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# Theoretical Study of Activation of Oxirane by Bidentate Acids

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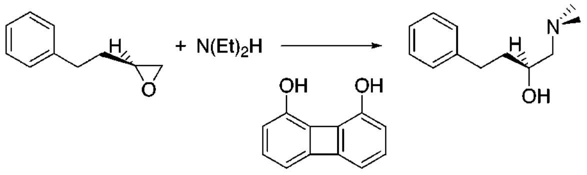
The reaction of oxirane with amines in the presence of some bidentate and monodentate Brønsted acids has been studied theoretically by taking some simplified reaction models. Acids have been shown to serve as temporary reservoirs of electronic charge during the reaction to strengthen the nucleophilicity of the substrate. The shift of electronic charges and enhancement of the nucleophilicity of oxirane have been represented by means of paired interaction orbitals and projected reactive orbitals. The reason the transition state appears at an earlier stage in the reaction catalyzed by 1,8-biphenylenediol relative to the reactions catalyzed by monodentate phenols and alcohols has been clarified.

## Introduction

Recently, the coordination chemistry of multidentate acids has attracted much attention, and their interesting features have been disclosed by several groups.[1,4−23] Hine and co-workers found that 1,8-biphenylenediol catalyzed the reaction of phenyl glycidyl ether with diethylamine[2,3] to a much higher extent than expected from the Brønsted correlation.[4d,e]



Wuest and his collaborators demonstrated that derivatives of 1,2-phenylenedimercury, such as dichloride,

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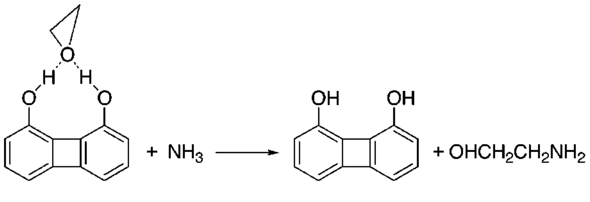
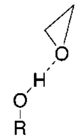
formed a doubly coordinated bimolecular adduct with carbonyl compounds.[5a] Ooi and Maruoka reported that a bidentate Lewis acid, (2,7-dimethyl-1,8-biphenylenedioxy)bis(dimethylaluminum), could enhance markedly the reactivity of carbonyl compounds toward tributylstannane, relative to monodentate Lewis acids.[6c] Kelly and co-workers disclosed that the Diels–Alder reactions of α,*β*-unsaturated ketones or aldehydes were highly accelerated in the presence of 4,5-dinitro-2,7-dipropyl-1,8-biphenylenediol.[7]

Undoubtedly, these intriguing experiments should be valuable for the design of new reagents based on the bidentate acids. Disappointedly, however, no report has provided any detailed analysis of the origin of activation of those basic substrates. In this sense, with regard to such reaction systems, it is of significance to perform theoretical studies to clarify the reaction paths and the causes of such remarkable increase in the reaction rates. Thus, we have carried out computational analysis of the 1:1 complex of oxirane and 1,8-biphenylenediol, **1**, and the reaction of **1** with ammonia, as a simplified model of the real system in the experiments reported by Hine.[4d,e]



**1**

To demonstrate the prominence of bidentate acids, similar analyses have been made on the complexes of oxirane and several monodentate acids, **2a–f**, and on catalyst-free oxirane.



**2**

| | |
|---|---|
| **2a** | R = Ph |
| **2b** | R = *p*-ClPh |
| **2c** | R = *p*-CNPh |
| **2d** | R = *p*-COHPh |
| **2e** | R = CH$_3$ |
| **2f** | R = H |

## Method of Calculations

Theoretical calculations were carried out by applying the Gaussian 94 program.[24] All of the geometrical parameters of the complexes and transition states for the reaction were determined by the density functional method of Becke's three parameters with Lee, Yang, and Parr's correlations (B3LYP).[25–27] The 6-31G** basis set was used to trace the path of the reaction between oxirane and ammonia in the presence of methanol as a model catalyst. The transition states were located at the B3LYP/6-31G* level of theory for the system with several other model catalysts, and the activation energies were estimated then by single-point calculations at the MP2/6-311++G** level. The orbital analysis was performed by utilizing the wave function obtained by the RHF/6-31G* calculations for the B3LYP-optimized structures.

