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Nonadiabatic Transitions in Photochemical Electrocyclic Reaction of Acrylaldehyde to Form 2*H*-Oxete

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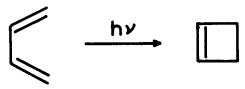
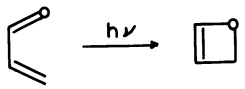
The photochemical electrocyclic reaction of *s-cis*-acrylaldehyde to form 2*H*-oxete was examined on the basis of the nonadiabatic interaction between potential energy surfaces. The nonadiabatic coupling *g* terms were calculated by the reduced classical-trajectory method along two postulated reaction paths, the concerted path and the step-by-step path. The calculated *g* terms were characteristic of the avoided crossing between the potential energy surfaces. The calculated *g* terms and the transition probabilities indicated that the step-by-step path was very efficient in the formation of 2*H*-oxete from the π-π^* state of acrylaldehyde.

The photochemical electrocyclic reaction of *s-cis*-butadiene, **1**→**2**, has been investigated theoretically by several researchers.[1,2] During the disrotatory mode of



1 2

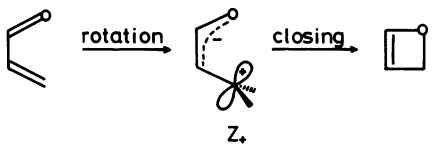
this isomerization reaction, there is an avoided crossing[3,4] between the ground state (S_0) and the lowest excited singlet state (S_1) surfaces. This avoided crossing plays a significant role in the isomerization reaction, and its existance can be easily predicted from an MO correlation diagram.[4] In the case of a formal electrocyclic reaction of *s-cis*-acrylaldehyde, **3**→**4**, such



3 4

a simple prediction is impossible because of a lack of symmetry in the molecular structure.

Since the **3**→**4** system is isoelectronic with the **1**→**2** system, the **3**→**4** reaction may be considered to proceed along the concerted reaction path as is expected for the **1**→**2** reaction. However, a recent analysis of the potential energy surfaces of the **3**→**4** reaction[5] has given evidence of the existance of another reaction path, a step-by-step path in which the ring closing occurs after a rotation of the methylene group. In this path, the Z_+



Z_+

zwitterion, in which the positive charge is localized on the terminal carbon atom, can undergo the ring closing very easily because of the strong attraction between the positive charge and the in-plane lone-pair electrons on the oxygen atom. It is thus very interesting to compare the efficiencies of the two reaction paths, the concerted path and the step-by-step path.

Since a photochemically-excited reactant molecule decays to the ground state of the reaction product *via* some nonadiabatic transitions, the transition-probability calculation as well as the potential-energy-surface analysis is necessary in order to understand the photochemical reaction processes. This is especially true for the **3**→**4** system, in which the symmetry argument of the MO correlation diagram is not effectively used. In our previous paper,[5] the **3**→**4** reaction paths were discussed on the basis of the potential energy surfaces obtained by the MINDO/3[6] CI calculations. In this paper, the nonadiabatic coupling term between the electronic states and the transition probability were calculated using the reduced classical-trajectory method,[2] and the efficiencies of the two postulated reaction paths, the concerted path and the step-by-step path, were examined on the basis of the nonadiabatic interaction between the potential energy surfaces.

Method

The method employed here is the reduced classical-trajectory method.[2] This method has been demonstrated to be a simple method for estimating nonadiabatic transition probabilities in polyatomic systems where transitions between the Ψ_1 and Ψ_2 states are induced, mainly, by the reaction-coordinate-coupling term:

$$g = \langle \Psi_2 | \partial/\partial s | \Psi_1 \rangle. \tag{1}$$

The reaction coordinate, *s*, is defined as the mass-weighted distance along the postulated reaction path A:[7]

$$s = \int_A ds. \tag{2}$$

The coupling term can be written as a sum of the CI and MO terms.[8] These terms were calculated by means of the finite-difference method for the reaction coordinate:[2]

$$g = g_{CI} + g_{MO}, \tag{3}$$

$$g_{CI} = \sum_m B_m(\partial A_m/\partial s),$$

$$g_{MO} = \sum_{\substack{m \\ (m \neq n)}} \sum_n B_m A_n \langle \Phi_m | \partial/\partial s | \Phi_n \rangle,$$

