the consumption of 0.04 mmol of 9α-ol and 0.13 mmol of 9β-ol. Analysis of mixtures of known composition of these three compounds by NMR indicated that the results were accurate to within 1%.

Acknowledgment. This work was supported by Grant DA-02634 from the National Institute on Drug Abuse. The JEOL FX-90Q NMR spectrometer was obtained through an NSF Support of Research Equipment Grant. We thank William H. Balke for carrying out the mass spectral determinations. We also acknowledge with gratitude the most helpful comments, suggestions, and information provided by Dr. Valentin Rautenstrauch, Firmenich SA.

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Theoretical Study on the Mechanism of the Thermal Decarboxylation of 2-Oxetanones

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The mechanism of the thermal decarboxylation of 2-oxetanone is investigated by the use of the MNDO method. The state correlation diagram shows that five heavy atoms of 2-oxetanone, three carbon and two oxygen atoms, are kept in the same plane in the decarboxylation. This is found to be a one-step reaction and to proceed via a zwitterionic transition state. The substitution effect and solvent effect on the reactivity are discussed.

The present paper deals with the mechanism of the thermal decarboxylation of 2-oxetanones, which yields olefin and carbon dioxide. The mechanisms of 2 + 2 reactions have received increasing attention during the past few years.[1] The decarboxylation of 2-oxetanones is one of them. This reaction has repeatedly been employed in the stereospecific synthesis of olefins because it proceeds with retention of geometrical configuration.[2] Recently, substitution effects on the thermal decarboxylation have been investigated, and the electronic effects of substituents attached at the C_3 or C_4 position have been clarified.[3] It is suggested that the reaction proceeds via a zwitterionic intermediate. However, it is still questionable how the bond scission takes place to give olefin and carbon dioxide. It is also not certain whether the zwitterionic species is really an intermediate or not, that is, the species is located on a local energy minimum in the reaction coordinate.

In this work, the decarboxylation path is examined by a correlation diagram[4] and then it is traced by the MNDO method[5] in order to clarify the reaction mechanism. The substitution effect and solvent effect on the obtained potential energy are investigated.

Simulation of the Reaction Path

The method of simulating the decarboxylation path is described. First, the fully optimized equilibrium geometries of 2-oxetanone and its decomposition products, ethylene and carbon dioxide, are obtained. Second, the state correlation diagram is drawn by the use of the molecular orbitals (MO's) of 2-oxetanone, ethylene, and carbon dioxide to judge whether the coplanarity formed by five heavy atoms, three carbon and two oxygen atoms, is kept or not throughout the reaction. Third, the energy-optimized path is calculated by the MNDO method.

Figure 1 shows the fully optimized geometry of 2-oxetanone obtained by the MNDO method together with the observed geometry.[6] The optimized geometry with the 4-31G basis set is also depicted.[7] In both MNDO and 4-31G calculations, bond lengths and angles are optimized within the accuracy of 0.005 Å and 0.1°, respectively. The calculated results are in fairly good agreement with the observed ones. Both experimental and computational data demonstrate that 2-oxetanone belongs to a point group of the C_s symmetry, which means that O_1, C_2, C_3, C_4, and O_5 are in the same plane.

Since 2-oxetanone is found to be planar, it is checked by a state correlation diagram as to whether the decarboxylation proceeds with retention of the planar structure. Figure 2 shows the state correlation diagram for the decarboxylation path with the C_s symmetry. The ground state of 2-oxetanone can connect with that of a product site without any avoided crossing, which is represented by a bold line in the figure. This means that the thermal decarboxylation is predicted to take place preserving the planarity of 2-oxetanone. The state correlation diagram also gives information on the photodecarboxylation. The

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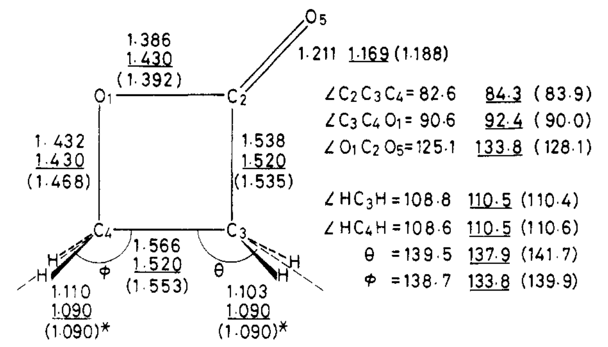

Figure 1. Geometry of 2-oxetanone optimized by the MNDO method. The underlined values are experimental ones, and those in parentheses are obtained by the 4-31G MO calculation. The values denoted by asterisks are kept constant during the optimization. Bond lengths are in Å and angles are in degrees. The total energy of 2-oxetanone optimized by the 4-31G basis set is −265.226 au, and this is 0.005 au lower than that obtained by using the MNDO-optimized geometry.

