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An MO Theoretical Study of the Photochemical Reaction of Alkanenitronate Anions to Form Hydroxamic Acids

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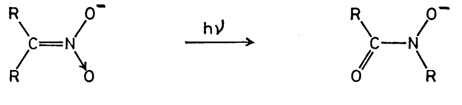
The reaction mechanism of the photochemical reaction of alkanenitronate anions to form hydroxamic acids was explored on the basis of the potential energy curves obtained by means of MINDO/3 CI calculations. The *O*-oxaziridine was calculated to be not an intermediate, but an unstable transient species in this photoreaction. This is different from the photoisomerization of methyleneamine *N*-oxide derivatives into the corresponding amides, in which the oxaziridine is considered to be an intermediate. The proposed reaction mechanism elucidates well the regioselectivity observed in the photochemical formation of hydroxamic acids from nitronate anions.

Although the photochemical reactions of aliphatic nitro compounds have been investigated extensively,[1] the photochemical reactions of alkanenitronate anions, which are formed from aliphatic nitro compounds in an alkaline solution, has not been reported before our recent studies.[2] The photolyses of nitronate anions, **1**, give hydroxamic acids, **2**. Since methyleneamine *N*-oxide derivatives, **3**, give, photochemically, the corresponding amides, **5**,[3] the **1**→**2** reaction may be considered to proceed by means of a mechanism similar to that of the **3**→**5** reaction. In the **3**→**5** reaction, the oxaziridine, **4**, is considered to be an intermediate; some oxaziridines have been isolated.[3] In the case of the nitronate anions, however, the corresponding *O*-oxaziridines are too unstable to be observed by spectroscopic methods.[2] Moreover, the regioselectivity observed in the photolysis of **6** is different from that observed in the **8**→**9** reaction. Thus, the **1**→**2** reaction mechanism can not be sufficiently understood by analogy with that of the **3**→**5** reaction; we therefore decided to perform MO theoretical calculation along the **1**→**2** reaction process to explore the reaction mechanism and to complement our experimental studies.



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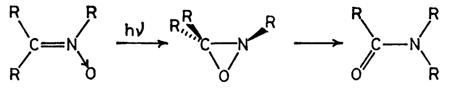

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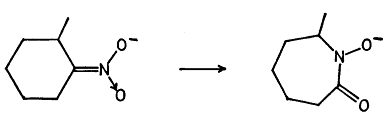

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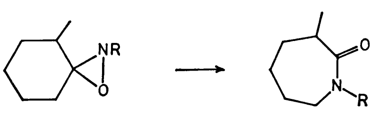

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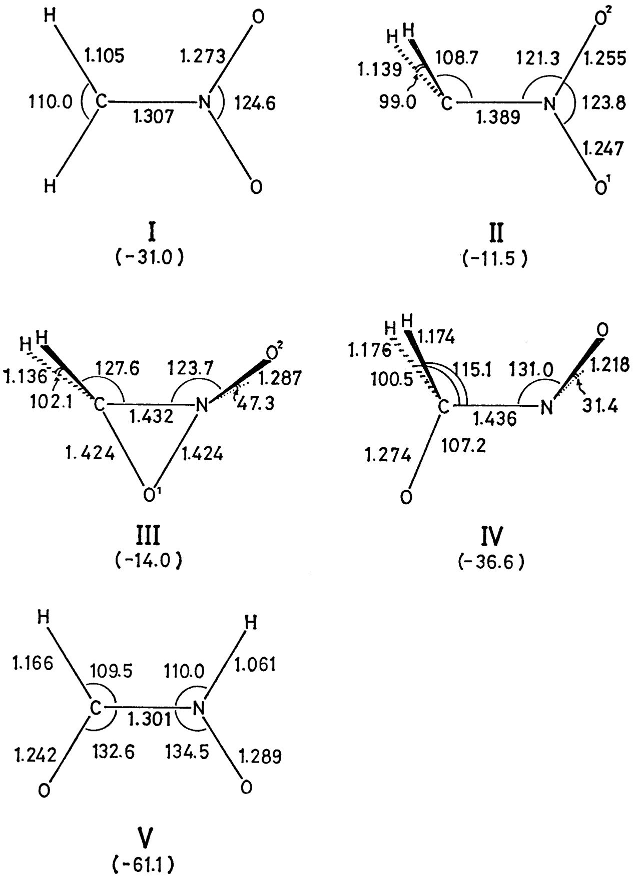


