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MO Studies on the Gas-Phase Reaction of Dypnone Oxide with Chloride Ion[†]

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The MNDO calculations were performed in order to investigate the gas-phase reaction mechanism of 2-propene-1-ol oxide, as a model compound of dypnone oxide(1,3-diphenyl-2-butene-1-one oxide) with the chloride ion. Optimized geometries and heats of formation for two probable concerted pathways, CHO and H migration, were determined and their activation energies were obtained. MO results show that although the formyl migration is thermodynamically more favorable than the hydride migration, the latter kinetically predominates over the formyl migration, which is contrary to the established migrating preferences. It is concluded that the hydride migratory propensity is catalyzed by the chloride ion by reducing the capability of the carbonyl π bond to participate in the migration.

Introduction

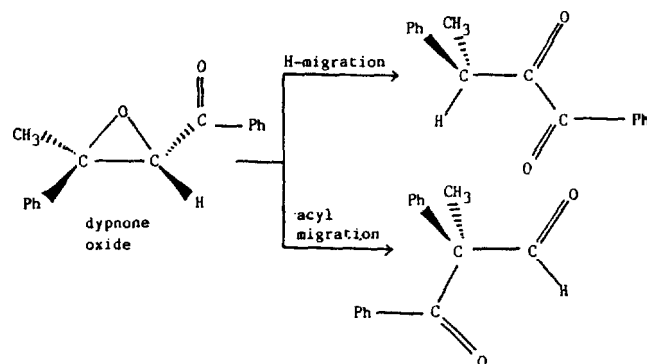
The acid-catalyzed ring-opening reactions of various epoxide derivatives have been a subject of numerous experimental and theoretical investigations.¹ The migratory propensity of the carbonyl group was first established by House in a series of mechanistic papers² and this intramolecular carbonyl group migration was reported with epoxy ketones, and so on.

Recently experimental studies on the Lewis acid catalyzed reaction of 1,3-diphenyl-2-butene-1-one oxides(dypnone oxides) were reported by Bach, *et al.*³ They suggested that the reaction mechanism involving the intramolecular migration as in scheme 1. The major findings were that while protic acids and mild Lewis acids readily induced the carbonyl group migration, nucleophilic Lewis acids led to the hydride migration.

The theoretical investigations of the chemical reaction mechanism must be attained from the determination of the transition state(TS) structure. Recently various MO theoretical methods to determine the TS structure have been developed and successfully applied to various organic reaction systems. Our efforts in this work will be directed toward establishing the migrating nature of the substituents in the ring-opening reaction of the epoxide by MO theoretical studies.

Calculation

In order to reduce the complexity of the molecular structure of the substrate, we chose the simplest reaction of 2-propene-1-ol oxide with the chloride ion as a model reaction. The calculations were carried out by the MNDO method.⁴ Ground state geometries of the reactants were optimized starting from the standard geometries. Transition states were



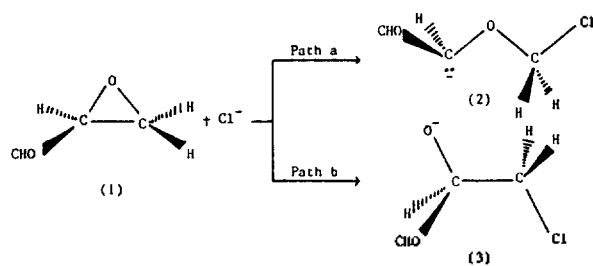
[†]Determination of Reactivity by MO Theory (Part 42).

found by the usual reaction coordinate method⁵ and were confirmed by checking the near-zero gradient norm and one negative eigenvalue in the diagonalized Hessian matrix.⁶

Results and Discussion

Optimized geometric parameters for 2-propene-1-ol oxide are summarized in Table 1 and numbering of atoms are given in Figure 1. This substrate may be attacked at either C₁ and C₂. Many experimental studies have shown that the substitution of the free epoxide under the neutral conditions usually involves an S_N2 mechanism⁷ in which the ambident substrate is attacked at the less sterically hindered carbon, and stereospecifically with inversion at that carbon. Therefore the chloride ion will attack at the C₂ atom. The positively developed charge on C₂ also indicates that C₂-attack has an advantage over C₁-attack by the chloride ion. The reason for the small negative charge on the C₂ atom, in spite of the electron-withdrawal by the CHO group, is that a little larger electron-withdrawing ability of the O₃ atom in the epoxide ring operates in the opposite direction. Moreover the fact that value of bond order between atoms C and O is larger in C₁-O₃ than in C₂-O₃ shows that the C₂-O₃ cleavage, followed by the attack of the Cl⁻ ion at C₂, might be more feasible than the C₁-O₃ cleavage.