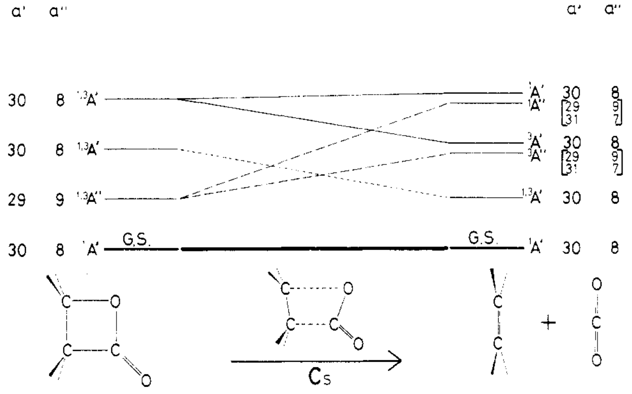

Figure 2. State correlation diagram for the decarboxylation with C_s symmetry. At both sides of this figure, all electrons of the system are assigned to two symmetry orbitals (a′ and a″); G.S. means the ground state.

lowest excited state of 2-oxetanone ($^{1,3}A''$, n → π*) goes up energetically (a broken line) as the reaction proceeds and cannot be connected with the lowest excited state of the product site of the different symmetry ($^{1,3}A'$). A reaction path with the C_s symmetry is, therefore, unfavorable for the decomposition in the lowest excited state. However, the second excited state of 2-oxetanone ($^{1,3}A'$, π → π*) slides down (a dotted line) toward the product site and is joined to the lowest excited state of the product site ($^{1,3}A'$). Therefore, 2-oxetanone in the second excited state can readily decompose with retaining its planar structure. The analysis of the state correlation diagram demonstrates that the energy-curve crossing between the ground and excited states is absent and consequently the thermal generation of the triplet state (furthermore chemiluminescence) is unlikely. This result is in contrast to the decomposition of the similar four-membered-ring compound, dioxetane.[8]

The reaction path in the ground state was obtained by the MNDO method. According to the result of the correlation diagram, the C_s symmetry is kept, which means that at the symmetry conserved stage of the reaction "bent-out-of-plane" motion is ruled out. A snapshot sequence of the reaction is shown in Figure 3. First, the O_1–C_4 bond (R) is enlarged from 1.43 Å (2-oxetanone) to 2.24 Å in order to reproduce the energy-optimized path. The reacting system is fully optimized at a given R. However, at $R > 2.24$ Å it is difficult to obtain the reasonable energy-optimized path, because small enlargement of R gives the drastic change of the geometry of the reacting system, and the obtained path begins to deviate from the "true" reaction coordinate.[9] Therefore, the energy-optimized path at $R > 2.24$ Å is obtained by using L (C_2–C_3 bond) instead of R as the main geometrical parameter.

According to the correlation diagram, the C_s symmetry (in-plane motion) is retained throughout the reaction. However, this is true only where the symmetry conservation is effective. At the large separation between carbon dioxide and ethylene (i.e., at the end of the reaction), the symmetry restriction is removed and these two species behave independently. In this region, the frontier-orbital theory[10] controls the reaction coordinate. The theory supports the bent-out-of-plane path rather than the bent-in-plane one.[1a] That is, while at a greater part of the reaction the symmetry-restriction rule gives the bent-in-plane path, at the final part the frontier-orbital theory gives the bent-out-of-plane path. This is schematically illustrated in Figure 4. When a bent-out-of-plane path is checked by the MNDO method, the in-plane motion is confirmed to be favorable in the greater part of the decarboxylation, although the bent-out-of-plane path becomes favorable at the final part (G and H in Figure 3) of the decarboxylation. Since we are interested in the electronic structure of the transition state, the bent-out-of-plane path is not traced here.