Fig. 1. Molecular structures and heats of formation (in parentheses) of the anions I—V obtained by MINDO/3. Bond lengths are in Å, bond angles in degrees, and heats of formations in kcal/mol (1 kcal=4.184 kJ).

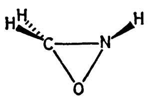
Method and Results

The unsubstituted compound, I, was employed as the model nitronate anion. The molecular structures of the anions, I—V, were optimized by MINDO/3[5]

SCF (without CI) calculation. The configuration of the H atoms in II and III was restricted to symmetrical with respect to the CNO^1 plane. The calculated structures and the heats of formation of these anions are shown in Fig. 1. The energy difference between I and II, 81.6 kJ/mol, agrees well with the STO-3G value (64.9 kJ/mol).[6)]

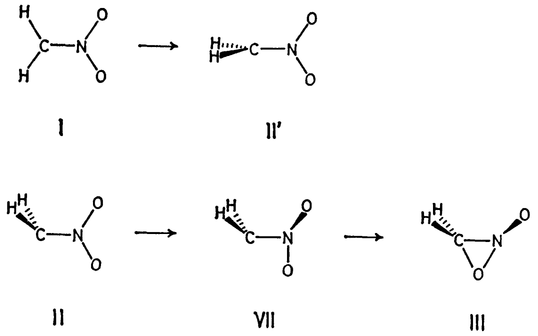
The HOMO of II is the CH_2 σ lone-pair orbital (carbanion type), while the LUMO of II is the NO_2 *anti*-bonding π orbital. The closed-shell configuration is the ground state of this twisted structure, and the HOMO→LUMO diradical structure is the excited state, as will be shown below. The CN bond of nitronate anions has a double-bond character. As may be expected from the electronic structure of the twisted ethylene,[7)] the lowest singlet state of the species obtained by 90° rotation about a double bond is the diradical state. The lowest state of the twisted methyleneamine *N*-oxide was calculated to be the diradical state.[8)] It is thus very interesting that the lowest singlet state of the twisted nitronate anion has a closed-shell electron configuration.

In the optimization of the bridged structure, III, the C–O^1 and N–O^1 distances were resticted to $R_{CO^1}=R_{NO^1}$. If this restriction is removed, the N–O^1 bond breaks spontaneously during the geometry optimization process, and the stable bridged structure cannot be obtained; the optimization gives an open structure, IV. Since the stable bridged structure is obtained for VI by the same optimization procedure,[8)] the instability of III may be said to be characteristic of the *O*-oxaziridine derived from nitronate anions. The reaction product V is very stable (105 kJ/mol more stable than IV), and the transformation from IV to V can be expected to occur very easily.



VI

The photochemical formation of V from I involves the methylene rotation, the oxygen migration from the nitrogen to carbon atoms, and the hydrogen migration in the reverse direction. The I→V process is thus too complex to be analyzed by the MO method. We restricted ourselves to considering three processes successively:



(1)

I II'

II VII III

Table 1. Lower electronic states of the planar CH_2=NO_2 anion

States	Energy/eV	Main configurations[a)]
$^1A_1$	0.000	Ground conf. (97%)
$^1B_2$	3.68	12→13(98%)
$^1A_1$	4.11	12→14(58%), 11→13(35%)
$^1B_2$	4.72	11→14(53%), 12→16(39%)
$^3A_1$	2.78	12→14(98%)
$^3B_2$	2.83	12→13(99%)
$^3A_1$	4.26	11→13(85%), 11→16(9%)

a) The highest occupied ϕ_{12} orbital is the C–N π orbital, the ϕ_{13} and ϕ_{16} orbitals are unoccupied σ orbitals, ϕ_{11} is the oxygen lone-pair σ orbital, and ϕ_{14} is the unoccupied π orbital.