## Results and Discussion

**Structures and Activation Energy.** It is known that oxirane and its derivatives undergo ring opening by an attack of a strong Lewis base.[28] Two mechanisms have been proposed, one being an S$_N$2-type mechanism with the inversion of conformation and the other being the

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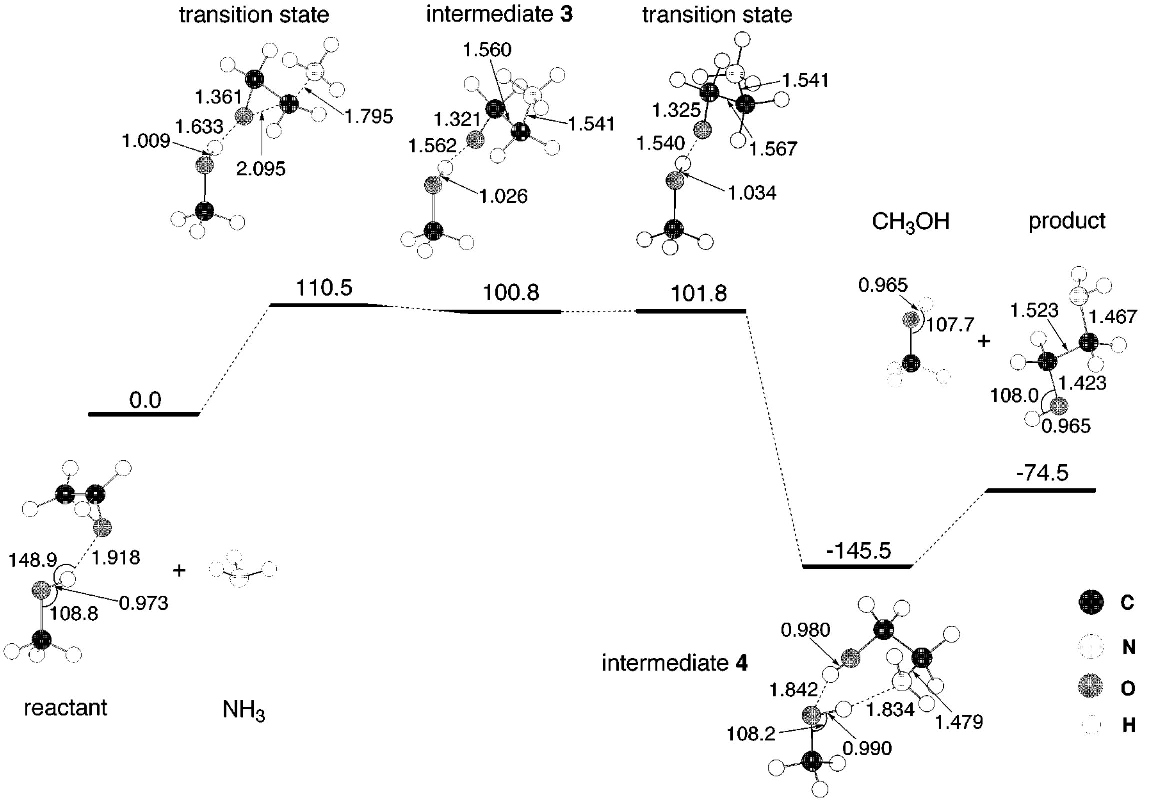

**Figure 1.** The energy change along the path for the reaction of oxirane with ammonia in the presence of methanol, derived from the B3LYP/6-31G** calculations.

mechanism that advocates the retention of conformation.[28b,d] We have carried out at first B3LYP/6-31G* calculations on a model reaction system, consisting of an oxirane molecule and an ammonia molecule. Though the transition state for the path with retention of conformation appeared to be stabilized by a hydrogen bond between the oxygen and one of the hydrogens in $NH_3$, it was shown that the activation barrier for the path with the inversion of conformation was lower by 38 kJ/mol. Thus, we examine only the path with the inversion of conformation in the present study.

Alcohols have been shown experimentally to accelerate the nucleophilic ring-opening reactions of oxiranes.[2] Thus, we have taken first a methanol molecule as a model catalyst to trace the reaction path by the B3LYP/6-31G** calculations. Figure 1 shows that methanol forms a stable 1:1 complex with oxirane. Then, ammonia attacks one of the C−O bonds of the oxirane to form an intermediate **3**. The barrier height is not so high. In **3**, the $NH_3$ unit has a large positive charge and the oxygen of the oxirane bears a large negative charge. From this polarized structure, rotation around the C−C bond takes place easily to allow one of the hydrogens in $NH_3$ to move onto the attached alcohol molecule, while the alcohol molecule transfers its hydrogen to the oxygen of the oxirane. The charge polarization has been neutralized in the intermediate **4**. Liberation of the alcohol molecule yields a ring-opened adduct of oxirane and ammonia as the product. The detailed mechanism has not yet been revealed experimentally, but the process shown in Figure 1 might also be possible in the reaction of phenyl glycidyl ether and diethylamine catalyzed by phenols.

Let us study next the roles of the catalysts. Figure 2 illustrates the structures of the 1:1 complex between oxirane and 1,8-biphenylenediol, **1**, and the complex between oxirane and phenol, **2a**, derived from the B3LYP/6-31G* calculations. In **1**, the oxygen of oxirane is located equidistant from the two phenolic hydrogens of the diol, having the oxirane ring perpendicular to the biphenylene framework. In **2a**, the oxirane ring is located also perpendicular to the phenyl ring. The O- - -H distance has been calculated to be 1.824 Å in **1** and 1.826 Å in **2a**, indicating that two species are bound by a normal hydrogen bond in these systems.