The potential energy profile by the MNDO method is depicted in Figure 5 (full line). It should be noticed that this potential energy profile has only one peak; that is, the decarboxylation is found to be a one-step reaction. The transition state of this reaction is located at $R = 2.24$ Å. To assure this, the SIGMA calculation using MINDO/3[11] is carried out. Although the geometry of the transition state obtained by the SIGMA calculation is somewhat different from that obtained by the MNDO calculation, it is ascertained that the decarboxylation has the transition state with the C_s symmetry like D in Figure 3. The activation energy is calculated to be 79.3 kcal/mol. The MNDO method is known to overestimate the stability of four-membered-ring compounds consistently with a mean error, 18.7 kcal/mol.[5a] The potential energy is recalculated with the 4-31G basis set by using the MNDO-optimized geometry to remove this MNDO error, and is also shown in Figure 5 (broken line). The marked difference between the two energies is found in the enthalpy changes, −18.6 kcal/mol (4-31G) vs. +8.9 kcal/mol (MNDO). When the 4-31G enthalpy change is accepted, the MNDO total energy of 2-oxetanone should be corrected (or scaled down) by 27.5 (= 8.9 − (−18.6)) kcal/mol. This correction decreases the MNDO activation energy to 51.8 (= 79.3 − 27.5) kcal/mol, which becomes closed to the 4-31G activation energy, 50.9 kcal/mol. The activation energy of the de-

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(9) In the strict sense, the reaction path should be sought, after the transition state is determined, in the direction of the normal mode associated with the imaginary frequency and by following the mass–weight gradient to the reactant and the product. In the present method of tracing the minimum energy path by the use of the internal coordinates, care should be taken to check whether the obtained path is coincident with the strict reaction coordinate. We have examined the shape of the energy hypersurface by taking many points for the energy calculation, and it is believed that the present minimum energy path is almost equal to the true reaction coordinate. If we take the C_2–C_3 distance (L) as a major geometrical parameter throughout the reaction, the C_2–C_3 bond fission requires more than 83 kcal/mol. This value is larger than that shown by the energy difference, $E_T(D) - E_T(A)$, in Figure 5. Thus, a geometrical parameter, L, can not describe the whole path, and the switch of the main geometrical parameter ($R \rightarrow L$) in the course of the distortion is necessary to simulate the reaction coordinate.

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Table I. Comparison of the Relative Activation Energies

no.	aryl (x)	1,[a] $(E_x - E_\phi)_{exptl}$ (T = 323 K)	3,[b] $(E_x - E_\phi)_{calcd}$	2,[a] $(E_x - E_\phi)_{exptl}$ (T = 433 K)	4,[b] $(E_x - E_\phi)_{calcd}$
i	p-$OCHC_6H_4$	−4.89	−0.954	0.08	0.018
ii	p-$CH_3C_6H_4$	−1.50	−0.094		−0.000
iii	C_6H_5	0	0	0	0
iv	m-ClC_6H_4	1.74	1.462	0.00	0.085
v	p-CNC_6H_4	2.79	2.147		0.100
vi	p-$NO_2C_6H_4$	3.31	4.564		0.192

[a] From $k_x = Ae^{-E_x/RT}$ and $k_\phi = Ae^{-E_\phi/RT}$, $(E_x - E_\phi)_{exptl} = RT\ln (k_\phi/k_x)$ under the assumption of the constant A. k_x and k_ϕ are taken from ref 3d. E_ϕ is the activation energy of phenyl-substituted-2-oxetanone, which is used as the standard value. [b] The finding that k_x of **1** is larger than k_x of **2** is reproduced by the MNDO activation energies of **3** and **4**. E_ϕ's of **3** and **4** are calculated to be 69.3 and 80.1 kcal/mol, respectively (see ref 3d). These values becomes 41.8 and 52.6 kcal/mol after the "27.5 kcal/mol correction" stated in the text.