where A_m and B_m are the coefficients of configurations Φ_m in each each state function, *i.e.*,

$$\Psi_1 = \sum_m A_m \Phi_m$$
$$\Psi_2 = \sum_m B_m \Phi_m.$$

The transition probability from the Ψ_2 state to the Ψ_1 state, $P_{2\to1}=|a_1|^2$, was obtained from the solution of the reduced classical-trajectory equations:[2b]

$$\dot{a}_1 = +g\dot{s}\exp\left[-(i/\hbar)\int^t \Delta E\,dt\right]a_2,$$
$$\dot{a}_2 = -g\dot{s}\exp\left[+(i/\hbar)\int^t \Delta E\,dt\right]a_1, \quad (4)$$

where ΔE is the energy gap between Ψ_1 and Ψ_2, *i.e.*, $\Delta E=E_2-E_1>0$. Thus the reduced classical-trajectory equations have a one-dimensional form for nuclear motions, and are derived by neglecting all of the 3N-7 vibrational-coupling terms in the N-atom system.[2b] The transition probability was estimated from the Landau-Zener model:[9]

$$P_{2\to1} = \exp\left[-(\pi/4)\xi\right], \quad (5)$$

with the Massey parameter,[10]

$$\xi = \Delta E(s_c)/\hbar\dot{s}_c g(s_c). \quad (6)$$

ξ was calculated for the s_c point where the g value becomes maximum. The velocity $\dot{s}_c$ was obtained from knowledge of the kinetic energy in the direction of the reaction coordinate, $T_s=(\dot{s}_c)^2/2$.

Linear reaction paths were assumed for the concerted and step-by-step paths of the **3→4** reaction. For the concerted path, all geometrical variables were varied simultaneously between the structures of acrylaldehyde and 2*H*-oxete. These values were first optimized using the MINDO/3 SCF calculation.[5] The step-by-step path was expressed by two linear paths. In the first linear path, only the twisting angle of the methylene group was varied to make the methylene CH_2 plane become perpendicular to the C-C-C-O skeleton. In the second linear path, all the geometrical variables, except for that of the methylene rotation, were simultaneously varied between the structures of the twisted acrylaldehyde and of 2*H*-oxete molecules.

Although the MINDO/3 parameters had been determined so as to well reproduce the ground-state properties of molecules, the MINDO/3 CI calculations gave reasonable results for several photochemical reaction processes.[5,11,12] We thus feel that the nonadiabatic coupling terms calculated with the MINDO/3 CI wavefunctions can be employed for the qualitative consideration regarding a decay process from the excited state.

Results and Discussion

Concerted Path. The total distance between the optimized structures of acrylaldehyde and 2*H*-oxete is **10.47** (atomic mass unit)$^{1/2}$ (bohr). This value was obtained by numerical integration of Eq. 2. The three lowest singlet states along this reaction path are shown in Fig. 1. The S_1 and S_2 states correspond to the $n\to\pi^*$ and $\pi\to\pi^*$ states of acrylaldehyde, respectively. Two avoided crossings were observed along the reaction path, *i.e.*, the A1 avoided crossing between the S_2 and S_1 state and the A2 avoided crossing between the $S_1$and S_0 states. The reaction proceeds from the $n\to\pi^*$ state of acrylaldehyde and reaches the ground state of 2*H*-oxete through the two avoided crossings. On the other hand, the 2*H*-oxete formation from the $\pi\to\pi^*$ is inefficient due to a potential barrier on the S_1 state. This agrees well with the experimental evidence reported by Friedrich and Schuster.[13] Therefore, the efficiency of the concerted path, which starts from the $\pi\to\pi^*$ state of acrylaldehyde, depends on the transition probabilities at the two avoided crossing regions.

The nonadiabatic coupling terms calculated along the concerted path are shown in Fig. 2. The coupling term between S_2 and S_1, which is related to the A1 avoided crossing, has a narrow shape and the CI term is dominant. On the other hand, a broad shape is observed for the coupling term between S_1 and S_0, which is related to the A2 avoided crossing; the MO term is dominant for the g shape. A remarkable observed feature in the concerted path is the overlapping between the two coupling regions. This overlapping indicates that nonadiabatic transitions are expected to occur over a wide range of the two coupling regions. Thus, the shape of the coupling term clearly reflects the property of the nonadiabatic interaction which is not directly observed from the potential energy curves.

