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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-al 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 papers[2] and this intramolecular carbonyl group migration was reported with epoxy ketones, and so on.

Scheme 1

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-al 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

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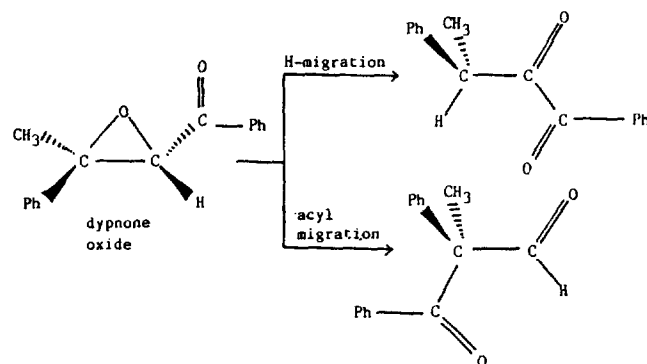
found by the usual reaction coordinate method[5] and were confirmed by checking the near–zero gradient norm and one negative eigenvalue in the diagonalized Hessian matrix.[6]

Results and Discussion

Optimized geometric parameters for 2–propene–1–al oxide are summarized in Table 1 and numbering of atoms are given in Figure 1. This substrate may be attacked at either C_1 and C_2. Many experimental studies have shown that the substitution of the free epoxide under the neutral conditions usually involves an S_N2 mechanism[7] 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 C_2 atom. The positively developed charge on C_2 also indicates that C_2–attack has an adventage over C_1–attack by the chloride ion. The reason for the small negative charge on the C_2 atom, inspite of the electron–withdrawal by the CHO group, is that a little larger electron–withdrawing ability of the O_3 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 C_1–O_3 than in C_2–O_3 shows that the C_2–O_3 cleavage, followed by the attack of the Cl^- ion at C_2, might be more feasible than the C_1–O_3 cleavage.

In competition with the C_2–O_3 cleavage, the backside attack of Cl^- toward C_2 may also lead to the C_1–C_2 cleavage as in scheme 2.
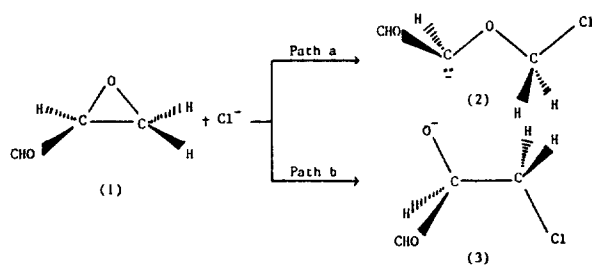
Scheme 2

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).
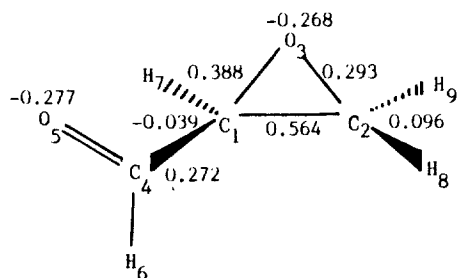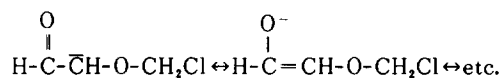
$$H\text{-}C\overset{\displaystyle O}{\underset{\displaystyle \|}{\text{-}}}\overline{C}H\text{-}O\text{-}CH_2Cl \leftrightarrow H\text{-}C\overset{\displaystyle O^-}{\underset{\displaystyle \|}{\text{-}}}= CH\text{-}O\text{-}CH_2Cl \leftrightarrow etc.$$

Figure 1. Atomic charges and bond orders of 2–propene–1–al oxide.