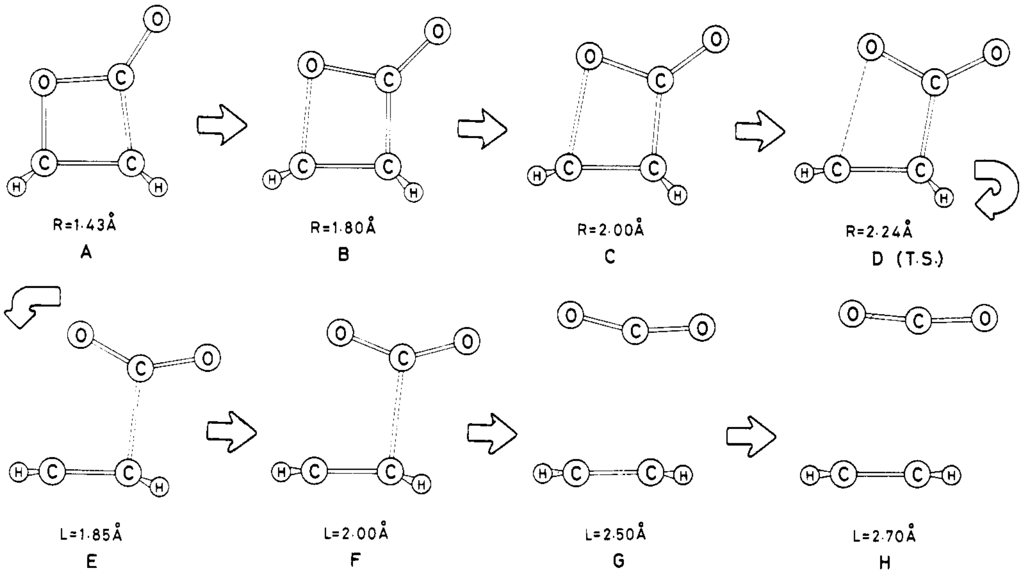


Figure 3. Snapshot sequence of the decarboxylation. R is the O_1–C_4 distance and L is the C_2–C_3 distance. At the point D, the energy maximum is obtained; T.S. denotes the transition state.

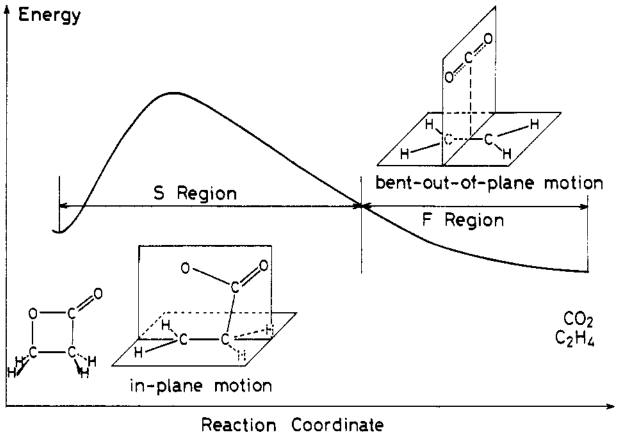


Figure 4. Schematic representation of the reaction coordinate. In the S region, the C_s symmetry is conserved. In the F region, the frontier-orbital control is effective, and the reaction path is free from the symmetry restriction.

carboxylation of 4-(p-nitrophenyl)-3,3-dimethyl-2-oxetanone is estimated by the MNDO correction method. The energy without the correction is calculated to be 72.3 kcal/mol, and that with the correction is 44.8 kcal/mol. The latter is in good agreement with the experimental energy, 36.9 kcal/mol.[3b] Thus, the MNDO method gives a good correspondence between the calculated and experimental activation energies when the correction is taken into account.

The lowest triplet state energies of B, C, D, E, F, and G in Figure 5 are also calculated.[5c] It is found that the energy curve of the triplet state does not cross that of the ground state. Therefore, it is considered that the triplet intermediate does not appear in the thermal decarboxylation as is predicted by the correlation diagram.