Step-by-step Path. The total distance, 3.76(amu)$^{1/2}$

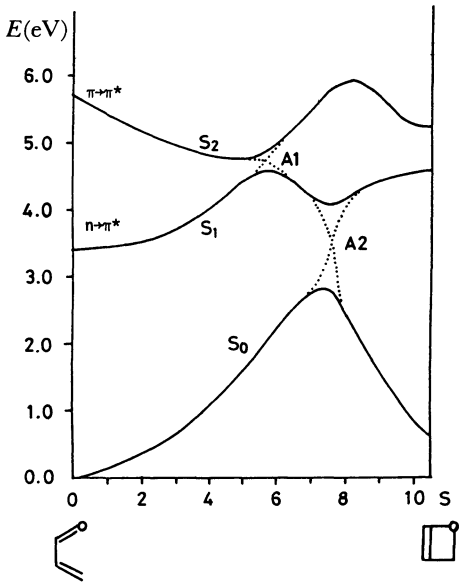


Fig. 1. Potential energy curves along the concerted path for the acrylaldehyde-2*H*-oxete system. Two avoided crossings, A1 and A2, are involved in the process. Unit of reaction coordinate is (amu)$^{1/2}$-(bohr).

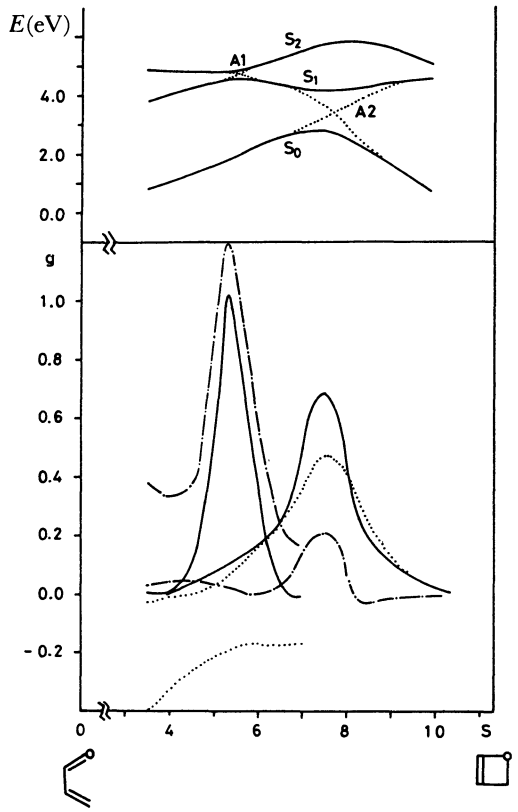


Fig. 2. Nonadiabatic coupling terms calculated along the concerted path(lower part) and the corresponding potential energy curves(upper part).
The lower part; (—·—): g_{CI}(CI term); (·····): g_{MO}(MO term); (——): $g=g_{CI}+g_{MO}$. Unit of g: $(amu)^{-1/2}(bohr)^{-1}$

(bohr), of the reaction coordinate in the first step is very short, since only hydrogen atoms with small masses move along the path. In the second step, the total distance, 9.62 $(amu)^{1/2}$ (bohr), is longer than that of the first step, since the heavy carbon and oxygen nuclei move. Figure 3 shows the potential energy curves along the step-by-step path. The rotation of the methylene group easily occurs in the $\pi\rightarrow\pi^*$ state of acrylaldehyde to give the twisted structure through the A3 avoided crossing between the S_1 and S_2 surfaces.

In the ring-closing step, the symmetry property with respect to the molecular plane is preserved. The S_1 and S_0 states are allowed to intersect since they belong to different symmetry representations.[5] If the symmetry property is destroyed, even slightly, an intersection between S_0 and S_1 is avoided. Such an intersection is called the conical intersection.[14] In order to investigate the nonadiabatic property of the conical intersection, the reaction path, in which the symmetry property was slightly destroyed, was adopted for the ring-closing step. The twisting angle of methylene group was fixed at 87.5° (not at 90°). The potential energy curves along this step-by-step path, therefore, involve two avoided crossings, A3 and A4, as shown in Fig. 3.

