

Perturbation of Molecules by Static Fields, Orbital Overlap, and Charge Transfer

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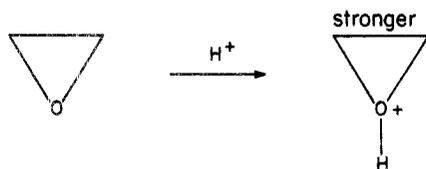
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Using a molecular orbital approach we discuss several modes by which a reagent could affect the reactivity of an organic molecule. Field effects, orbital overlap, charge transfer, and polarization are analyzed. The model substrate molecule is oxirane or acrolein, the model perturber a fixed point charge or an acceptor orbital of varying energy. The mixing of substrate orbitals by the perturbation can cause highly specific and localized changes in the electron distribution in the substrate.

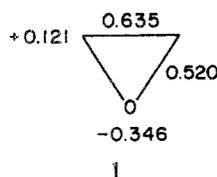
The ever-improving computational capability of the theoretical chemist must be accompanied by an enhanced analytical ability. To transform calculation into understanding we need sharpened analytical tools with which we may extract the essential physical features which made a calculation come out the way it indeed did. This paper is part of our effort in this direction. It presents no novel conclusions of experimental interest. However in the context of explaining some new and older theoretical results, it develops further the methodology available for analyzing molecular orbital calculations. Our special focus is on external perturbations caused by point charges and donor or acceptor orbitals.

Electrostatic, Orbital Overlap, and Charge Transfer Interactions in the Protonation of Oxirane

It was recently pointed out that the overlap population, and therefore presumably the bond strength, of the carbon-carbon bond of oxirane (ethylene oxide) increases upon protonation.¹ Although there is no experimental observation allowing a direct comparison of carbon-carbon bond length or strength before and after protonation, there is some indirect supporting information in the literature.² The problem has a broader context in that it represents a model system for the study of solvent effects and acid catalysis.



We first consider the simple electrostatic effect of the external field. The reference is an iterative extended Hückel (EH) calculation on oxirane.³ Resulting charges and overlap populations are shown in 1.

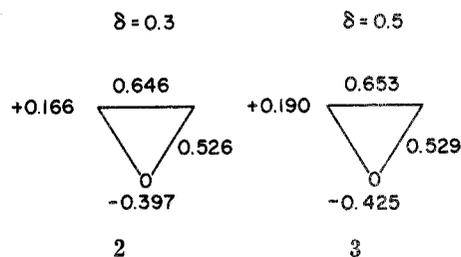


To study the electrostatic effect of the external field we placed a point charge δe 3.0 Å away from the oxygen atom.

It was not obvious from which direction such a positive probe should approach oxirane. One possibility is to use the Bonaccorsi-Scrocco-Tomasi potential.⁴ Another possibility, followed by us, is to calculate first the composition of the in-plane lone pair orbital of oxirane, using the criterion of Ruedenberg.⁵ That orbital is found to be an $sp^{0.56}$ hybrid on oxygen, possessing maximum extension away from the ring. Taking a one-to-one linear combination of this hybrid with the out-of-plane, pure 2p lone pair orbital of oxygen, we found $\sim 118^\circ$ for the angle between the two hybrids. To see the qualitative effect of the charge, we took 60° for θ , as shown in Figure 1. Corrections to the Coulomb integrals of the atomic orbitals (AO) were made in the following approximate way

$$h_{ii} = h_{ii}^0 + \Delta_{ii} \quad \Delta_{ii} = -\delta e^2/r_i \quad (1)$$

where h_{ii}^0 is the Coulomb integral without perturbation and r_i is the distance between the center of the AO i and the point charge δe .⁶ The atomic and overlap populations are given in 2 and 3 for $\delta = 0.3$ and $\delta = 0.5$, respectively. A significant change in the carbon-carbon overlap populations is observed.



