An MO-theoretical Study of the Nucleophilic Bimolecular Ring-opening of Ethylene Oxide

Hiroshi Fujimoto, Motohiro Katata, Shinichi Yamabe, and Kenichi Fukui
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received October 30, 1971)

The results of an approximate molecular orbital (MO) calculation of the interaction energy of the ring-opening of ethylene oxide by a hydride ion are presented. The method of calculation is based upon the isolated-molecule approximation. The interaction energy was divided into the Coulomb, exchange, delocalization, and polarization interaction terms, and the changes in these four terms with the progress of the reaction were investigated. The wave function of the combined system of ethylene oxide and a hydride ion was obtained by the configuration interaction (CI) procedure. The changes in the electron populations of ethylene oxide and the hydride ion were calculated from the ground-state CI wave function. Among the unoccupied MO's of ethylene oxide, two low-lying unoccupied MO's were shown to be of special importance in the electron transfer from the attacking anion to ethylene oxide. The effect of the deformation of the molecular shape upon the interaction energy and the intermolecular bond formation is also discussed.

In order to elucidate the origin of the stereoselectivity in chemical reactions, several MO calculations of intermolecular interaction have been carried out.[1-5] These approaches have all intended to discuss the favorable path of several kinds of reaction in light of our knowledge of the MO's of the two reactants in an isolated state. Although the applications of these studies have been limited to the early stage of chemical interaction, they have been believed to be able to give rather detailed information about chemical reactions. The interaction energy between two systems can reasonably be divided into several terms,[4,6,7] to examine what kinds of interactions are important in a given reaction. We previously represented the interaction energy as approximately the sum of four terms, the Coulomb, exchange, delocalization, and polarization interaction energies.[8] Some succinct expressions for these terms were obtained by adopting LCAO SCF MO's. A discussion has also been presented on the role of each of these four terms in determining the favorable path of the bimolecular nucleophilic substitution reaction of methyl chloride, based upon the results of approximate numerical calculations.[9]

It is well known that the bimolecular nucleophilic ring-opening reaction of epoxides takes place stereoselectively, with the preferential occurrence of the inversion at the carbon atom to be attacked by the anion.[10] In the present paper we will discuss the effect of the four energy terms on the determination of the favorable path of the ring-opening of ethylene oxide. The attacking anion is simply represented by a hydride ion. A possible influence of the molecular deformation upon the ease of interaction will also be investigated.

Interaction Energy

The method of the present calculation is based on the concept of the isolated-molecule approximation. That is, the interaction energy between a hydride ion and ethylene oxide, and the changes in the electron populations due to the interaction, are expressed in terms of MO's, which are obtained with respect to each of the two species in the isolated state. We represent the wave function of the interacting system composed of a hydride ion and ethylene oxide as approximately (the symbols are the same as those in Ref. 8);

$$\Psi = C_0\Psi_0 + \sum_{j}^{\text{uno}} C_{h\to j}\Psi_{h\to j} + \sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}} C_{i\to j}\Psi_{i\to j} \tag{1}$$

where i and j denote the occupied and unoccupied MO's of ethylene oxide, and where h denotes the doubly-occupied orbital of the hydride ion. Although it may be interesting to include outer-shell orbitals, tentatively we do not regard unoccupied orbitals for the hydride ion. Then, the interaction energy, ΔW, between the two may be given approximately by:

$$\Delta W = \varepsilon_Q + \varepsilon_K - D - \Pi \tag{2}$$

where ε_Q is the Coulomb interaction energy, ε_K is the exchange interaction energy, D is the delocalization interaction energy, and Π is the polarization interaction energy. The last two terms can be expressed in the second-order perturbation forms, provided the interaction is not yet strong.[8]

Calculation on Isolated Molecules

The MO's of ethylene oxide were obtained by a semi-empirical valence-electrons SCF MO method. The method of calculation and the approximations employed are the same as those used in the previous calculation.[9] In Fig. 1 are shown the MO levels.

---

[1] a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965). b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).

[2] K. Fukui and H. Fujimoto, This Bulletin, **39**, 2116 (1966).