In competition with the C₂-O₃ cleavage, the backside attack of Cl⁻ toward C₂ may also lead to the C₁-C₂ cleavage as in scheme 2.



Scheme 2

Correspondingly MNDO results show that attacking through path (a) and path (b), respectively, causes the C-C and the C-O bond cleavage and that the heat of formation for the intermediate (2) produced by the C-C bond cleavage is smaller than that for the intermediate (3). This is because the mesomerically electron-withdrawing CHO group stabilizes the negative charge in the structure (3).

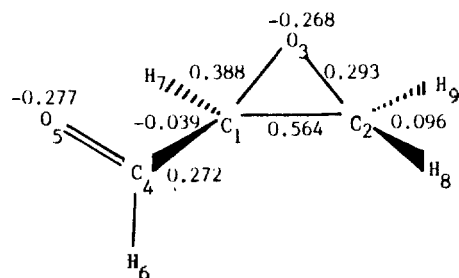
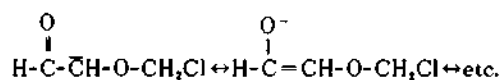


Figure 1. Atomic charges and bond orders of 2-propene-1-ol oxide.

Table 1. The MNDO Geometries of 2-propene-1-ol Oxide

| bond length(Å) | bond angle(deg.) | dihedral angle(deg.) |
|-------------------------------------|--|---|
| C ₁ C ₂ 1.519 | C ₂ C ₁ C ₄ 125.0 | O ₃ C ₂ C ₁ H ₁ 100.3 |
| C ₁ O ₃ 1.421 | C ₂ C ₁ C ₃ 120.0 | O ₃ C ₂ C ₁ C ₄ 259.3 |
| C ₁ C ₄ 1.518 | C ₁ C ₂ H ₈ 124.6 | C ₂ C ₁ C ₄ O ₃ 261.5 |
| C ₂ O ₃ 1.413 | C ₁ C ₂ H ₉ 123.9 | C ₂ C ₁ C ₄ H ₆ 83.1 |
| C ₄ O ₃ 1.220 | C ₁ C ₄ H ₆ 115.9 | |
| | C ₁ C ₄ O ₃ 122.2 | |

Table 2. Heats of Formation for the Various Species Involved in the Reaction of Epoxide with Cl⁻ in the Unit of kcal/mol

| (1) | (2) | (3) | TS(2) | TS(3) | E _a (a) | E _a (b) | |
|-----------------|---------|---------|---------|---------|--------------------|--------------------|-------|
| R = H | -99.69 | -104.36 | -99.56 | -87.27 | -76.99 | 12.42 | 22.70 |
| CH ₃ | -112.94 | -119.04 | -112.87 | -102.26 | -89.84 | 10.68 | 23.10 |