The total wave function of the perturbed system can be expanded in terms of the various electronic configurations of the unperturbed states.⁷ They are for $\delta = 0.3$

$$\begin{aligned} \Psi' &= \frac{1}{\sqrt{18!}} |a_1 \bar{a}_1' a_2 \bar{a}_2' \dots a_9 \bar{a}_9'| \\ &= 0.9988 \Psi_0 + 0.0333 \Psi_{7-10} + \\ &\quad 0.0126 \Psi_{2-15} + \dots \quad (2) \end{aligned}$$

where

$$\Psi_0 = \frac{1}{\sqrt{18!}} |a_1 \bar{a}_1 a_2 \bar{a}_2 \dots a_9 \bar{a}_9| \quad (3)$$

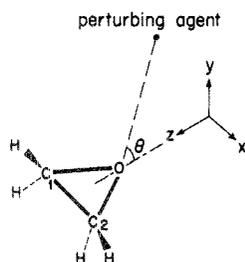


Figure 1. The model used to calculate the electrostatic effect of a perturbing point charge on oxirane.

$$\Psi_{7-10} = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{18!}} |a_1 \bar{a}_1 \dots a_7 \bar{a}_{10} a_8 \dots \bar{a}_9| - \frac{1}{\sqrt{18!}} |a_1 \bar{a}_1 \dots \bar{a}_7 a_{10} a_8 \dots \bar{a}_9| \right] \quad (4)$$

and

$$a_i = \sum_r c_{ri} \chi_r \quad \text{unperturbed MO}$$

$$a_i' = \sum_r c_{ri}' \chi_r \quad \text{perturbed MO}$$

The numbering refers to the ground state configuration of oxirane. For $\delta = 0.5$

$$\Psi' = 0.9970 \Psi_0 + 0.0515 \Psi_{7-10} + 0.0201 \Psi_{2-15} + \dots$$

Thus the wave function of the perturbed system is expressed as a combination of the original state and excited states of the unperturbed system. The leading term outside of the ground configuration involves a promotion of an electron from occupied orbital $a_7(3b_2)$ to the lowest unoccupied molecular orbital (LUMO) of the isolated molecule, $a_{10}(4b_2)$. These orbitals, both antisymmetric with respect to the mirror plane bisecting the CC bond, are shown schematically in Figure 2.⁸ They are obviously related to the Walsh orbitals of cyclopropane.

The electron density of ethylene oxide perturbed by 0.3e is given by

$$\rho' = \rho + (0.0333)^2 (-a_7^* a_7 + a_{10}^* a_{10}) + 0.9988 \times 0.0333 \times \sqrt{2} \times (a_7^* a_{10} + a_{10}^* a_7) + \dots \quad (5)$$

where ρ is the unperturbed electron density

$$\rho = 2 \sum_i^{\text{occ}} a_i^* a_i \quad (6)$$

Although the third term of ρ' vanishes upon integration over all space, it brings about a reorganization of the electron density distribution.⁹

The MO's a_7 and a_{10} which do not interact in the isolated state of oxirane are forced to intermix by the external perturbation. The mode of mixing is drawn schematically in Figure 2. It is clear that a_7' of perturbed ethylene oxide has less p_z - p_z antibonding character. We can attribute the increase in the carbon-carbon overlap population mainly to the increase in the p_z - p_z bond population. Table I gives the specific change in the AO overlap populations of the car-

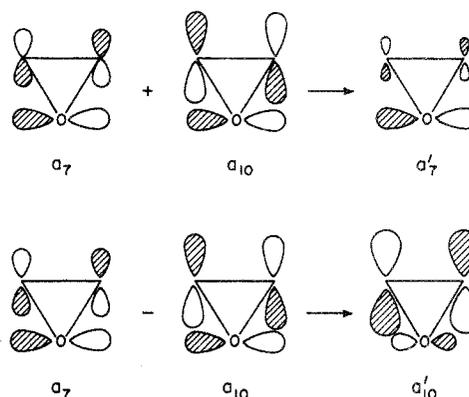


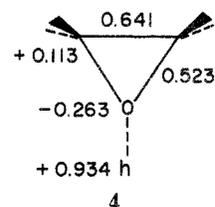
Figure 2. A schematic representation of the mixing of two b_2 orbitals of oxirane, induced by a static charge. In reality the mixing coefficients are not equal.

TABLE I: Differences in the Carbon-Carbon Overlap Populations between Unperturbed Oxirane and the Molecule Perturbed by a Static Charge

	C_{1s}	C_{1z}	C_{1y}	C_{1z}
C_{2s}	-0.0024	0.0015	0	0
C_{2z}	0.0015	-0.0014	0	0
C_{2y}	0	0	0.0001	0
C_{2z}	0	0	0	0.0121

bon-carbon bond when oxirane is under the influence of a static charge of +0.3e. A relatively large increase in $2p_z$ - $2p_z$ overlap population is observed.