The calculated nonadiabatic coupling terms for the two avoided crossing regions are shown in Fig. 4. The

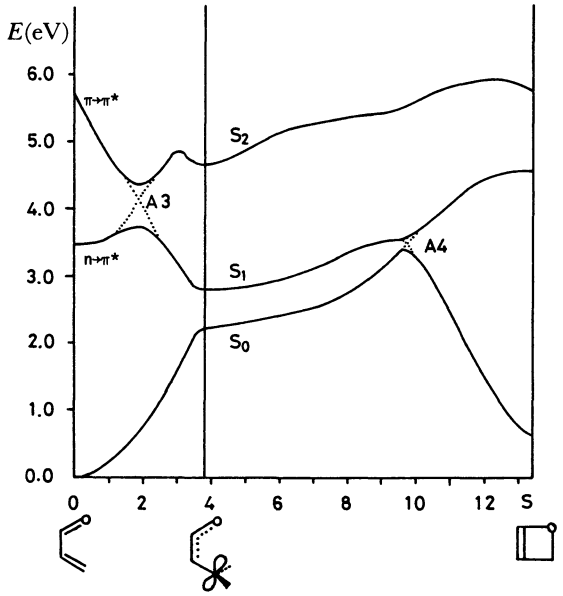


Fig. 3. Potential energy curves along the step-by-step path for the acryaldehyde-2*H*-oxete system. Two avoided crossings, A3 and A4, are involved in the process.

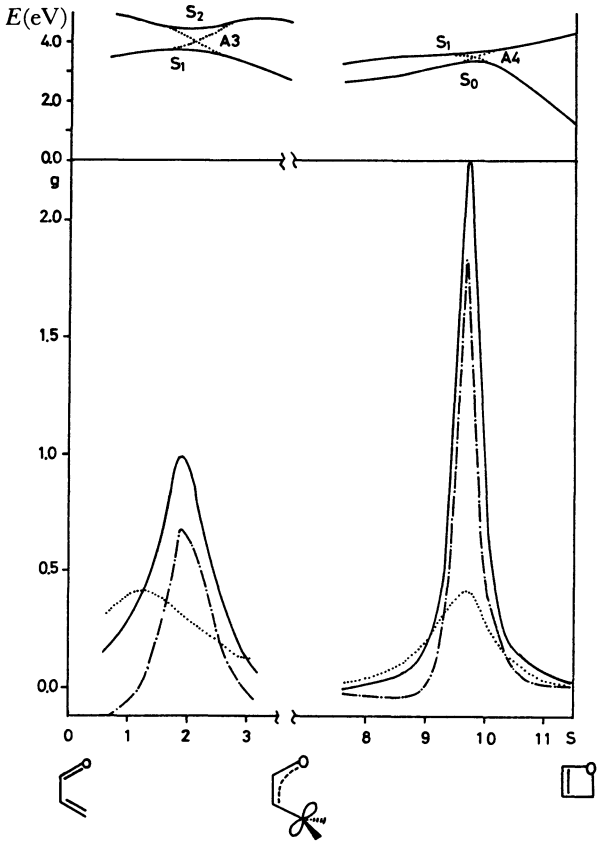


Fig. 4. Nonadiabatic coupling terms calculated along the step-by-step path(lower part) and the corresponding potential energy curves (upper part).
The lower part; (—·—): g_{CI}; (·····): g_{MO}; (——): $g=g_{CI}+g_{MO}$. Unit of g: $(amu)^{-1/2}(bohr)^{-1}$

total g shape for the A3 avoided crossing is similar to that of the A1 avoided crossing in the concerted path, although the shape of the MO and CI components are

TABLE 1. TRANSITION PROBABILITIES AND THEIR RELATED QUANTITIES FOR THE CONCERTED AND STEP-BY-STEP PATHS IN THE ACRYLALDEHYDE-2*H*-OXETE SYSTEM.