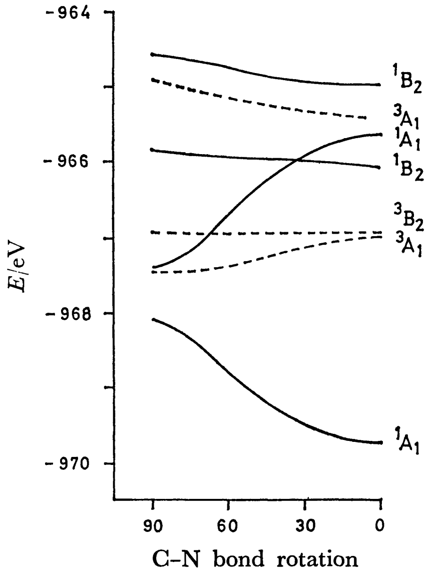
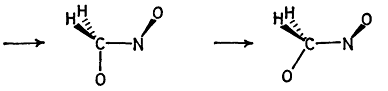
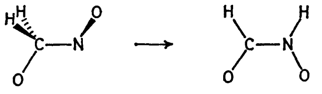


Fig. 2. Energy variations of several lower electronic states of the nitronate anion I along the rotation about the CN bond.



(2)

VIII IV



(3)

IV V

The potential curves along the methylene rotation, Eq. 1, were calculated by means of the CI method, in which 30 and 27 configuration functions were selected from singly- and doubly-excited configurations for the singlet and triplet states respectively. Several lower states of I are listed in Table 1, while their energy variations along the methylene rotation are shown in Fig. 2.

In order to determine the potential curves for the oxygen-migration reaction, the CI calculations were

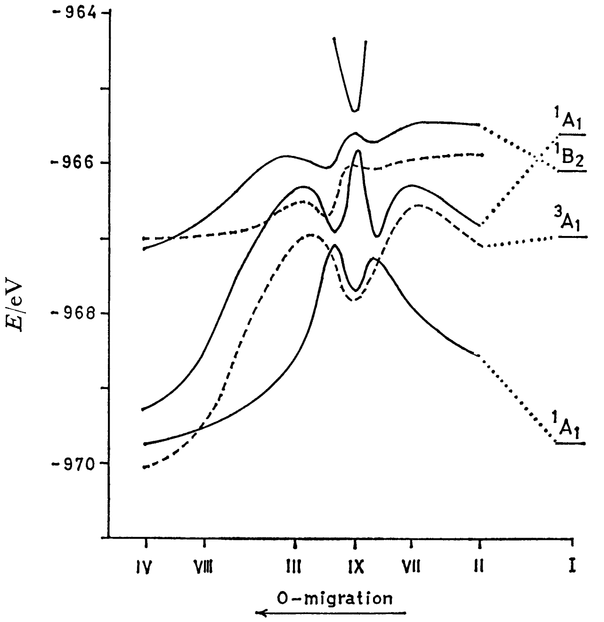
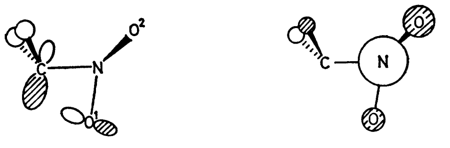


Fig. 3. Energy variation of lower electronic states along the oxygen migration process II→IV.



