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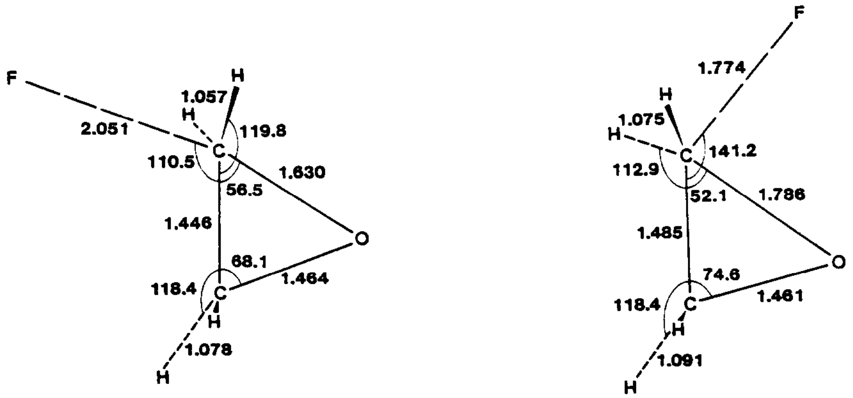
RING-OPENING OF OXIRANE BY NUCLEOPHILIC ATTACK. TRANSITION STATES AND PAIRED INTERACTING ORBITALS.

Hiroshi Fujimoto,* Itaru Hataue, Nobuaki Koga[1] and Terumasa Yamasaki
Division of Molecular Engineering, Kyoto University,
Kyoto 606, Japan

Abstract: The transition state structures for ring-opening of oxirane initiated by the attack of a fluoride ion have been calculated by means of the ab initio molecular orbital method to elucidate why the path with inversion of configuration is favoured.

Nucleophilic substitution is one of the most extensively studied reactions in chemistry. *Among the various reaction schemes proposed so far,* S_N1 *and* S_N2 *mechanisms* are located at either extreme of the wide spectrum.[2] The stereochemistry is related closely with the mechanism, inversion of configuration at the reaction center being regarded as specifying the bimolecular processes. Analogous to the direct displacements in alkyl halides, openings of epoxide rings proceed with almost complete inversion of configuration at the carbon atom under attack.[3] Molecular orbital (MO) theory is a powerful tool to study the charge redistribution and changes in chemical bondings in the course of reactions. In particular, recent developments in ab initio MO calculations made it possible to locate the transition state and trace the reaction path on the potential energy surface. With a view to providing a clearer insight into the mechanisms of nucleophilic substitutions and related reactions, we report here the result of our ab initio MO calculation on the ring-opening of oxirane.

For simplicity of calculations, we took a fluoride ion as the attacking nucleophile. The transition state geometry was determined by applying a commonly used technique[4] with the 3-21G basis functions for an attack of the anion from the backside of a C-O bond (path (i)) and for an attack from the same side as the C-O bonds (path (ii)). The calculated structures are shown in Figure 1.[5] In both cases, the anion approaches one of the carbon atoms in the plane of the three-membered ring. The transition state structure for the path (i) looks



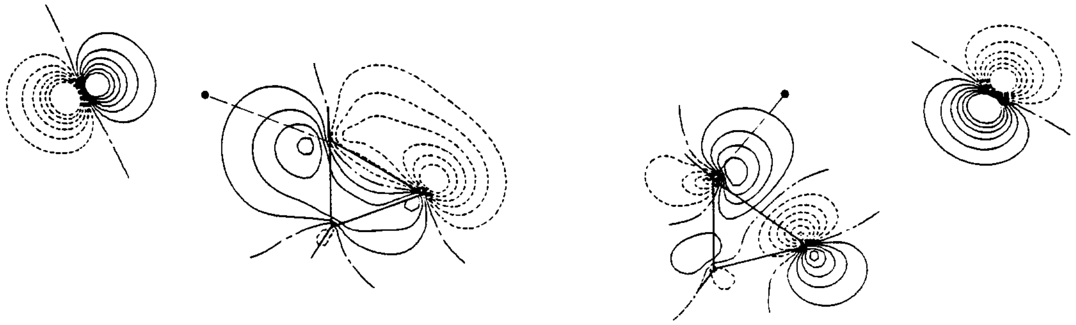
path with inversion of configuration path with retention of configuration

Figure 1. Transition state structures of ring-opening of oxirane.
Bond distances are in Å and bond angles are in degree.

similar to the structure which has been accepted for bimolecular nucleophilic substitution reactions in alkyl halides. The carbon and oxygen of oxirane and the attacking fluoride ion are placed approximately on a line and the configuration about the carbon under attack is halfway to becoming inverted. The distance between the carbon atom and the fluoride ion is shorter and the ring is more distorted in the path (ii) at the transition state.