The summary of the calculated results is given as follows. The decarboxylation of 2-oxetanone is a one-step reaction, but two bonds (O_1–C_4 and C_2–C_3) are successively broken. At the initial stage (before the transition state), the O_1–C_4 bond is weakened, and then it is broken at the transition state. The C_2–C_3 bond is not so weakened yet at the transition state (L = 1.538 → 1.572 Å). The reaction coordinate is represented mainly by the elongation of the O_1–C_4 bond (R). After the transition state, however, the reaction coordinate is composed chiefly of the change of the C_2–C_3 bond (L). Therefore, the main component of the reaction coordinate is switched at the transition state. The potential energy profile has only one maximum in spite of the successive bond scission. This is explained as follows. Although the C_2–C_3 bond fission destabilizes the reacting system, the formation of two π bonds inside ethylene and carbon dioxide overwhelms the destabilization, and totally the reacting system is stabilized. As for the reaction path, the essential part of the decarboxylation has the C_s symmetry. Since the path is described by an in-plane motion, the decarboxylation proceeds stereospecifically.[2]

Comparison with Experimental Data

In this section, the calculatd results are compared with the experimental data obtained so far.[3] First, the substituent effect is discussed. Rate constants of the ther-

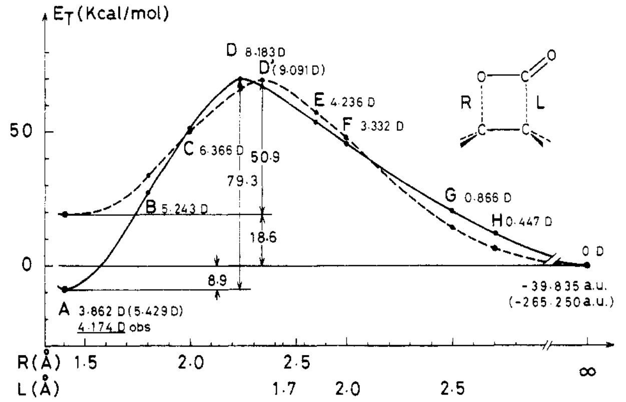
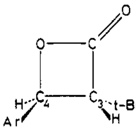


Figure 5. Potential energy profile of the thermal decarboxylation obtained by the MNDO (full line) and 4-31G (broken line) methods. The number at each point denotes the calculated dipole moment in debye by the MNDO method. The numbers in parentheses are the dipole moments calculated by the 4-31G MO calculation. E_T stands for the total energy. The zero of the vertical axis corresponds to $E_T(C_2H_4 + CO_2)$. E_T in parentheses is calculated by the 4-31G basis set.



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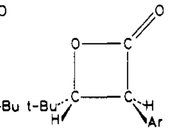

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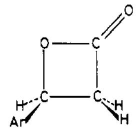

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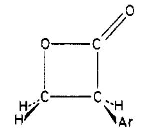

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molysis of *trans*-3-*tert*-butyl-4-aryl-2-oxetanones (*1*) and *trans*-4-*tert*-butyl-3-aryl-2-oxetanones (*2*) are available,[3d] although the activation energies for a series of 2-oxetanones were not measured. The substituent on the para or ortho position of the phenyl ring changes the rate constant considerably. Since the substitution on the phenyl ring is expected to be almost independent on the preexponential factor, *A*, of the Arrhenius equation, the difference of the activation energies is estimated by the use of the rate constants. It is compared with the calculated energy barrier (E_ϕ and $E_x = E_T$ (the transition state − E_T(2-oxetanone)) of the MNDO MO calculation. For the computational simplicity, 4-aryl-2-oxetanones (**3**) and 3-aryl-2-oxetanones (**4**) are used as models for the MO calculation instead of **1** and **2**.

Table I summarizes the calculated results. For **1** and **3**, the present calculation gives a fairly good correspondence between $(E_x - E_\phi)_{\text{exptl}}$ and $(E_x - E_\phi)_{\text{calcd}}$. An electron-donating group attached to the phenyl of the C_4 position (i and ii) makes the rate constant larger, whereas an electron-accepting group (iv, v, and vi) makes it smaller. For **2**, the substitution at the C_3 position shows a minor effect on the rate constant,[3] which is well reproduced by $(E_x - E_\phi)_{\text{calcd}}$ of **4**. The charge distribution of the transition state is analyzed to see the origin of the difference of the reactivity. Figure 6 shows the charge distribution. The transition state of the parent molecule shows a significant