Table 3. The MNDO Geometries of the Intermediate (3) and the TS(3)*

| bond length (Å) | bond angle (deg.) | dihedral angle (deg.) | charge |
|-------------------------------------|--|---|-----------------------|
| TS(3): | | | |
| C ₁ C ₂ 1.506 | C ₂ C ₁ C ₄ 120.4 | H ₉ C ₂ C ₁ C ₄ 172.2 | C ₁ 0.693 |
| C ₁ O ₃ 1.363 | C ₂ C ₁ H ₁ 116.2 | H ₉ C ₂ C ₁ H ₁ 38.1 | C ₂ 0.322 |
| C ₁ C ₄ 1.533 | C ₁ C ₂ H ₈ 119.2 | H ₉ C ₂ C ₁ O ₃ 285.6 | O ₃ -0.643 |
| C ₂ O ₃ 1.800 | C ₁ C ₂ H ₉ 118.8 | XC ₁ C ₂ H ₈ ** 149.8 | C ₄ 0.270 |
| C ₄ O ₃ 1.244 | C ₁ C ₄ H ₆ 115.5 | XC ₁ C ₂ H ₈ 0.0 | O ₃ -0.345 |
| C ₂ Cl 2.120 | C ₁ C ₄ O ₃ 125.0 | XC ₁ C ₂ Cl 254.7 | Cl -0.737 |
| | C ₁ C ₂ Cl 112.6 | | |
| (3): | | | |
| C ₁ C ₂ 1.591 | C ₂ C ₁ C ₄ 110.0 | H ₉ C ₂ C ₁ C ₄ 180.0 | C ₁ 0.267 |
| C ₁ O ₃ 1.298 | C ₂ C ₁ H ₁ 104.0 | H ₉ C ₂ C ₁ H ₁ 69.1 | C ₂ 0.101 |
| C ₁ C ₄ 1.570 | C ₁ C ₂ C ₄ 113.4 | H ₉ C ₂ C ₁ O ₃ 305.1 | O ₃ -0.704 |
| C ₄ O ₃ 1.226 | C ₁ C ₂ H ₈ 111.1 | XC ₁ C ₂ H ₈ 123.7 | C ₄ 0.217 |
| C ₂ Cl 1.842 | C ₄ C ₃ H ₆ 116.7 | XC ₁ C ₂ H ₈ 0.0 | O ₃ -0.363 |
| | C ₁ C ₄ O ₃ 125.5 | XC ₁ C ₂ Cl 243.0 | C ₁ -0.350 |
| | C ₁ C ₂ Cl 115.1 | | |

* Numbering of atoms is the same as in Figure 1. ** X refers to the dummy atom, normal to the C₁-C₂ bond.

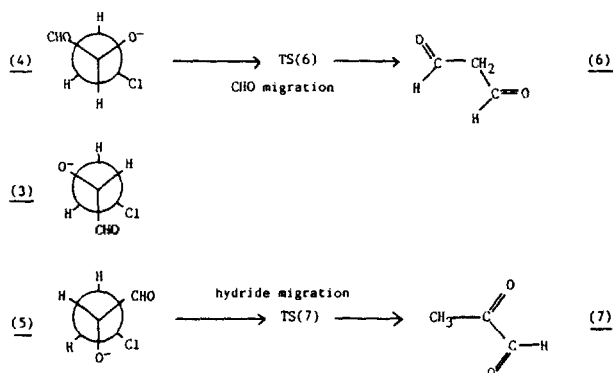
The heat of formation calculated for the TS(2) and (3) are -87.23 and -76.99 kcal/mol, respectively, and the activation barrier for path (a) is lower than that for path (b) by 10.28 kcal/mol. These results are summarized in Table 2.

Again on replacing the hydrogen atom attached to the C₂ atom with the electron-donating CH₃ group, the activation energy for path (a), E_a(a), is obtained to be reduced by 1.74 kcal/mol. From this result, we confirm that the direction of the bond cleavage is dependent on the electrical property of substituents.

Optimized geometrical parameters for the intermediate (3) and the TS(3) are summarized in Table 3. From Figure 1 and Table 3, we find that the positive charge on C₂ increases in the TS(3) but subsequently decreases in the structure (3). For the O₃ atom, there is a fairly large increase in the negative charge in the TS(3) and a little increase in the structure (3).

This means that in the transition state the C₂-O₃ bond cleavage precedes the C₂-Cl bond formation. That is, it appears that the cleavage of the C₂-O₃ bond rather than the attack of the Cl⁻ ion, might have a greater influence on the ring-opening reaction of the epoxide and therefore that the catalytic metallation and protonation of the oxygen atom in the epoxide ring by the Lewis acids and the protic acids respectively give an exclusive C₂-O₃ bond cleavage. In this light, we discuss the migrating propensity of substituents on the assumption that the attack of Cl⁻ leads to the exclusive C-O bond cleavage.

Since the migrating group is antiperiplanar to the leaving group in the migrating step,⁸ the intermediate (3) must carry the internal rotation as in scheme 3.



Scheme 3

Two kinds of migration are possible; one is the acyl(in this work, formyl) group migration from the intermediate (4), and the other is the hydride migration from (5). Rotational barriers obtained from heats of formation for conformers (4) and (5) are 0.37 and 2.8 kcal/mol, respectively, resulting in stabilizing the conformer (4) by the amount of 2.4 kcal/mol. In this calculation, the carbonyl(C=O) bond is oriented upward from the paper and this spatial arrangement is assumed to be retained during rotation.