Within this level of calculation, the transition state for the path (ii) is shown to be 157.2kJ mol^{-1} higher in energy than the transition state for the path (i). Though the calculated energy difference is apparently too large as is often the case with such systems being studied,[6] the calculation indicates anyhow that the transition state for the path with retention of configuration should be quite unstable. Now, the concept of paired interacting orbitals may be utilized conveniently in order to elucidate the origin of such a difference in the interactions between the path (i) and the path (ii).[7] A single bond is formed between a carbon atom and the attacking fluoride ion in the reaction and, therefore, the orbital interactions are condensed well in a single pair of interacting orbitals.

One of the factors which governs reaction pathways is electron delocalization between the two fragment species. Figure 2 illustrates the interacting orbitals of oxirane and the anion which play the dominant role in charge transfer from the latter to the former at the transition state. The interacting orbitals demonstrate completely different patterns for the path (i) and for the path (ii). In the path (ii), the orbital of oxirane that takes part in

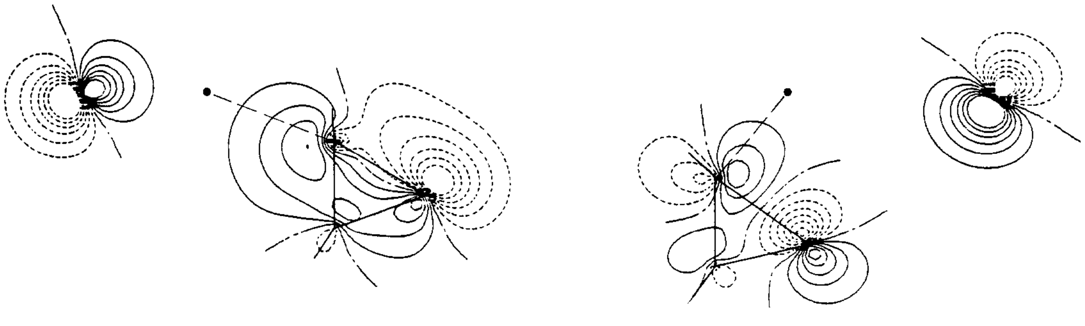


path with inversion of configuration path with retention of configuration

Figure 2. Principal pair of interacting orbitals taking part in delocalization interaction.

the delocalization interaction is seen to be localized well around the reaction site and has the maximum extension toward the incoming anion. This suggests that a sufficient stabilization can be obtained even when a fluoride ion attacks the carbon atom from the same side of the C-O bond. Though the oxygen atom participates in the interaction in an antibonding manner, the population analysis shows that the bonding interaction between the interacting orbital of the oxirane and the paired counterpart of the anion is stronger in the path (ii) than in the path (i).

Another interaction of importance is the overlap repulsion between occupied MOs of the two species. Figure 3 illustrates the paired orbitals which cover electron delocalization, overlap repulsion and also charge polarization. In the path (i), the interacting orbitals do not change much. In other words, the overlap repulsion is not so crucial as to make the reaction unfavourable. In the path (ii), on the other hand, the bonding lobe on the carbon atom is contracted significantly and, in addition, the antibonding lobe around the oxygen atom



path with inversion of configuration path with retention of configuration

Figure 3. Principal pair of interacting orbitals participating in orbital interactions.

is somewhat expanded. As discussed above, the C-O bond is found to be more stretched at the transition state in the path (ii) than in the path (i). This distortion of the ring takes place in order to reduce the antibonding interaction between the oxygen in oxirane and the attacking anion by increasing their separation. This distortion is accompanied, however, by a destabilization of the oxirane fragment.

Now, the unfavoured path with retention of configuration is rationalized first of all in terms of strong overlap repulsion between the oxirane ring and the attacking nucleophile and second in terms of the forced distortion of three-membered ring at the transition state.[8] One of the C-O bonds should be weakened beforehand to suppress this destabilization. An electron acceptor is suggested immediately to be a possible perturber. In experiments, however, ring-opening of epoxides catalyzed by Lewis acids proceeds in most cases with inversion of configuration at the carbon under attack.[3] The acid catalyst adds the out-of-plane lone-pair orbital of oxygen and, accordingly, can not eliminate effectively the electron density of the orbitals having the direction of extension in the plane of ring.

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5. The frequency of the vibration along the reaction coordinate was calculated to be -438.9i cm^{-1} for the path (i) and -700.4icm^{-1} for the path (ii).
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8. Electrostatic interaction does not favour the path with retention either.

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