At the transition state of the reaction with ammonia, the C−N distance has been calculated to be 1.975 Å for **1**, which is considerably longer than that for **2a**, 1.856 Å. The oxirane ring is less distorted in the reaction of **1**. These calculations imply that the transition state appears at an earlier stage in the reaction catalyzed by 1,8-biphenylenediol, compared with the reaction catalyzed by phenol. As illustrated in Figure 2, the C−N bond is even shorter, 1.646 Å, and the oxirane ring is highly distorted at the transition state of the reaction between oxirane and ammonia in the absence of an acid. It is clear that the acid affects significantly the reaction profile.

We have also carried out the calculations on other species, **2b**−**f**. The calculated barrier heights for the reaction with ammonia are given in Table 1. It is seen that 1,8-biphenylenediol lowers the activation barrier of the reaction more effectively than phenols. The electron-attracting groups, −CN and −CHO, attached to the para position of phenol lower the activation barrier. Methanol is less effective, but accelerates the reaction. These results agree well with experimental observations.[4d,e] Though the difference in barrier height between an acid-catalyzed system and the reacting system without catalyst has been shown to be smaller in the MP2/6-

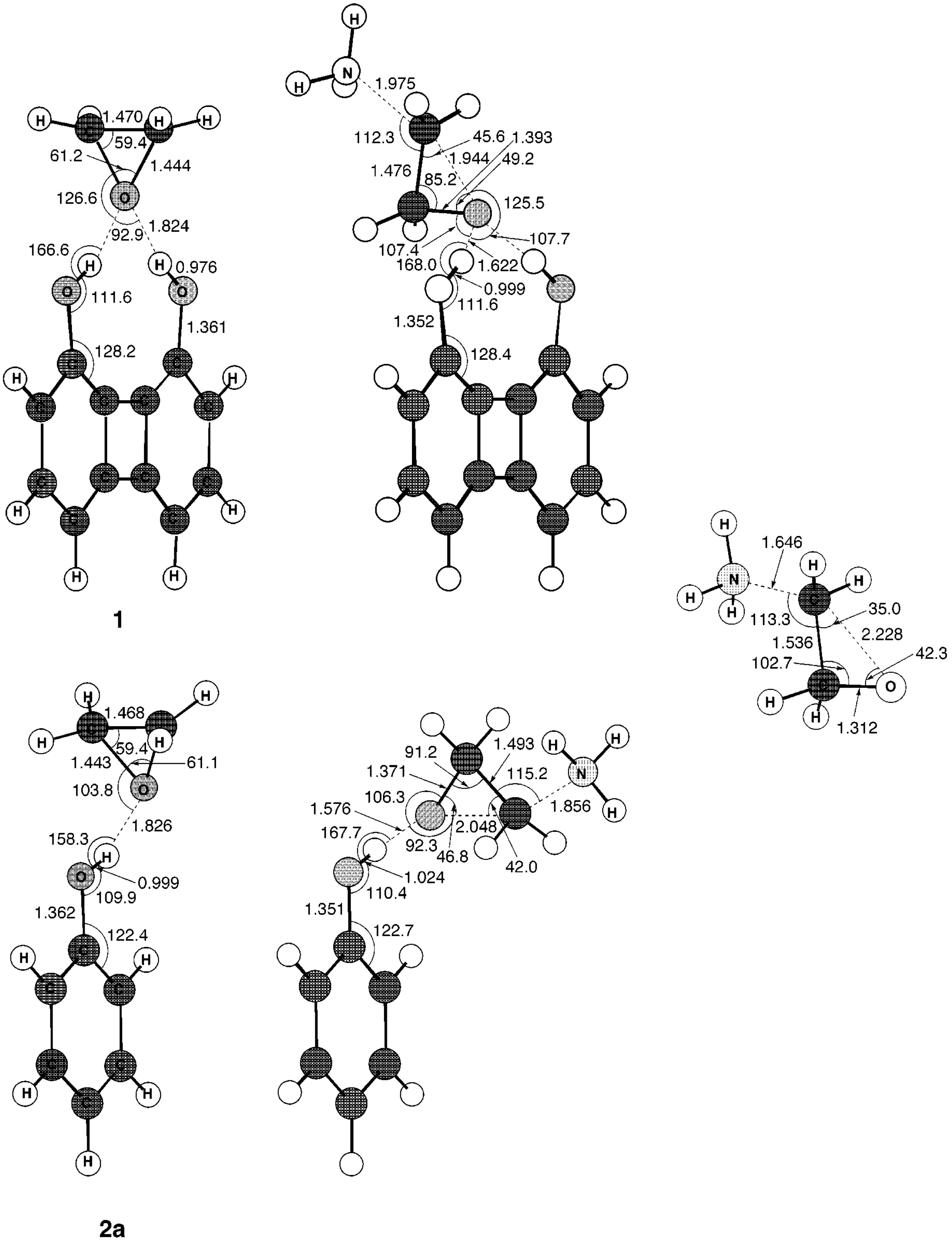