[3] L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

[4] A. Devaquet and L. Salem, *ibid.*, **91**, 3797 (1969).

[5] R. Sustmann and G. Binsch, *Mol. Phys.*, **20**, 1, 9 (1970).

[6] J. N. Murrell, M. Randić, and D. R. Williams, *Proc. Roy. Soc.* (London), **A284**, 566 (1965).

[7] G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

[8] K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).

[9] a) H. Fujimoto, S. Yamabe, and K. Fukui, *ibid.*, **44**, 971 (1971). b) H. Fujimoto, S. Yamabe, and K. Fukui, *Tetrahedron Lett.*, **1971**, 439, 443.

[10] See, for instance, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y. (1959).

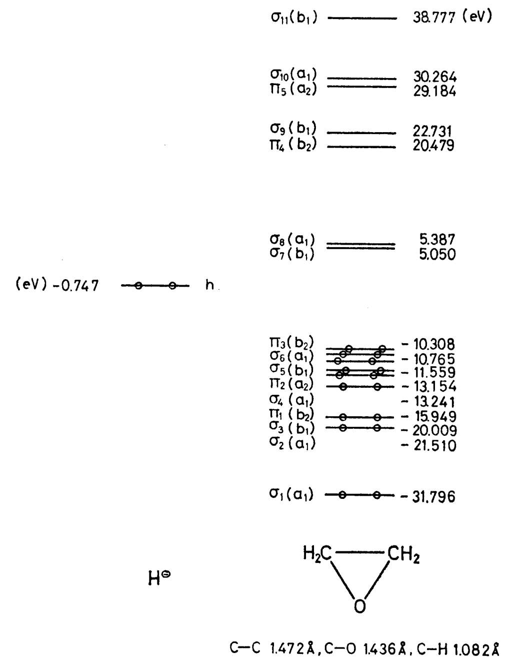

Fig. 1. MO energy levels of ethylene oxide and hydride ion.

The calculated ionization potential is 10.31 eV, showing a good agreement with the observed value, 10.562 eV.[11] There exist two relatively low-lying unoccupied MO's, having almost the same energy. Here, both of these two MO's may be regarded as the lowest unoccupied (LU) MO's. One of them belongs to the irreducible representation, a_1, and the other, to b_1, of the C_{2v} point group. The shapes of these two MO's are illustrated in Fig. 2. It is noted that both of these two MO's have nodes between carbons and oxygen. The energy level of the hydride ion was taken to be -0.747 eV, equal to the minus electron affinity value of hydrogen atom. In Fig. 3 are shown the atomic populations and atomic-bond populations of ethylene oxide in an isolated state.

Table 1. Calculated interaction energies

Model No.	(x, y, z)[a)]	ε_Q, eV	ε_K, eV	D, eV	Π, eV
Ia	(3.3, 0.000, 0)	−0.815	0.138	0.128	0.104
IIa	(3.3, 0.368, 0)	−0.809	0.137	0.132	0.105
IIIa	(3.3, 0.736, 0)	−0.789	0.135	0.138	0.106
IVa	(3.3, 1.472, 0)	−0.715	0.111	0.116	0.104
Va	(3.3, 2.208, 0)	−0.608	0.066	0.061	0.091
Ib	(3.0, 0.000, 0)	−0.937	0.332	0.333	0.146
IIb	(3.0, 0.368, 0)	−0.929	0.331	0.347	0.147
IIIb	(3.0, 0.736, 0)	−0.905	0.324	0.367	0.149
IVb	(3.0, 1.472, 0)	−0.811	0.264	0.295	0.145
Vb	(3.0, 2.208, 0)	−0.677	0.149	0.135	0.122
Ic	(2.8, 0.000, 0)	−1.034	0.587	0.691	0.188
IIc	(2.8, 0.368, 0)	−1.025	0.586	0.726	0.190
IIIc	(2.8, 0.736, 0)	−0.997	0.573	0.776	0.193
IVc	(2.8, 1.472, 0)	−0.887	0.461	0.584	0.186
Vc	(2.8, 2.208, 0)	−0.729	0.254	0.233	0.152
VI	(−1.532, 3.316, 0)	0.228	0.386	0.281	0.162
VII	(−2.149, 2.948, 0)	0.553	0.262	0.283	0.156