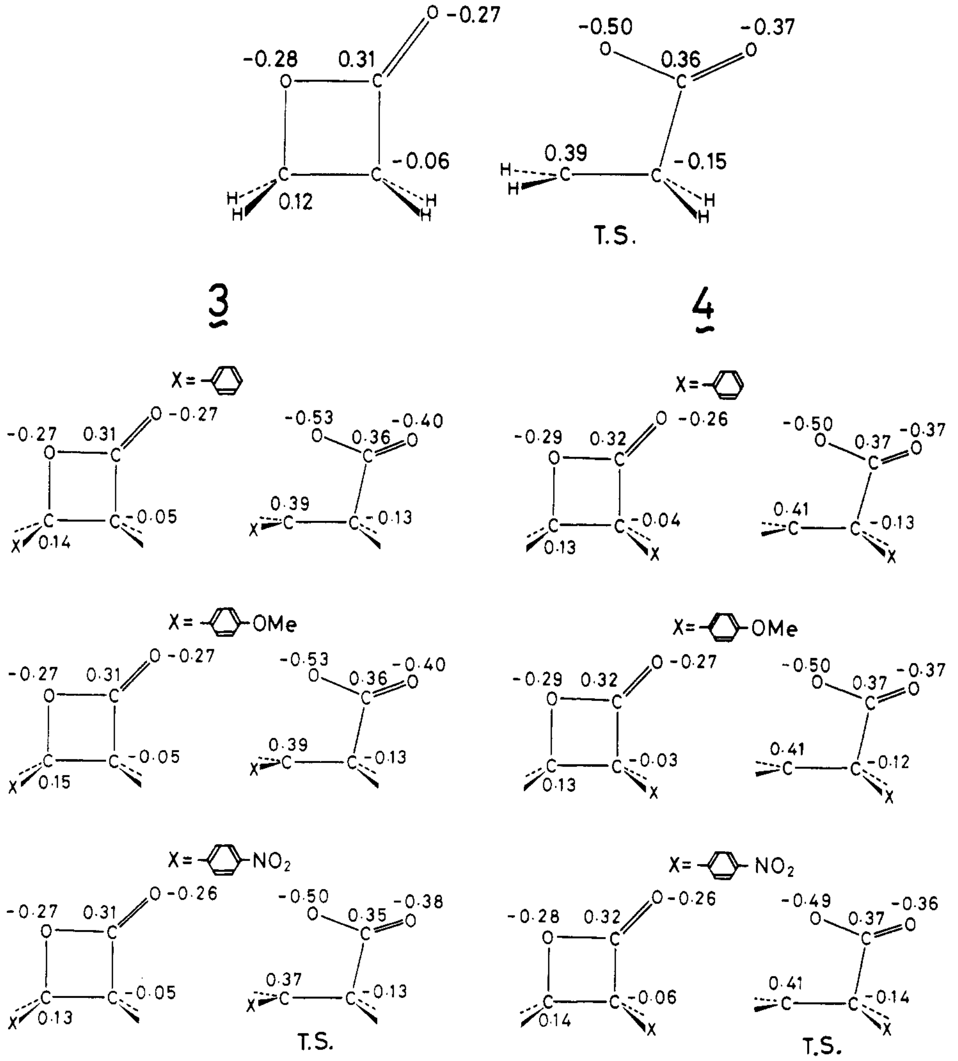

Figure 6. Charge distribution of 2-oxetanones and point D (transition state). For **3** and **4**, the geometry is assumed to be the same as that of the parent molecule (top) except at the substituted site.

positive charge (electron deficient) on the C_4 position and a significant negative charge (electron sufficient) on the O_1 position.[12] The good correspondence of $(E_x - E_\phi)_{\text{exptl}}$ with $(E_x - E_\phi)_{\text{calcd}}$ ascertains the presence of the zwitterionic transition state.

The solvent effect on the rate constant is discussed. Mulzer and Zippel determined the decarboxylation rates of 1_{iii} in several solvents, for example, decalin, anisole, and formanilide.[3d] They obtained a satisfactory correlation of the rate constants with polarities of the solvents. The rate constant is large in polar solvents. Figure 6 shows the large localization of the positive and negative charges on the C_4 and O_1 positions, respectively, in the transition state. The transition state is stabilized by the Coulombic attraction between the cationic site of a polar solvent and the O_1 atom of the reactant. In addition, the zwitterionic nature of the transition state gives the large polarity of the reactant. Figure 5 shows the dipole moment of 2-oxetanone and the reacting system. The calculated dipole moment of 2-oxetanone at point A (3.862 D) is in good agreement with the observed one (4.174 D).[6] The dipole moment is found to be largest at the transition state (8.183 D). Therefore, the transition state is most stabilized by the long-range dipole–dipole interaction between solvent molecules and the reactant. Consequently, polar solvents make the activation energy small and the rate constant large by the Coulombic and dipole–dipole interactions. This analysis supports the finding by Mulzer and Zippel. Therefore, the solvent effect also ascertains the presence of the zwitterionic transition state.