Avoided crossing		T_s[a] / eV	$\Delta E(s_c)$ / eV	$g(s_c)$[b] / R	ξ	P
Concerted	A1	1.25	0.25	0.980	1.32	0.35
	A2	1.95	1.32	0.686	7.96	0.0019
Step-by-step	A3	1.63	0.66	0.974	3.07	0.090
	A4	2.46	0.18	2.23	0.30	0.79

a) T_s is the nuclear kinetic energy. The velocity $\dot{s}_c$ in the Massey parameter ξ was obtained from T_s by the equation. $\dot{s}_c=(2T_s)^{1/2}$. b) $g(s_c)$ indicates the maximum value of coupling term in each avoided crossing region, and the unit, (R), is equal to $(\text{amu})^{-1/2}$ $(\text{bohr})^{-1}$.

quite different between the A1 and A3 regions. A very sharp peak is observed in the variation of the coupling term between S_0 and S_1. The character of the conical intersection is clearly reflected in the *g* shape. It can be seen from the *g* shape that the nonadiabatic interaction suddenly increases near the allowed crossing, and the nonadiabatic transition occurs, effectively, in the very narrow region. If the symmetry property with respect to the molecular plane is preserved during the ring-closing step, the *g* shape would be that of a delta function at the crossing point.

Figure 3 may indicate that the $S_1 \rightarrow S_0$ transition occurs, effectively, at the twisted form of acrylaldehyde ($s=3.76$). This transition is induced by the rotation of the terminal methylene group and can be understood by the analogy of the photochemical *cis-trans* isomerization process of simple olefins.[15] The nonadiabatic coupling for this transition was not calculated, since this process is not important for the 2*H*-oxete formation.

Transition Probability. The reaction was assumed to start from the $\pi \rightarrow \pi^*$ state of acrylaldehyde, and the transition probability was calculated for each avoided crossing according to Eq. 5. The results are summarized in Table 1. The kinetic energy, T_s, was calculated from the difference between the energies of the upper state at each avoided crossing point and of the $\pi \rightarrow \pi^*$state of acrylaldehyde. The excitation energy of acrylaldehyde was assumed to be 6 (eV); this value was determined so as to be slightly higher than that of the calculated $\pi \rightarrow \pi^*$ state of acrylaldehyde.

Let us compare the possibility of the step-by-step path with that of the concerted path. If the reaction starts from the $\pi \rightarrow \pi^*$ state of acrylaldehyde, two nonadiabatic transitions are involved in each reaction path. In the first transition from the S_2 state to the S_1 state, the probability of the A1 avoided crossing in the concerted path is higher than that of the A3 avoided crossing in the step-by-step path. In the second transition from S_1 to S_0, however, the A4 avoided crossing has a much higher transition probability than that of the A2 avoided crossing. By the large difference in the probabilities of the second transition, the step-by-step path is considered to be the more effective reaction path in the two postulated paths.

It is noted that some shortcomings are involved in the above consideration. One of them involves the estimation of the kinetic energies employed in the transition-probability calculation. The kinetic energy along the reaction coordinate was estimated from the $\pi \rightarrow \pi^*$ excited-state energy, and the energy distribution among several degrees of nuclear freedom was not taken into account. This may be unrealistic and more reliable statistical methods[16] are necessary to determine the decay-rate constant.

The efficiencies of the two postulated reaction paths were compared on the basis of the nonadiabatic interaction, and the effect of the potential energy barriers on the S_0 and S_1 surfaces was not quantitatively considered. The discussion is, thus, a qualitative one and the most probable reaction path was not determined by the present treatment, although the step-by-step path was expected to be involved in the isomerization reaction.

The possibility of the existance of the step-by-step path in the photochemical electrocyclic reaction of acrylaldehyde was supported by means of the reduced classical-trajectory method. The step-by-step path *via* a zwitterion has been proposed not only for the **3**→**4** reaction but also for the various types of hetero-atom conjugated systems.[11] The present study indicates the importance of this reaction path in the photochemical electrocyclic reaction of heteroatom conjugated systems.

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7) The infinitesimal distance, ds, can be given by $ds^2=\sum_i$

dx_i^2, if the reaction path is represented with the mass-weighted Cartesian coordinates of the N-atom system, $A=(x_1, x_2, \ldots, x_{3N})$. For a more general definition of reaction coordinate, see A. Tachibana and K. Fukui, *Theor, Chim. Acta,* **49**, 321 (1978); P. G. Mezey, *ibid., 54*, 95 (1980).

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