetene system. Only three lower singlet states are shown. θ is the rotation angle of the terminal methylene and *d* represents the simultaneous change in all the geometrical variables other than θ.

vibration energy, it can cyclize to form the oxetene *via* the C_7 crossing.

An important role of the zwitterion has been pointed out by Dauben *et al.*[14,17] and by Salem[18] in the photochemical cyclization of non-symmetric polyenes. In



the **5**→**6** reaction, the primary step is the photoinduced rotation of the terminal methylene, which gives the zwitterion. This step is followed by the 1,3 ring closing of the anionic allyl group by another rotation about the C–C bonds. The reaction scheme of the zwitterion in the present **3**→**4** reaction is clearly different from that proposed for the **5**→**6** process. In the **3**→**4** reaction, the ring closing occurs between the positive carbon atom and the lone-pair electrons of the terminal hetero atom, without another rotation. This path can occur only if the terminal atom has the lone-pair electrons and is characteristic of the hetero-atom conjugated system.

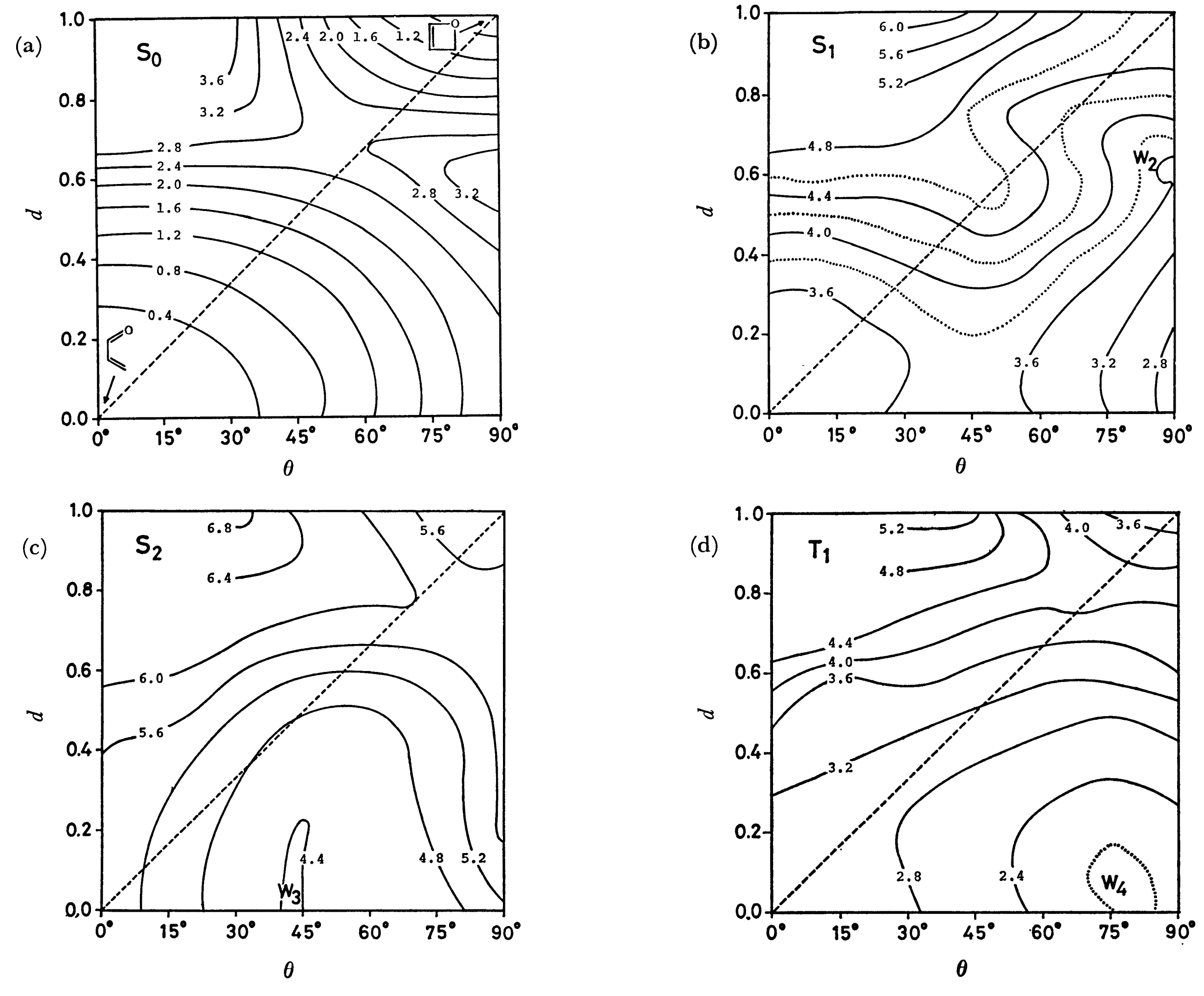


Fig. 7. Two-dimensional potential surfaces of (a) S_0, (b) S_1, (c) S_2, and (d) T_1 states of the acrylaldehyde–oxetene system. The energies (eV) are relative values with respect to that of the ground state of *s-cis*-acrylaldehyde.