Thus, the present calculation demonstrates that the reactivity of the thermal decarboxylation is determined by the extent of the $O_1 \cdots C_4$ polarity. The reaction rate is enhanced by the lowering of the activation barrier through the polarized transition state···solvent interaction.

Concluding Remarks

In this paper, the thermal decarboxylation mechanism for 2-oxetanones is investigated by the MNDO method. Although the energetics of the decarboxylation is not so accurate, the significant feature of this reaction is obtained. It is found that five heavy atoms of 2-oxetanones, three carbons and two oxygens, are preserved on the same plane in the essential part of the reaction. The decarboxylation is a one-step reaction with successive bond fission. First, the O_1–C_4 bond is broken at the transition state, and then the C_2–C_3 bond is broken. The transition state of the reaction has a largely polarized character, the extent of which is a crucial factor of the reactivity. The electron-donating substituent on the aryl of C_4 position enhances this polarity, which deserves both intramolecular ($O_1^{\delta-} \cdots C_4^{\delta+}$) Coulombic attraction and reactant–solvent interaction. The state correlation diagram demonstrates that the triplet spin state does not concern the thermal decarboxylation.

Acknowledgment. We thank the Computer Center, Institute for Molecular Science, for the use of the HITAC M-200H computer. We also express our gratitude to Miss Minako Hirata for her assistance in the MO calculation.

Registry No. **3i**, 85005-04-5; **3ii**, 85005-05-6; **3iii**, 4287-98-3; **3iv**, 85005-06-7; **3v**, 85005-07-8; **3vi**, 35202-08-5; **4i**, 85005-08-9; **4ii**, 85027-94-7; **4iii**, 27150-91-0; **4iv**, 85005-09-0; **4v**, 85005-10-3; **4vi**. 85005-11-4.

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[12] The charge distribution of 2-aminoethanoic acid ($NH_3^+CH_2COO^-$) is calculated by the MNDO method as an example of the ion-pair species. The calculated result shows that the electronic charge on the carboxylic oxygen is −0.57 and that on amino group is +0.63 (the charge on the nitrogen is only +0.05). In view of these values for the typical ion-pair molecule, we may say analogously that the transition state of the decarboxylation obtained here has a zwitterionic nature.

Reaction of *N*,*N*-Dimethylaniline Derivatives with Cumene Hydroperoxide. Oxazolidine Formation via Addition of α-Aminomethyl Radicals to Formaldehyde

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Received July 1, 1982

The reactions of *N*,*N*-dimethylaniline derivatives (1) with cumene hydroperoxide in acetonitrile at 100 °C produce significant amounts of the corresponding *N*-aryloxazolidine (6). Oxazolidine formation occurs by addition of α-aminomethyl radicals (7) to formaldehyde to give the alkoxy radical (8), followed by intramolecular 1,6 H-atom abstraction, oxidation, and cyclization. The results of labeling experiments and the dependence of the oxazolidine yield on the formaldehyde concentration support this mechanism. Alkoxy radical 8 was generated by an alternative route and does give the oxazolidine. Radical addition to the carbonyl carbon of formaldehyde is a reflection of the electron-rich, nucleophilic nature of the α-aminomethyl radical 7 and rapid trapping of the resulting alkoxy radical 8 via intramolecular H-atom abstraction through a six-membered transition state.

One of the characteristic reactions of alkoxy radicals is the β-scission to give a carbonyl compound and a new, usually carbon-centered radical.[1] The reverse of this process, addition of a radical to a carbonyl group to give an alkoxy radical, is rare and only a few examples can be found in the literature.[2] We now report that α-aminomethyl radicals, generated in the reaction of *N*,*N*-dimethylaniline derivatives with cumene hydroperoxide (CHP), add to formaldehyde at the carbonyl carbon to give

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