Hartree-Fock energy can be divided into one-electronic term($2 \Sigma \epsilon_i$) and two-electronic(steric) term($V_{NN} - V_{ee}$).⁹ These energy components for the rotational conformers are summarized in Table 4. Also, Table 4 shows that both energy components favor the conformer (4) over the conformer (5), with somewhat larger contribution of the steric term.

If the ratio of the products, (6) and (7), produced from in-

Table 4. Energy Components for the Rotational Conformers (3)-(5)

| | (3) | (4) | (5) |
|----------------------------|---------|---------|---------|
| ΔH_f (kcal/mol) | -99.56 | -99.19 | -96.74 |
| $2 \Sigma \epsilon_i$ (eV) | -519.09 | -518.39 | -517.68 |
| $V_{NN} - V_{ee}$ (eV) | 920.92 | 921.61 | 923.21 |

terconverting species depends on the relative isomeric populations in the ground state, (4) and (5), the main product is given by the formyl migration. Heats of formation for the TS(6) and the TS(7) are calculated as -63.9 and -66.7 kcal/mol respectively and hence their corresponding activation energies are obtained as 35.3 and 30.0 kcal/mol. If the activation energies of interconverting species are large compared to the barrier to interconversion, the ratio of the products from the two species depends only on the difference in the energies of the respective transition states from the two species according to the Curtin-Hammett principle.¹⁰ Therefore the Curtin-Hammett principle is applicable to this situation and so the main product is given as the product (7) passing through the TS(7) of the lower activation energy. Optimized geometries for these transition states are given in Table 5 and their formal atomic charges and the coefficients of the highest occupied MO(HOMO) in Figure 2.

Table 5 shows that the coefficients of C₂ is larger than that of C₁ and the positive charge at C₁ is larger than that at C₂ both in the TS(6) and in the TS(7). From these, we confirm that the hydride and the CHO group migrate significantly from C₁ and C₂ in each transition state. Also, results show that the bond cleavage of C₂-Cl is more advanced in the TS(7) and, consequently, change in charges and coefficients at the positions concerned are also larger in the TS(7) than in the TS(6). This means that the hydride migration is more effective than formyl migration but that this involves the early transition state, leading to the lower activation energy.

In most cases the carbonyl migration predominates over the hydrogen migration, with the migrating preferences of carbonyl > alkyl > hydrogen.¹¹ But our MNDO result is contrary to this established migrating trend.

Table 5. The MNDO Geometries of the TS(6) and (7)

| structure | bond length (Å) | bond angle (deg.) | dihedral angle (deg.) | |
|-------------------------------|-------------------------------|-------------------|--|---|
| TS(6) | C ₁ C ₂ | 1.493 | C ₁ C ₂ C ₃ , 68.8 | X ₂ C ₁ C ₂ Cl 293.1 |
| | C ₁ C ₃ | 2.157 | C ₁ C ₂ C ₃ , 64.6 | X ₁ C ₁ C ₂ H ₈ 189.9 |
| | C ₂ C ₃ | 2.091 | C ₁ C ₂ O ₄ , 126.3 | X ₂ C ₁ C ₂ H ₆ , 39.4 |
| | C ₁ O ₄ | 1.239 | C ₁ C ₂ Cl 107.2 | X ₂ C ₁ C ₂ O ₃ , 119.8 |
| | | | | X ₁ C ₁ C ₂ O ₄ , 162.7 |
| | C ₂ Cl | 2.009 | C ₁ C ₂ H ₈ , 118.1 | C ₁ C ₂ C ₃ H ₄ , 98.3 |
| | | | C ₁ C ₂ H ₆ , 119.5 | C ₂ C ₁ C ₃ H ₈ , 253.6 |
| ΔH_f : -63.9 kcal/mol | | | | |
| TS(7) | C ₁ C ₂ | 1.491 | C ₁ C ₂ H ₈ , 110.5 | X ₂ C ₁ C ₂ H ₈ , 326.9 |
| | C ₁ H ₃ | 1.861 | C ₁ C ₂ H ₈ , 118.3 | X ₂ C ₁ C ₂ O ₃ , 161.9 |
| | C ₁ C ₃ | 1.537 | C ₁ C ₂ H ₈ , 118.8 | X ₂ C ₁ C ₂ H ₈ , 192.6 |
| | C ₂ H ₃ | 1.110 | C ₁ C ₂ Cl 110.2 | X ₂ C ₁ C ₂ Cl 298.2 |
| | C ₂ Cl | 2.072 | C ₁ C ₂ H ₈ , 45.5 | X ₂ C ₁ C ₂ H ₈ , 40.6 |
| | | | C ₁ C ₂ C ₃ , 116.9 | X ₁ C ₂ C ₁ O ₄ , 125.1 |
| | ΔH_f : -66.7 kcal/mol | | | |