**Figure 2.** Stable structures of the 1:1 complexes of oxirane with 1,8-biphenylenediol (left top) and with phenol (left bottom) and the transition-state structures for the reaction of these complexes with ammonia (center). The transition-state structure of the reaction between oxirane and ammonia is shown for comparison (right).

311++G** level calculations compared with that in the B3LYP/6-31G* calculations, the calculated activation barrier for the reaction in the absence of acids is very high.

**Nucleophilicity of Oxirane.** It is attracting to investigate the reason 1,8-biphenylenediol catalyzes more effectively the reaction than phenols or alcohols do so. We first look at the interaction between oxirane and the acids, by utilizing the method of paired interaction orbitals.[29] In the frontier orbital scheme, one assumes from the beginning that the interaction is governed by

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[29] (a) Fujimoto, H.; Koga, N.; Fukui, K. *J. Am. Chem. Soc.* **1981**, *103*, 7452. (b) Fujimoto, H.; Koga, N.; Hataue, I. *J. Phys. Chem.* **1984**, *88*, 3539. (c) Fujimoto, H.; Yamasaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157. (d) Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578.

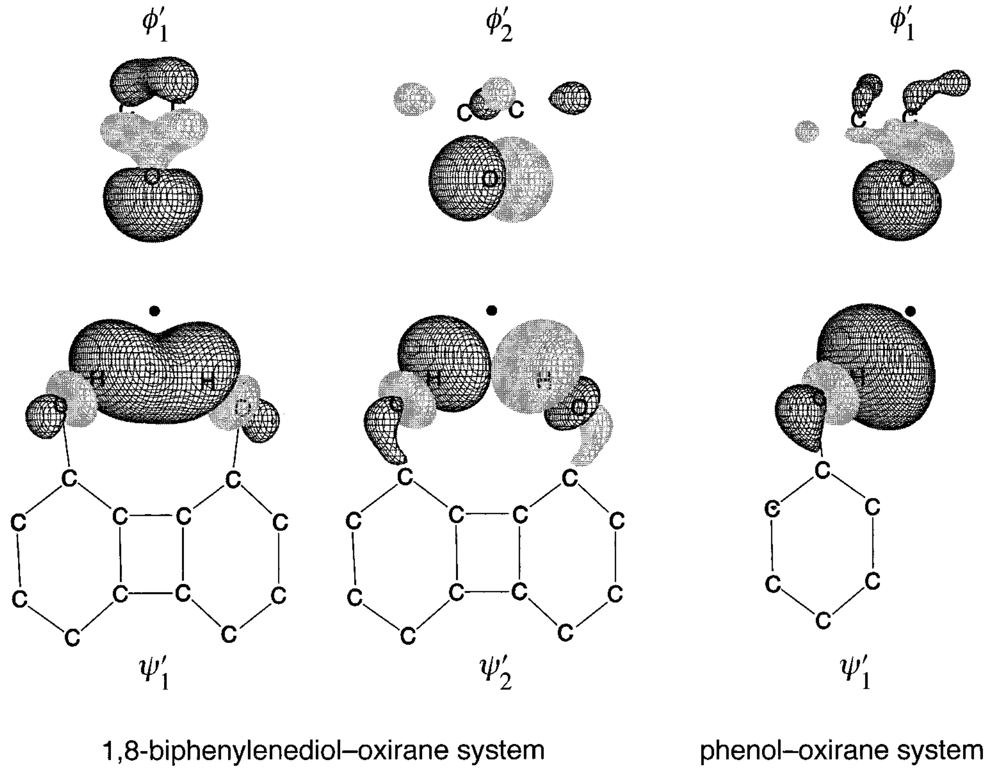


**Figure 3.** Interaction orbitals responsible for electron delocalization from the oxirane part to the acid part in the 1:1 complex of oxirane and an acid. The orbital $\phi'$s are given by the combination of the occupied MOs of the oxirane part, and $\psi'$s are given by the combination of the unoccupied MOs of the acid part. Two orbital pairs on the left-hand side are for the (oxirane + 1,8-biphenylenediol) system and a pair on the right-hand side is for the (oxirane + phenol) system.