a) in Å

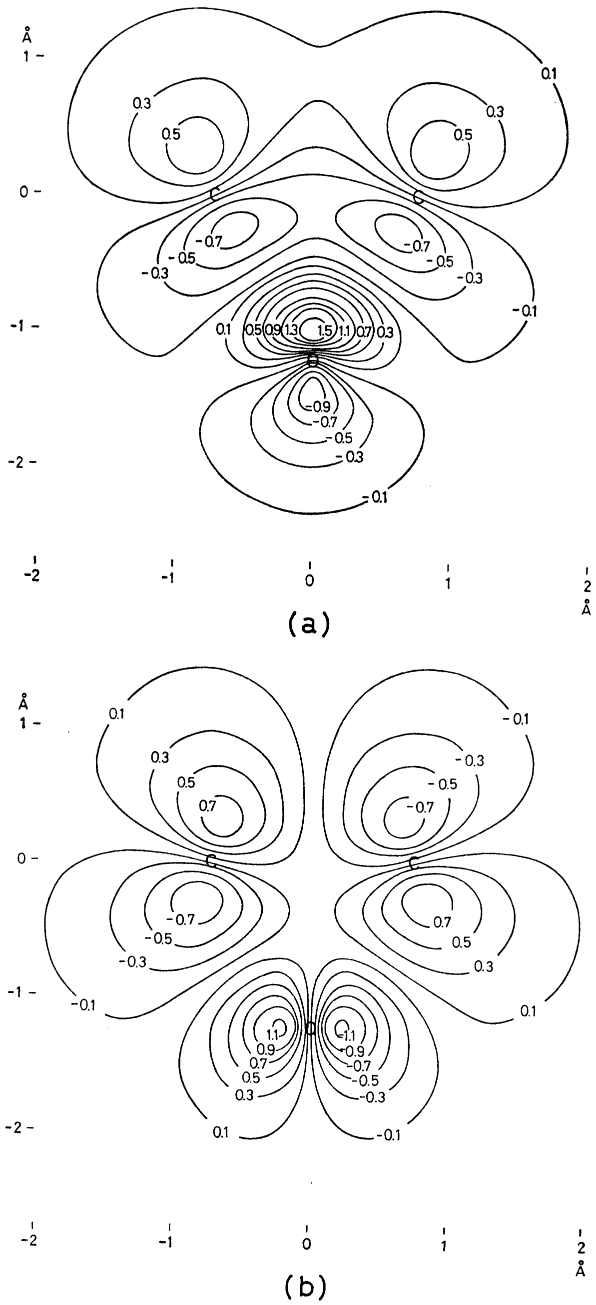

Fig. 2. The LUMO's of ethylene oxide. The figures indicate the values of the real MO's in the molecular plane.
(a): a_1 LUMO (b): b_1 LUMO

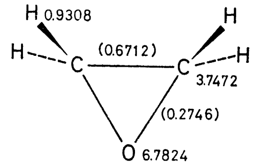

Fig. 3. The atomic populations and atomic bond populations of ethylne oxide.

Calculation of the Interaction Energy

Table 1 gives the results of the calculation of the

---

[11] A. Lowrey, III and K. Watanabe, *J. Chem. Phys.*, **28**, 208 (1958).

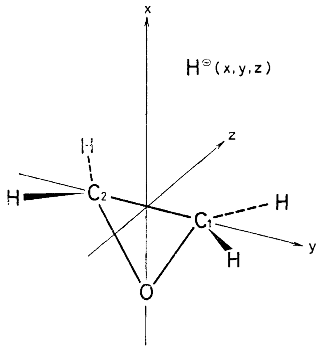

Fig. 4. A schematic representation of assumed reaction models.