Table 1. The MNDO Geometries of 2–propene–1–al Oxide

bond length(Å)		bond angle(deg.)		dihedral angle(deg.)	
C_1C_2	1.519	$C_2C_1C_4$	125.0	$O_3C_2C_1H_7$	100.3
C_1O_3	1.421	$C_2C_1C_7$	120.0	$O_3C_2C_1C_4$	259.3
C_1C_4	1.518	$C_1C_2H_8$	124.6	$C_2C_1C_4O_5$	261.5
C_2O_3	1.413	$C_1C_2H_9$	123.9	$C_2C_1C_4H_6$	83.1
C_4O_5	1.220	$C_1C_4H_6$	115.9		
		$C_1C_4O_5$	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_1C_2	1.506	$C_2C_1C_4$	120.4	$H_9C_2C_1C_4$	172.2	C_1	0.693
C_1O_3	1.363	$C_2C_1H_7$	116.2	$H_9C_2C_1H_7$	38.1	C_2	0.322
C_1C_4	1.533	$C_1C_2H_8$	119.2	$H_9C_2C_1O_3$	285.6	O_3	−0.643
C_2O_3	1.800	$C_1C_2H_9$	118.8	$XC_2H_8^{**}$	149.8	C_4	0.270
C_4O_5	1.244	$C_1C_4H_6$	115.5	XC_2H_9	0.0	O_5	−0.345
C_2Cl	2.120	$C_1C_4O_5$	125.0	XC_1C_2Cl	254.7	Cl	−0.737
		C_1C_2Cl	112.6				
(3):							
C_1C_2	1.591	$C_2C_1C_4$	110.0	$H_9C_2C_1C_4$	180.0	C_1	0.267
C_1O_3	1.298	$C_2C_1H_7$	104.0	$H_9C_2C_1H_7$	69.1	C_2	0.101
C_1C_4	1.570	$C_1C_2C_8$	113.4	$H_9C_2C_1O_3$	305.1	O_3	−0.704
C_4O_5	1.226	$C_1C_2H_9$	111.1	XC_2H_8	123.7	C_4	0.217
C_2Cl	1.842	$C_4C_5H_6$	116.7	XC_2H_9	0.0	O_5	−0.363
		$C_1C_4O_5$	125.5	XC_1C_2Cl	243.0	C_1	−0.350
		C_1C_2Cl	115.1				

* Numbering of atoms is the same as in Figure 1. ** X refers to the dummy atom, normal to the C_1–C_2 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 C_2 atom with the electron–donating CH_3 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.

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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 C_2 increases in the TS(3) but subsequently decreases in the structure (3). For the O_3 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 C_2-O_3 bond cleavage precedes the C_2-Cl bond formation. That is, it appears that the cleavage of the C_2-O_3 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 C_2-O_3 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.
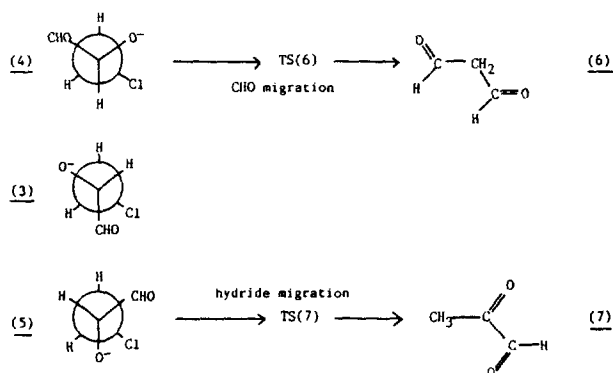
Scheme 3

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($2 \Sigma \varepsilon_i$) 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-