**Table 1. Calculated Energy of the Complexes between Oxirane and Acid and of the Transition States (in au) and the Activation Energy for the Reaction with Ammonia (in kJ/mol)**

| species | complex | $NH_3$ | transition state | activation energy |
|---|---|---|---|---|
| **1** | −766.26854 | −56.54795 | −822.79413 | 58.7[a] |
| | −764.33485 | −56.41536 | −820.71819 | 84.0[b] |
| **2a** | −461.26524 | −56.54795 | −517.77774 | 93.1[a] |
| | −460.08606 | −56.41536 | −516.45751 | 115.3[b] |
| **2b** | −920.86167 | −56.54795 | −977.37649 | 87.0[a] |
| | −919.14581 | −56.41536 | −975.51863 | 111.7[b] |
| **2c** | −553.51264 | −56.54795 | −610.02959 | 81.4[a] |
| | −552.12706 | −56.41536 | −608.50124 | 108.1[b] |
| **2d** | −574.59416 | −56.54795 | −631.11052 | 82.9[a] |
| | −573.17075 | −56.41536 | −629.54464 | 108.9[b] |
| **2e** | −269.51290 | −56.54795 | −326.01974 | 107.9[a] |
| | −268.86154 | −56.41536 | −325.22709 | 130.8[b] |
| **2f** | −230.20742 | −56.54795 | −286.71366 | 109.5[a] |
| | −229.69116 | −56.41536 | −286.05563 | 133.6[b] |
| oxirane | −153.78626 | −56.54795 | −210.27228 | 162.6[a] |
| | −153.40557 | −56.41536 | −209.75913 | 162.3[b] |

[a] B3LYP/6-31G* calculations. [b] MP2/6-311++G**//B3LYP/6-31G* calculations.

the highest occupied (HO) and lowest unoccupied (LU) MOs. It may be difficult, however, to apply the scheme to compare the interactions in the systems that differ in size and structure. Here, we try to take the contributions of all the occupied and unoccupied MOs of the two fragments into account. For this purpose, we expand first the MOs of the system consisting of an oxirane molecule and an acid molecule in a linear combination of the MOs of the two species. We carry out next the unitary transformations of the fragment orbitals simultaneously within the occupied MO space of one fragment and within the unoccupied MO space of the other fragment, referring to the strengths of orbital interactions calculated from the wave function of the system that consists of an oxirane molecule and an acid molecule.[29] By this treatment, electron delocalization is represented compactly by a few pairs of the fragment interaction orbitals ($\phi'_f$; $\psi'_f$), including not only the combination of the highest occupied MO of the donor part and the lowest unoccupied MO of the acceptor part, but also all the occupied MOs of the former and all the unoccupied MOs of the latter. That is, the new orbital $\phi'_f$ is given by a linear combination of the occupied canonical MOs of the donor part, and the paired orbital $\psi'_f$ is given by a linear combination of the unoccupied canonical MOs of the acceptor part.

Figure 3 illustrates two pairs of interaction orbitals that represent donation of the oxirane lone pair of electrons to 1,8-biphenylenediol. Each of the orbitals $\phi'_1$ and $\phi'_2$ consists of the occupied MOs of the oxirane fragment, whereas each of the paired orbital $\psi'_1$ and $\psi'_2$ consists of the unoccupied MOs of the 1,8-biphenylenediol fragment. One sees that the orbitals $\psi'_1$ and $\psi'_2$ are localized completely on the two O−H bonds of the diol. The orbitals $\psi'_1$ and $\psi'_2$ overlap *in-phase* with the orbitals $\phi'_1$ and $\phi'_2$ for the lone pairs of electrons of oxirane, respectively. One pair is symmetric and the other is antisymmetric with respect to the $\sigma_v$ plane bisecting the biphenylene framework. By means of these two pairs of orbitals, the diol can accept the electronic charge from the oxygen, and the two hydrogen bonds are formed. The orbitals $\psi'_1$ and $\psi'_2$ are antibonding between the oxygens and the hydrogens in the diol, and accordingly, the O−H bonds are weakened upon the acceptance of electronic charge from the oxirane.

On the other hand, an unoccupied interaction orbital localized on the O−H bond of phenol participates in