interaction energy terms with respect to several assumed models. Each model corresponds to a location of the approaching hydride ion, as is indicated in Fig. 4. The interaction energies have been obtained in a manner similar to that used in previous calculations.[9,12] In the early stage of interaction, in which the hydride ion is distant, the Coulomb interaction term is dominant among the four energy terms. As the hydride ion gets near to ethylene oxide, the exchange and delocalization interaction terms rapidly increase. Because of the crudeness of the approximations employed, the relative magnitudes of the four energies are not trustworthy in a quantitative sense. The present calculation may, rather, be regarded as disclosing, only qualitatively, the possible directing effects of the four energy terms in this reaction. That is, it may be said that the Coulomb term favors the attack of the anion along the principal axis, while the other three require the approach of the anion apart from that axis. The delocalization interaction energy depends greatly on the nodal properties of the LUMO's. When the anion approaches ethylene oxide in a manner like Models Ia, Ib, Ic, ···, the 1*s* orbital of the hydride ion interacts with only one of the LUMO's with the a_1 symmetry, while in the course IIa, IIb, IIc, ···, or IIIa, IIIb, IIIc, ···, the hydride 1*s* orbital can overlap with both of the two LUMO's. The polarization interaction is found to be less important than the delocalization interaction as hydride comes nearer to ethylene oxide. The comparison of Models VI and VII with Models Ib—Vb seems to indicate the preference of inversion at the carbon atom to be attacked by the anion; this is in accordance with the experimental results.[10]

As the reaction proceeds, the initial molecular geometry of the reactant changes. The deformation in the molecular structure is accompanied by changes in the interaction energy terms through the changes in spatial functions and MO energy levels. In order to examine this problem, we have carried out further calculations while altering the shape of ethylene oxide. Here, we tentatively stretch the C_1–O bond by 0.2 Å. Although this value is arbitrary, such a configuration would be rather in conformity with the deformation along the reaction path. By this deformation, the LUMO's, which are nearly degenerate in ethylene oxide of the symmetrical configuration, split by about 3.8 eV. The shape of the LUMO of the deformed ethylene oxide is shown in Fig. 5. Table 2 presents the results of the calculation of the interaction energy for some assumed locations of the approaching hydride ion with respect to the deformed ethylene oxide. The results in Table 2 seem to indicate that the departure of the hydride ion from the bisecting axis of the C–C bond is assisted by the deformation of the ring. We find the most significant influence of the molecular deformation on the energy term *D*. It is interesting that the delocalization energy is large when the hydride ion approaches from the direction of the maximum extension of the LUMO of ethylene oxide. The effect of the molecular deformation appears to be a matter of gerat significance in applying the isolated-molecule approximation.

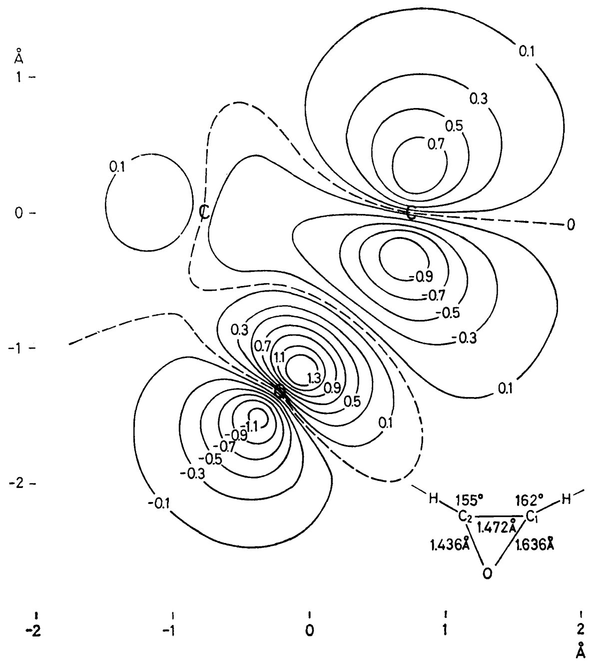

Fig. 5. The LUMO of ethylene oxide with a deformed nuclear configuration. The figures idicate the values of the real MO in the molecular plane.