ϕ_{σ^*} ϕ_{π^*}

carried out for the five optimized structures involved in Eq. 2, as well as for several intermediate structures between VII and III. The potential curves obtained are shown in Fig. 3. An interesting shape of potential curves was observed between VII and III. In this region, two occupied orbitals, the carbanion-type σ lone-pair orbital on the carbon atom and the in-plane oxygen one-pair orbital, interact with each other to form the C–O^1 ϕ_σ and ϕ_{σ^*} occupied orbitals. When this interaction increases, the orbital energy of the occupied ϕ_{σ^*} orbital increases rapidly and crosses with the unoccupied ϕ_{π^*} orbital of the NO_2 group. Since the O^1 migration is accompanied by the deviation of the NO bond out of the CNO^1 plane, the ϕ_{σ^*} and ϕ_{π^*} orbitals mix to give the HOMO and LUMO in this region (Eqs. 4 and 5). According to Salem,[7]

$$\Psi_{12}(\text{HOMO}) = \frac{1}{\sqrt{2}}(\phi_{\sigma^*}+\phi_{\pi^*}) \tag{4}$$

$$\Psi_{13}(\text{LUMO}) = \frac{1}{\sqrt{2}}(\phi_{\sigma^*}-\phi_{\pi^*}) \tag{5}$$

the lowest singlet state in this region is a diradical state whose electron configuration is $(\phi_{\sigma^*})^1(\phi_{\pi^*})^1$. The wavefunction of the pure diradical singlet state of this electron configuration is:

$$\frac{1}{\sqrt{2}}(\Psi_{12}^2-\Psi_{13}^2).$$

Thus, the lowest singlet state in this region should be expressed by the two-configuration wavefunction. The CI calculation in this region was carried out for the diradical IX, whose molecular structure was optimized by using the double-configuration wavefunction. The IX structure corresponds to the deep minimum point in Fig. 3, and the CI wavefunction of the lowest singlet

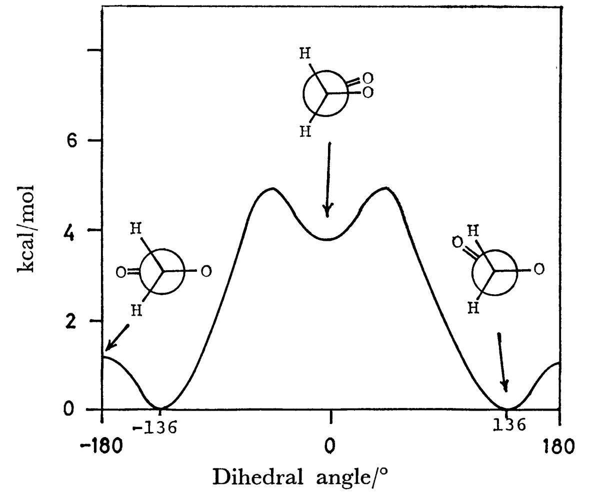


Fig. 4. Energy variation of IV along the rotation about the C–N bond. The structure is optimized at each rotational angle.

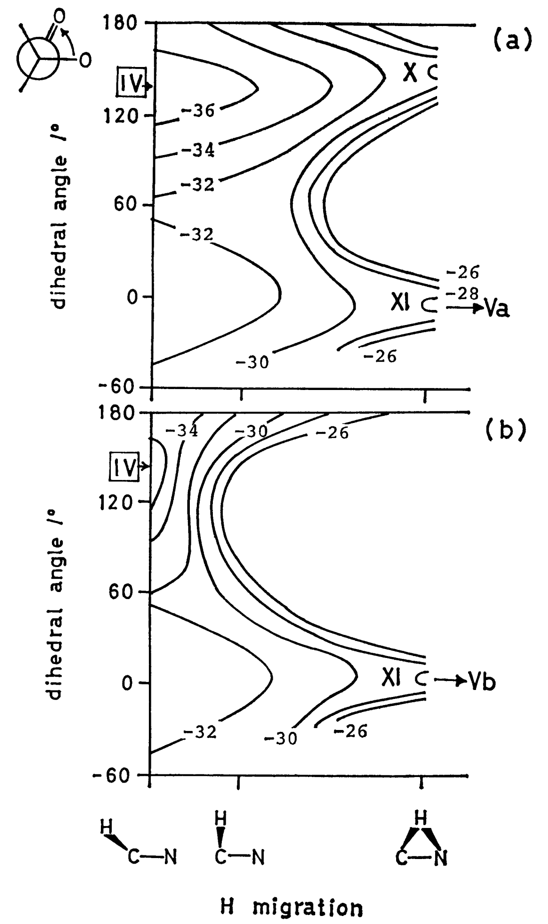
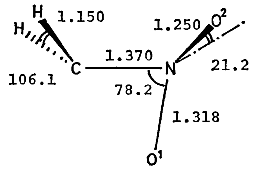