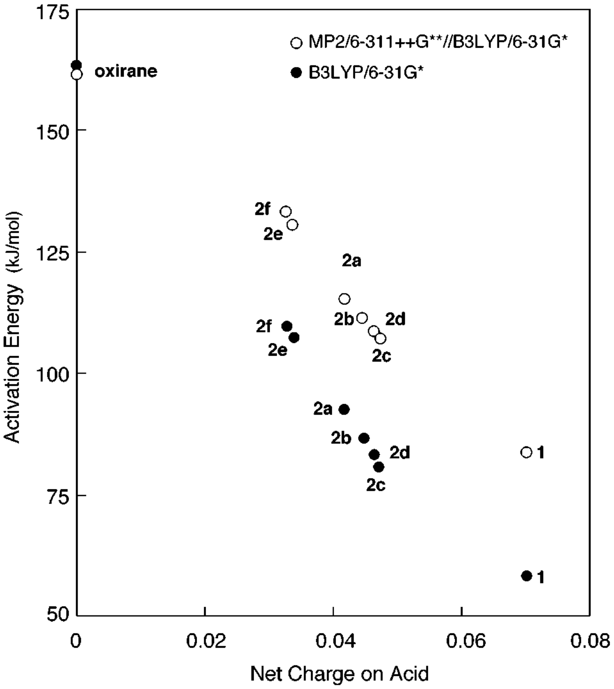
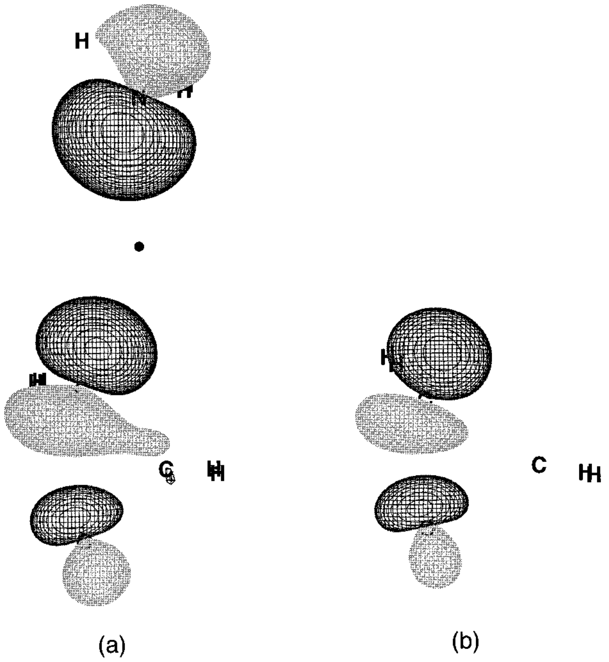


**Figure 4.** Relation between the calculated activation energy and the amount of electronic charge transferred from the oxirane part to the acid part.



(a) (b)

**Figure 5.** Pair of interaction orbitals that plays the dominant role in electron delocalization from the attacking ammonia to oxirane at the transition state (a) and the projected unoccupied reactive orbital of oxirane at the initial state (b).

electron acceptance in the oxirane−phenol complex, **2a**, as illustrated on the right-hand side of Figure 3. We have calculated the electron population shifted from the oxirane part to the acid part through the pairs of interaction orbitals for **1** and **2a**−**f**.[30,31] The relation between the calculated activation energy and the electron population transferred from the oxirane to the acids is illustrated in Figure 4. It is suggested here that the acids activate oxirane by removing its electron population.

The removal of electronic charge may enhance nucleophilicity of the oxirane ring. To see more directly the effect of the acid, we have applied the orbital analysis adopted above to the interaction between an ammonia molecule and an oxirane molecule coordinated to an acid. In this case, one fragment is the attacking ammonia and the other fragment is the combined system of an oxirane molecule and an acid molecule. Figure 5 illustrates the pair of orbitals that plays the dominant role in electron delocalization from the ammonia to **1** at the transition state. The biphenylene framework has been omitted for simplicity of presentation. The orbital of the oxirane−biphenylenediol part is seen to be localized completely on the C−O bond under attack, being given by a linear combination of the unoccupied canonical MOs of the complex **1**. The MOs that originate mainly from the LUMO and the next LUMO of oxirane are the dominant components of the interaction orbital. We have also obtained the interaction orbitals for other systems **2a**−**f** and oxirane without an acid. They look very similar to that given in Figure 5.

The transition state appears at an earlier stage in the reaction catalyzed by 1,8-biphenylenediol, compared with the reactions catalyzed by monodentate acids. The structure of the oxirane ring is considerably different at the transition states of these reactions. Then, to make a comparison between these systems meaningful, we have derived the unoccupied reactive orbital for each oxirane−acid system in its stable structure without an attacking ammonia. The interaction orbital of the oxirane part is given by a linear combination of the unoccupied MOs and, therefore, is expressed in terms of the atomic orbitals (AO). We have taken the carbon and oxygen AO components of the interaction orbital as the reference orbital function and have projected this function, fixing the signs and magnitudes of the coefficients, onto the unoccupied MO subspace in each of the complexes **1** and **2a**−**f**.[32] In this manner, we can trace the origin of the interaction orbital at the transition state to the oxirane-acid systems in the initial reactant state. As shown on the right-hand side of Figure 5 for **1**, the projected reactive orbital bears a close resemblance to the interaction orbital obtained above, being localized well on the C−O bond to be attacked.