TABLE 2. CALCULATED INTERACTION ENERGIES

Model No.	(x, y, z)[a]	ε_Q, eV	ε_K, eV	D, eV	Π, eV
I′	(3.0, −0.736, 0)	−0.898	0.331	0.502	0.171
II′	(3.0, 0.000, 0)	−0.913	0.319	0.676	0.188
III′	(3.0, 0.736, 0)	−0.867	0.297	0.911	0.204
IV′	(3.0, 0.828, 0)	−0.858	0.292	0.917	0.205
V′	(3.0, 0.920, 0)	−0.848	0.287	0.914	0.205
VI′	(3.0, 1.472, 0)	−0.775	0.236	0.701	0.199

a) in Å

---

[12] One-center core attraction integrals $v_{\alpha tt}=\int t(1)(-Z_\alpha e^2/r_{\alpha 1})t(1)dv(1)$ (the AO *t* belongs to the nucleus α) were evaluated in a different way from the previous calculation. They were modified so as to make the quantity $\{v_{\alpha tt}+\sum_{t'}^{\alpha} n_{t'}(t't'|t't')\}$ give the same value both for the non-empirically calculated and for the semi-empirically estimated cases, where $n_{t'}$ means the occupation number of the AO *t′* of the atom α.

Table 3. The coefficients of the ground-state CI wave functions

Model No.	C_0	$C_{h\to j}$						
		$j=\sigma_7$	$j=\sigma_8$	$j=\pi_4$	$j=\sigma_9$	$j=\pi_5$	$j=\sigma_{10}$	$j=\sigma_{11}$
IIa	0.9867	0.0332	0.1261	0	0.0019	0	0.0211	0.0022
IIIa	0.9860	0.0591	0.1193	0	0.0036	0	0.0213	0.0046
IVa	0.9881	0.0750	0.0929	0	0.0062	0	0.0215	0.0093
IIb	0.9654	0.0582	0.2077	0	0.0016	0	0.0239	0.0022
IIIb	0.9634	0.1024	0.1957	0	0.0030	0	0.0245	0.0050
IVb	0.9701	0.1248	0.1505	0	0.0056	0	0.0262	0.0117
VI	0.9655	0.1760	0.1205	0	0.0072	0	0.0182	0.0282
III′	0.8817	0.4247	0.0391	0	0.0021	0	0.0236	0.0005
IV′	0.8811	0.4262	0.0315	0	0.0025	0	0.0238	0.0012
V′	0.8813	0.4260	0.0246	0	0.0028	0	0.0241	0.0019
VI′	0.9008	0.3900	0.0025	0	0.0046	0	0.0268	0.0064

Table 4. The intermolecular AO bond populations of the AO's of ethylene oxide with hydride 1*s* orbital

Model No.	$1C_s$	$1C_x$	$1C_y$	$1C_z$	$2C_s$	$2C_x$	$2C_y$	$2C_z$
IIb	−0.0130	0.0197	−0.0006	0	−0.0075	0.0064	−0.0025	0
IIIb	−0.0138	0.0241	0	0	−0.0052	0.0022	−0.0027	0
IVb	−0.0111	0.0197	−0.0004	0	−0.0021	−0.0002	−0.0017	0
III′	−0.0172	0.0427	0	0	−0.0041	0.0020	−0.0026	0
V′	−0.0173	0.0427	0.0004	0	−0.0036	0.0015	−0.0025	0
VI′	−0.0151	0.0349	0.0007	0	−0.0015	0.0002	−0.0017	0

Electron Populations

The coefficients of Eq. (1) calculated for the lowest energy state of the combined system of two reacting species are shown in Table 3. We can see that the most contributing term to Ψ except Ψ_0 is the charge-transferred configuration from the hydride ion into the a_1 LUMO, and that the next contributing is that from the hydride orbital into the b_1 LUMO of the symmetrical-form ethylene oxide. The preferential contribution of a_1 MO to b_1 MO is attributable to the nodal properties of these MO's. The deformation of the nuclear configuration also promotes the mixing of charge-transferred states, as is clear from the comparison of Models IIIb and III′ in Table 3. In obtaining the wave functions, the locally-excited configurations of ethylene oxide were tentatively neglected, since they were thought to have little influence upon the intermolecular electron transfer.