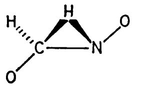
Fig. 5. Potential energy surfaces for the H-migration reaction from IV to the bridged structure. a) H^t migration. b) H^c migration. The values are heats of formation in kcal/mol (1 kcal=4.184 kJ).



IX

state of IX is $0.759\Psi_{12}^{2}-0.569\Psi_{13}^{2}+\cdots$.

The hydrogen migration and the N=O group rotation are involved in Eq. 3. Figure 4 shows the energy variation in IV with respect to the dihedral angle between the OCN and CNO planes. Figure 5 shows the potential energy curves as a function of the dihedral angle and the H-migration coordinate. Two bridged structures, X and XI, were predicted for the transition states; X and XI give the *trans* and *cis* isomers of the final product respectively. As may be seen from Fig. 4, the two hydrogen atoms in IV are not equivalent; one is *trans*, and the other is *cis*, with respect to the N=O bond. There are two possible paths leading to the *cis* isomer of the final product which corresponds to **7**. The potential energy surfaces in Fig. 5 indicate that the H^t migration is preferable to the H^c migration.



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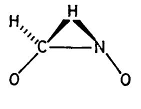
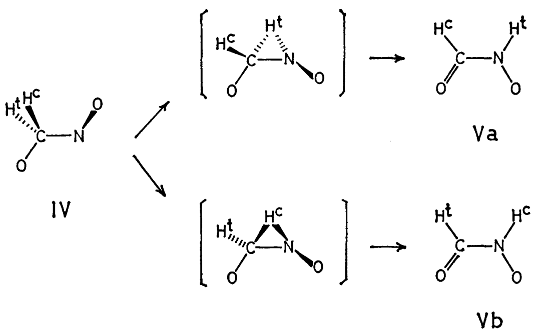


XI



Discussion

The strong absorption of alkanenitronate anions observed in the 230—240 mμ region[2] can be assigned to the transition from the ground state to the $^1A_1(\pi\rightarrow\pi^*)$ excited state, since this is a symmetry-allowed transition. The rotation of the methylene group about the CN bond of I can occur in this excited state (Fig. 2). The nitronate anions can undergo photochemical isomerization from their $\pi\rightarrow\pi^*$ excited state. In the present calculation, two processes, the rotation of methylene and the oxygen migration, were treated separately; a concerted path of these two processes may be possible in the actual system. These steps do not occur from the ground state, since the activation energy required is more than 210 kJ/mol (Figs. 2 and 3).