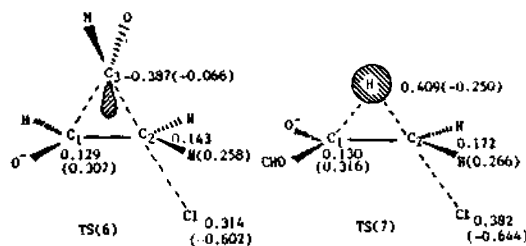


Figure 2. Coefficients of HOMO and atomic charges(in parentheses) for the TS(6) and the TS(7).

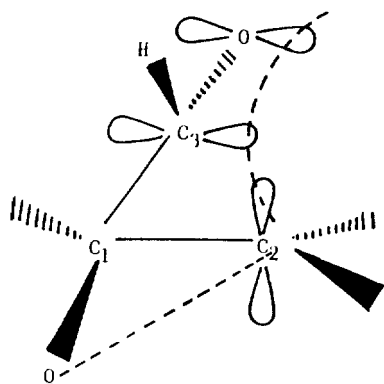


Figure 3. Homoallylic participation of the carbonyl bond with the p orbital at the C_2 atom.

Bach, *et al.*³ proposed for this preference of the carbonyl migration that the Walsh orbitals of the cyclopropyl ring provides a stabilizing influence on the transition state as in Figure 3. The overall concepts involved are quite analogous to those involved in the homoallylic neighbouring group participation.¹² Thus nonnucleophilic protic acids and very mild Lewis acids must readily induce the carbonyl migration. But it is expected that nucleophilic Lewis acids or large concentrations of mild acids effect the hydride migration. We attribute this to a polarization of the carbonyl π bond toward oxygen which reduces the capability of this π bond to participate by complexing the carbonyl group with the Lewis acid. Thus the epoxide will exhibit competing hydride migration.

In our reaction system calculated in which the C_2 atom is already attacked by Cl^- in order to catalyze the C-O bond cleavage, the p orbital is developed to a small degree at the

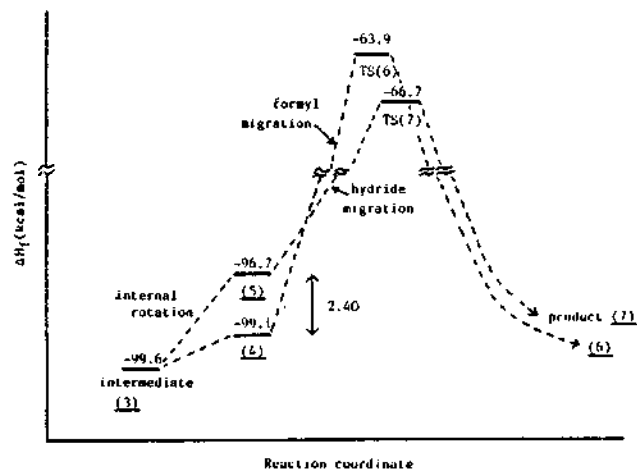


Figure 4. Schematic presentation of the thermodynamic energy profile.

C_2 atom so that the contribution of the orbital interaction, as mentioned above, will be reduced. This is attributed for the relative preference of the hydride migration over the CHO group migration.

The bond cleavage of C_2-Cl in the TS(7) is more advanced and therefore more polarizable than in the TS(6), which is the early transition state. That is when the epoxide is attacked by Cl^- as a nucleophile prior to migration, the epoxide exhibits the competing hydride migration to a relatively large extent.

Finally we summarize the results schematically in a thermodynamic energy profile in Figure 4.

Energy profile shows that while the ground state of the interconverting species is favorable for the formyl migration, the transition state favors the hydride migration. Since the barrier to interconversion is much small compared to the difference in the activation barriers in the migrating step, we conclude that this intramolecular migration is not thermodynamic-controlled but kinetic-controlled.

Acknowledgement. We wish to thank Ministry of Education for a grant of financial support for this work.

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