The projected reactive orbital is given by a linear combination of the unoccupied MOs (LCMO) of the oxirane-acid system, and therefore, nucleophilicity of the C−O bond can now be estimated by taking the sum of the orbital energies $\epsilon_j$ of the constituent MOs, weighted by the square of the LCMO coefficients, $d_j$.

$$\lambda_{\text{unoc}} = \Big(\sum_{j}^{\text{unoc}} d_j^2\, \epsilon_j\Big)\Big/\Big(\sum_{j}^{\text{unoc}} d_j^2\Big)$$

Here, a smaller $\lambda_{\text{unoc}}$ value indicates that the oxirane has the unoccupied reactive orbital located lower in energy. The relation between the calculated activation energy and the $\lambda_{\text{unoc}}$ value of the C−O bond is illustrated

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(30) Mulliken overlap population analysis based on transformed fragment orbitals.

(31) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

(32) (a) Fujimoto, H.; Mizutani, Y.; Iwase, K. *J. Phys. Chem.* **1986**, *90*, 2768. (b) Fujimoto, H.; Satoh, S. *J. Phys. Chem.* **1994**, *98*, 1436.

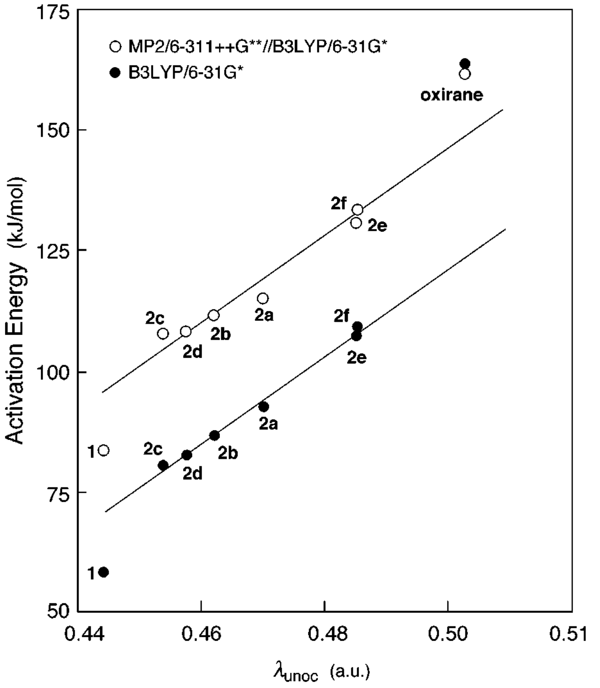

**Figure 6.** Relation between the calculated activation energy and the theoretically estimated nucleophilicity of the C−O bond in oxirane.

in Figure 6. It is seen that the theoretically estimated nucleophilicity gives a nice correlation with the activation energy for the monodentate catalysts, phenols and methanol. It is noted that the C−O bond of oxirane coordinated to 1,8-biphenylenediol gives the unoccupied reactive orbital which is located considerably lower in energy, compared with those of phenols. This means clearly that the coordination of 1,8-biphenylenediol enhances nucleophilicity of the oxirane more effectively than monodentate acids do so.

The electronic charge shifted from the attacking ammonia is 0.255 at the transition state of the reaction of **1**, whereas it is 0.336 in the reaction of **2a** in the present calculation.[33] A larger amount of charge has been transferred at the transition state of the reaction of **2a**. It is obvious that this result is ascribed to the stronger interaction between **2a** and an attacking ammonia at the transition state. To see the effect of the acids, we have frozen the structure of the acid part and the position of the oxygen in oxirane to those at the transition state and have optimized other geometrical parameters for several selected values of the C−N bond length. It has been shown that electron delocalization is more effective in the reaction of **1**. At $r_{\mathrm{C-N}} = 2.0$ Å, for instance, the charge shifted from ammonia to **1** has been calculated to be 0.230, while it is 0.192 in **2a**. This is in line with the discussion made above that nucleophilicity of the C−O bond in oxirane has been enhanced to a greater extent in **1**.

One sees in Figure 6 that the activation energy is considerably lower than that expected from the $\lambda_{\mathrm{unoc}}$ value in the reaction of **1**. It is suggested that a part of the electronic charge shifted from the attacking ammonia to the oxirane should be transferred further onto the acid, through the interaction orbitals that are very similar to those presented in Figure 3. This should bring an additional stabilization to the system, by reducing the overlap repulsion between the oxirane occupied orbitals and the lone pair of electrons of the attacking ammonia. It is supposed here that the charge shift in the reaction should be proportional to that in the initial oxirane-acid complexes, **1** and **2a**−**f**, presented in Figure 2. It is not straightforward, however, to show this by numbers. The transition state appears at an earlier stage in the reaction catalyzed by 1,8-biphenylenediol and the amount of charge shifted from the attacking ammonia is smaller, compared with the reaction catalyzed by phenol, as seen above.