The changes in the electron populations due to the interaction can be calculated by the use of Eq. (1).[13] The AO bond populations between the hydride 1*s* orbital and the AO's of the carbon atoms of ethylene oxide, obtained from the ground-state CI wave function, are shown in Table 4. The bond formation between the hydride ion and the carbon atom of ethylene oxide under attack is most effective in the model in which the delocalization interaction energy is the largest. The AO of the carbon atom 1, which plays the most dominant role in the formation of the intermolecular bond with the hydride ion, is the p_x orbital, which has its maximum extension in the direction of the approach of the anion. In order to calculate the AO populations of both reactants, we should divide the effused fraction of electrons over the intermolecular region through the overlapping of the AO's *h* of hydride and *t* of ethylene oxide into two parts, the one constituting a part of the AO population of the AO *h*, and the other, that of the AO *t*. This partitioning may be an extension of Mulliken's population analysis to intermolecular AO pairs.[14] The changes in the atomic populations and in the atomic-bond

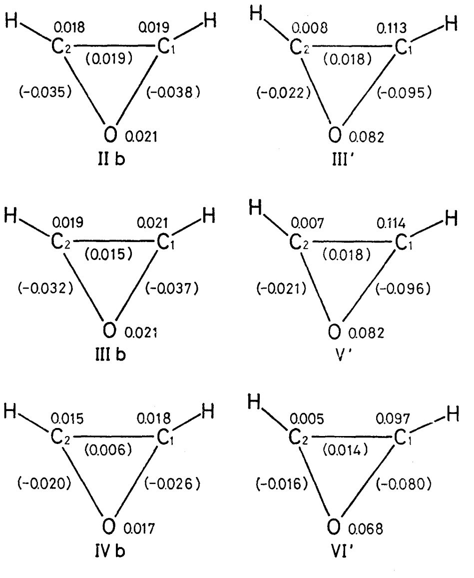

Fig. 6. The changes in the atomic populations and in the atomic bond populations of ethylene oxide due to the interaction with a hydride ion.

---

[13] H. Fujimoto, S. Yamabe, and K. Fukui, This Bulletin, **44**, 2936 (1971).

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

populations of ethylene oxide are shown in Fig. 6 with respect to some of the models mentioned before. The figures in parentheses indicate the changes in atomic-bond populations from those in an isolated state. The atomic-bond populations of the C–O bonds decrease in the case of the interaction with the hydride ion. The results in Table 4 and in Fig. 6 demonstrate that both the formation of new bonds and the weakening of old bonds are accelerated by the molecular deformation. This result is consistent with our previous proposition that the cooperation of the electron delocalization with the change in the molecular shape is a possible driving force in chemical reactions.[15]

Conclusion

We have presented the results of a semi-empirical calculation of the chemical interaction energy and the bond interchange in the ring-opening reaction of ethylene oxide with a hydride ion. Because of the simplification of the reaction model and the crudeness of the calculation, we must refrain from drawing any decisive conclusion about the reaction path from our present results. We can only remark that the path of the approach of the hydride ion to ethylene oxide is very likely to be governed by a delicate balance of the four energy terms presented here. Among charge-transferred states, the one in which an electron of the hydride ion is transferred into the LUMO of ethylene oxide is most important. Molecular deformation along the reaction path appears to be of considerable significance, influencing the ease of the chemical interaction. The effect has been found to be striking in the delocalization interaction energy. The present calculation should not be looked upon as necessarily intending to search for the reaction coordinate leading to the transition state of this special reaction. They will better serve to provide a rough estimate of the directing effect of the four energy terms, and of the bond interchange with respect to some locations of the attacking anion, in the early stage of the reaction. We hope only that we can extend the calculations to a region of moderate interaction.

It is a pleasure to express our gratitude to the Data Processing Center, Kyoto University, for its generous permission to use the FACOM 230·60 computer.

---

15) K. Fukui and H. Fujimoto, This Bulletin, **42**, 3399 (1969).