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–Hammet 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 C_2 is larger than that of C_1 and the positive charge at C_1 is larger than that at C_2 both in the TS(6) and in the TS(7). From these, we confirm that the hydride and the CHO group migrate significantly from C_1 and C_2 in each transition state. Also, results show that the bond cleavage of C_2-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) ΔH_f: −63.9 kcal/mol	C_1C_2 1.493	$C_1C_2C_3$ 68.8	$X_2C_1C_2Cl$ 293.1
	C_1C_3 2.157	$C_2C_1C_3$ 64.6	$X_2C_1C_2H_8$ 189.9
	C_2C_3 2.091	$C_2C_1O_6$ 126.3	$X_2C_1C_2H_9$ 39.4
	C_1O_6 1.239	C_1C_2Cl 107.2	$X_2C_1C_2O_3$ 119.8
			$X_1C_2C_1O_6$ 162.7
	C_2Cl 2.009	$C_1C_2H_8$ 118.1	$C_2C_1C_3H_4$ 98.3
		$C_1C_2H_9$ 119.5	$C_2C_1C_3H_5$ 253.6
TS(7) ΔH_f: −66.7 kcal/mol	C_1C_2 1.491	$C_1C_2H_9$ 110.5	$X_2C_1C_2H_8$ 326.9
	C_1H_3 1.861	$C_1C_2H_8$ 118.3	$X_2C_2C_1O_5$ 161.9
	C_1C_5 1.537	$C_1C_2H_3$ 118.8	$X_2C_1C_2H_9$ 192.6
	C_2H_3 1.110	C_1C_2Cl 110.2	$X_2C_1C_2Cl$ 298.2
	C_2Cl 2.072	$C_2C_1H_3$ 45.5	$X_2C_1C_2H_3$ 40.6
		$C_2C_1C_5$ 116.9	$X_1C_2C_1O_4$ 125.1

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

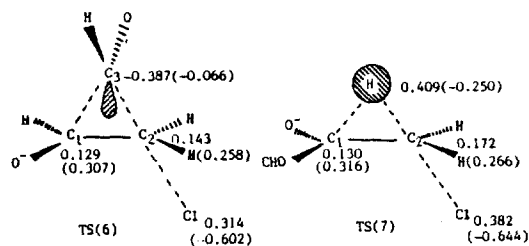|	(3)	(4)	(5)
ΔH_f (kcal/mol)	− 99.56	− 99.19	− 96.74
$2 \Sigma \varepsilon_i$ (eV)	− 519.09	− 518.39	− 517.68
$V_{NN}-V_{ee}$ (eV)	920.92	921.61	923.21

Figure 2. Coefficients of HOMO and atomic charges(in parentheses) for the TS(6) and the TS(7).
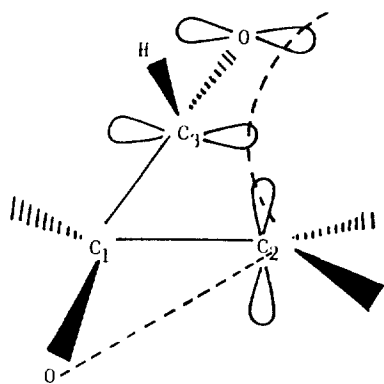
Figure 3. Homoallylic participation of the carbonyl bond with the p orbital at the C_2 atom.

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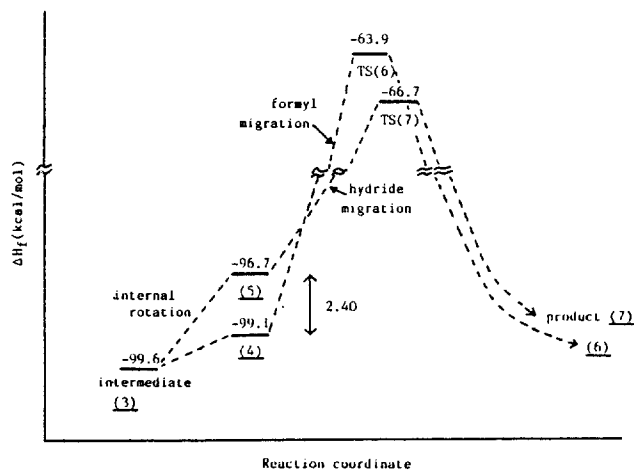
C_2 atom so that the contribution of the orbital interaction, as mentioned above, will be reduced. This is attributed for the relative preference of the hydride migration over the CHO group migration.

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.

Figure 4. Schematic presentation of the thermodynamic energy profile.

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