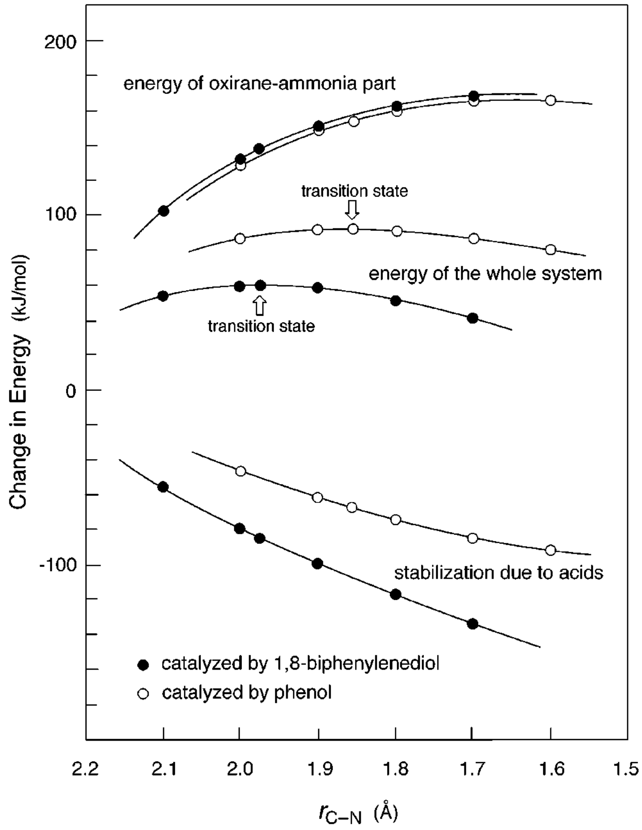

**Figure 7.** Changes in the energy of an oxirane−ammonia reacting system and those in the presence of an acid. The structure of the acid part and the location of the oxygen in oxirane were frozen to those at the transition state, and other variables were optimized for the given C−N distances.

To show the effect of acids on the strength of charge shift, we have carried out above the calculations on the reacting system by freezing the structure of the acid part and the position of the oxygen in oxirane to those at the transition state and by optimizing the oxirane and ammonia parts for some given values of the C−N bond length. These calculations may provide the energy change of the reacting system along an approximate reaction coordinate around the transition state. We have also carried out calculations on the system composed only of an oxirane molecule and an ammonia molecule with the same geometry as that in the acid-catalyzed system. By subtracting the energy of the oxirane-ammonia system from the energy of the whole system, we can estimate the stabilization brought about by adding the acids. Figure 7 illustrates that the ammonia−oxirane system

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[33] Natural population analysis (NPA), see: (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

is destabilized with the progress of the reaction to reach the transition state, which is similar to the one depicted in Figure 2. The oxirane–ammonia part is almost the same in structure both in the biphenylenediol-catalyzed case and in the phenol-catalyzed case for a given C–N distance. It should be noted here that the stabilization arising from the presence of an acid does not remain constant, but increases with the progress of the reaction. Since the structure of the acid part and the lengths of the O- - -H bonds were frozen, this result indicates that the acid relaxes the reacting system by housing temporarily the electronic charge of the oxirane part on its orbitals. The activation barrier should be lowered and the transition state should appear at an earlier stage on the reaction path. It is seen in Figure 7 that the stabilization increases more rapidly in **1** than in **2a**. Thus, the activation barrier is lower and the transition state comes earlier in the reaction of **1**. The reason the reaction of oxirane in the absence of catalyst costs such a high activation energy is also understandable in the same context.

## Conclusion

We have studied the ring-opening reaction of oxirane in the presence of some acids by means of the density functional and molecular orbital theoretical calculations and by applying the method of paired interaction orbitals. The acids have been shown to have two effects. One is to enhance nucleophilicity of the C–O bond by removing the electronic charge from oxirane before the attack of a nucleophile. A nice correlation has been found to exist between the electronic charge shifted from the oxirane part to an acid through paired interaction orbitals and the calculated activation energy. A measure of nucleophilicity evaluated theoretically shows a good linear correlation with the calculated values of activation energy for phenols and alcohols. Our model bidentate acid catalyst, 1,8-biphenylenediol, has been shown to enhance the nucleophilicity of a C–O bond in oxirane to a higher extent, compared with monodentate acids. The second effect of acids is to relax the reacting system by lifting the electronic charge that has been shifted from the attacking nucleophile to the oxirane ring further onto the acid framework. That is, acids serve as temporary reservoirs of electronic charge during the reaction to maintain high nucleophilicity of oxirane and to reduce overlap repulsion between the substrate and the attacking nucleophile. The stabilization has been demonstrated to increase with the progress of the reaction. Thus, the coordination of an acid to oxirane makes the activation energy lower and, more importantly, brings the transition state earlier on the reaction path. Bidentate acids remove the electronic charge by utilizing two pairs of orbitals and, accordingly, activate the reacting system more efficiently than monodentate phenols.

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**Supporting Information Available:** Tables listing geometries and energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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