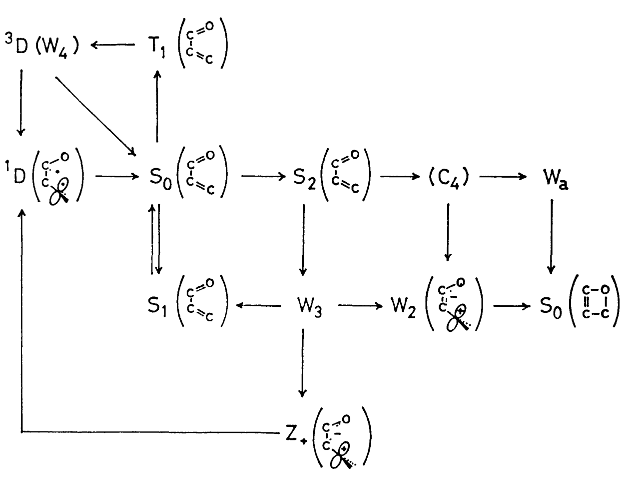
Two-dimensional Potential Surfaces. The potential surfaces of several electronic states of the acrylaldehyde–oxetene system were obtained as the function of two geometrical parameters, θ and d. They are shown in Fig. 7. Although two-dimensional surfaces are still only a distant approximation of the real multidimensional hypersurfaces, they give much more information than one-dimensional ones; they are useful as confirmation of and complement to the results obtained from the one-dimensional potential curves. The n→π* singlet state of acrylaldehyde is located at the energy minimum on the S_1 surface and is stable even when the molecular structure is deformed (Fig. 7-b). An important characteristic of this S_1 surface is the absence of the W_a well which appears in one-dimensional curves (Fig. 3). Instead, the W_a well in Fig. 3 is a part of the shallow well, W_2, the minimum point of which is located at the C_7 crossing point in Fig. 6. The transition from the W_2 region to the ground state occurs very easily to form the oxetene.

From Fig. 7-c, it may be seen that acrylaldehyde in its π→π* excited state can move around most ($0.0<\theta<0.6$, and $0° < d < 90°$) of the S_2 surface. The transition from the W_3 well to the S_1 state produces the normal acrylaldehyde or the twisted acrylaldehyde. However, Fig. 7-b indicates that the S_1 species formed from the W_3 well is capable of access to the W_2 well. In this case, the oxetene is formed *via* the Z_+ zwitterion. The smallest energy separation between the S_1 and S_2 surfaces is observed at the central region of the two-dimensional maps; this region corresponds to the C_4 crossing region in Fig. 3. The strong coupling between S_1 and S_2 is suggested by the calculated CI coefficients, and an appreciable transition from S_2 to S_1 is expected in this region. As may be seen from Figs. 7-b and 7-c, the Z_+ zwitterion (corresponding to the W_2 well) is formed from the S_1 species generated from S_2 through the C_4 crossing. From the analysis of the two-dimensional surfaces, it is confirmed that there is a path through the Z_+ zwitterion in the **3**→**4** photochemical process.

Figure 7-d shows the potential surface of the T_1 triplet state. The acrylaldehyde side of this surface corresponds to the π→π* triplet state of acrylaldehyde. The rotation of methylene occurs easily in this state and gives the twisted acrylaldehyde, the triplet diradical, $^3D_{\sigma\pi}$. The crossing of this surface with the lowest S_0 state occurs near the W_4 well, and the reproduction of the ground state of acrylaldehyde proceeds from the triplet T_1 state through this singlet-triplet crossing. This path corresponds to the photochemical *cis-trans* isomerization of acrylaldehyde. The intersystem crossing rate between the $^3D_{\sigma\pi}$ and $^1D_{\sigma\pi}$ states is not expected to be particularly fast, but the intersystem crossing is still an efficient process, since the triplet is at a minimum.[14]