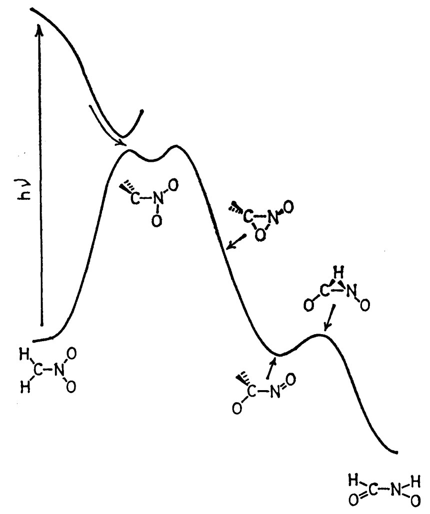
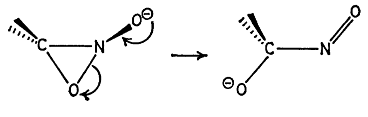
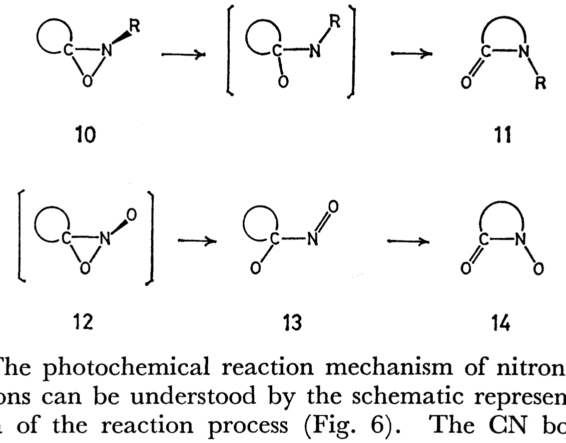


Fig. 6. Schematic representation of the photochemical process of alkanenitronate anions to form hydroxamic acids.

The most clear-cut finding is the unstable property of the *O*-oxaziridine. In the photochemical **3**→**5** process, the oxaziridine, **4**, is an intermediate.[3] The difference in stability between III and VI originates from the difference in their electronic structures. In the case of III, the electron migration occurs very easily to give the stable structure IV, while this type of electron migration is not expected in the oxaziridine, VI.

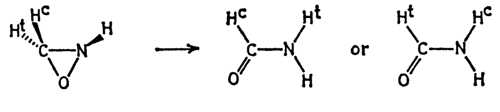


In the photochemical isomerization of cyclic oxaziridines into amides, **10**→**11**, an alkyl migration after the N–O bond cleavage has been proposed.[9] This mechanism is not applied to the present system, however, since the bridged structure, **12**, is a transient species. The ionic mechanism, in which **13** is an intermediate, is more appropriate for the present system. The alkyl migration, **13**→**14**, involved in this step is similar to the benzilic acid rearrangement[10] in an alkaline solution.



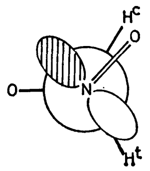
The photochemical reaction mechanism of nitronate anions can be understood by the schematic representation of the reaction process (Fig. 6). The CN bond rotation and the oxygen migration occur from the $\pi\rightarrow\pi^*$ excited state. The transition from the excited state to the ground state occurs near the diradical structure (XI), and the stable anion (IV) is produced very easily. The oxaziridine is not an intermediate in this step. The alkyl migration requires only a small activation energy to form the final reaction product.

Oliveros *et al.*[9] have well explained the regioselectivity observed in the **8**→**9** reaction on the basis of theoretical calculations for the model system, **15**→**16**.

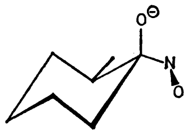


15 16a 16b

Their results indicated that the CH bond in the *cis* position with respect to the N–H hydrogen atom breaks easier than that in the *trans* position. In the case of nitronate anions, the nitroso compound, **13**, is an intermediate, and the regioselectivity observed in the **6**→**7** reaction may be explained by the selectivity expected in the **13**→**14** reaction. The model calculation for the IV→Va and IV→Vb processes suggested that the migration of the *trans* alkyl group is preferable to that of the *cis* one (Fig. 5). In the IV→V step, the hydrogen atom bearing a pair of electrons migrates to the nitrogen atom, and the interaction between the C–H bond and the N=O *anti*-bonding π orbital is very important. This stereoelectronic effect is why the H^{t} hydrogen atom migrates more



easily than the H^{c} atom. If the XII conformation, in which the steric interaction between the N=O oxygen atom and the ring substituent is minimized, is assumed to hold for the anion derived from **6**, the present model calculation predicts the formation of **7**, which is observed experimentally.



XII

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