Conclusion

The possible decay paths for the photochemically excited *s-cis*-acrylaldehyde have been considered on the basis of the potential surfaces obtained by MINDO/3 CI calculations. Two possible paths have been predicted for the photochemical electrocyclic reaction of *s-cis*-acrylaldehyde into oxetene. The concerted type of cyclization proceeds from the π→π* state: acrylaldehyde →S_2→C_4→W_a→oxetene. The step-by-step path, in which the Z_+ zwitterion is involved, also proceeds from the π→π* state: acrylaldehyde→S_2→(C_4 or W_3)→W_2→oxetene. Since no quantitative examinations were performed for the transition probability between the electronic states, the efficiency of the above two possible paths to form the oxetene can not be determined from the present study. The W_a well appearing in the concerted path is actually a part of the W_2 well which corresponds to the Z_+ zwitterion. Therefore, the Z_+ zwitterion also plays an important role in the concerted-type pathway. The path *via* the Z_+ zwitterion proposed in this study is a new type of mechanism for the formal photochemical electrocyclic reactions. Since the lone-pair electrons play a key role in the ring-closing step, this path can not be deduced by analogy or a simple extension of the concepts established for the all-hydrocarbon conjugated systems.



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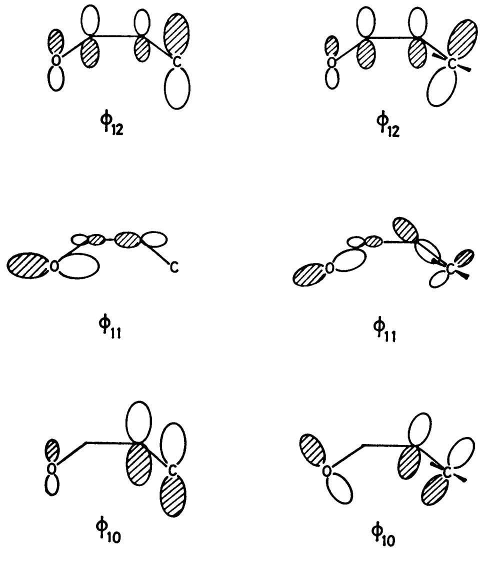
9) Since only one methylene group is involved in acrylaldehyde, there is no distinction between the conrotatory and disrotatory modes, which can be defined by means of the relative motion of the two terminal methylene groups. However, it may be interesting to illustrate the change in the orbital shape on the oxygen atom, which is induced by the rotation of the terminal methylene. The two highest occupied MO's, ϕ_{10} and ϕ_{11}, and the lowest unoccupied MO, ϕ_{12}, are shown here for acrylaldehyde, and also for the structure in which the terminal methylene group is twisted by 30°. When the terminal methylene group is rotated, the lone-pair orbital (ϕ_{11}) and the occupied π orbital (ϕ_{10}) of acryladehyde mix well to give the ϕ_{10} and ϕ_{11} MO's of the twisted structure, while the OCC part of the LUMO is unchanged. From these MO shapes, we may say that the orbital fragments on the oxygen atom in the occupied ϕ_{10} and ϕ_{11} MO's rotate in a disrotatory-like manner with respect to the methylene group. However, it should be noted again that we cannot define the methylene rotation in acrylaldehyde as the disrotatory rotation: only one kind of rotation exists in acrylaldehyde,.



10) The value was obtained from the potential curves for the conrotatory mode of the isomerization of butadiene.

11) L. Salem and C. Rowland, *Angew. Chem. Int. Ed. Engl.*, **11**, 92 (1972).

12) The Z_+ zwitterion has the same symmetry property as the $D_{\sigma\sigma}$ diradical, in which two unpaired electrons occupy the carbon 2p AO and the lone-pair orbital of the oxygen atom. The Z_+ zwitterion is lower in energy than the $D_{\sigma\sigma}$ diradical in the twisted acrylaldehyde.

13) The correlation between the twisted structure and the cyclic one can be determined simply by counting the σ and π electrons on the reaction centers.[14]

14) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).

15) The HOMO of the A($\theta=90°$, $d=0$), B($\theta=90°$, $d=0.5$), or C($\theta=90°$, $d=2/3$) conformation is the second (nonbonding type) π orbital, and the LUMO is the σ AO of the terminal carbon atom. The net charges at the terminal carbon atom in the A, B, and C conformations are in the range of $+0.65$—$+0.75$.

16) The experimental evidence reported by Friedrich and Schuster[4a] suggests that the photochemical cyclization of methyl-substituted acrylaldehyde occurs from the $\pi\rightarrow\pi^*$ state.

17) W. G. Dauben and J. S. Ritsher, *J. Am. Chem. Soc.*, **92**, 2925 (1970).

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