We turn to an analysis of the interaction of oxirane with a high-lying hole or acceptor orbital. It was shown above that the bond strengthening due to perturbation by a point charge was brought about by the mixing of two antisymmetric MO's. In that case no orbital overlapping was assumed between the MO's of oxirane and the perturbing agent. In general a reagent interacting with a substrate will bear not only a charge but a set of orbitals. To see the effect of this we placed a vacant hole consisting of a single 1s orbital,¹⁰ in the vertical mirror plane, 1.5 Å from the oxygen. The angle θ was again taken as 60° (see Figure 1). In order to avoid strong charge transfer, the hole was placed high in energy at -5 eV. The resultant population analysis is given in 4. We can see an increase, albeit not large, of the carbon-carbon overlap population.



In this instance, unlike the case mentioned above, only the MO's symmetric with respect to the mirror plane can interact with the hole orbital. Antisymmetric MO's remain unchanged. Since the hole is indeed empty, charge transfer is unidirectional from oxirane to the hole. This in turn implies that the symmetric MO's of oxirane will lose some fraction of their electron pairs, leading to a weakening of the carbon-carbon bond. However the observed net result is a strengthening of that bond. The increase in the overlap population comes from the second-order mixing of two symmetric MO's through their overlap with the hole orbital.⁹ The wave function of the system composed of oxirane

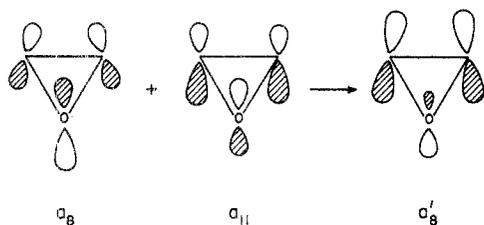


Figure 3. Formation of the perturbed a_8' ($6a_1$) MO of oxirane.

TABLE II: Changes in the Carbon-Carbon Overlap Populations between Unperturbed Oxirane and the Molecule Perturbed by a High-Lying Vacant Orbital

	C_{1s}	C_{1x}	C_{1y}	C_{1z}
C_{2s}	0.0012	0.0007	0	0
C_{2x}	0.0007	-0.0001	0	0
C_{2y}	0	0	0.0002	0
C_{2z}	0	0	0	0.0032

and the vacant orbital is given by

$$\Psi = 0.9499\Psi_0 + 0.1383\Psi_{8 \rightarrow h} + 0.0944\Psi_{9 \rightarrow h} + 0.0172\Psi_{8 \rightarrow 11} + 0.0121\Psi_{9 \rightarrow 11} + \dots$$

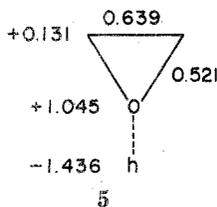
where $\Psi_{i \rightarrow h}$ means a charge-transferred state from a_i to the orbital of the hole h

$$\Psi_{i \rightarrow h} = \frac{1}{\sqrt{2}} \left\{ n | a_1 \bar{a}_1 \dots a_i \bar{h} \dots a_9 \bar{a}_9 | - n | a_1 \bar{a}_1 \dots \bar{a}_i h \dots a_9 \bar{a}_9 | \right\}$$

We can see that locally excited states $\Psi_{8 \rightarrow 11}$ and $\Psi_{9 \rightarrow 11}$ come to mix into Ψ . The contribution of $\Psi_{9 \rightarrow 11}$ to the bond strengthening is small because $a_9(2b_1)$ is a π -type lone pair orbital, while $a_{11}(7a_1)$ is a σ -type MO. The intermixing of these orbitals yields an electron distribution unsymmetrical with respect to the molecular plane.

The mode of orbital overlap interaction may be analyzed schematically as shown in Figure 3. Orbitals 8 and 11 are both in-plane σ orbitals. It is evident that the mixing of these two symmetric MO's can increase the carbon-carbon overlap population. The changes in the AO populations of the bond, given in Table II, support this conclusion.

In the case discussed above, the charge-transfer from the three-membered ring to the vacant perturber orbital was rather small, since the hole was placed high in energy compared to the highest occupied MO (HOMO) of oxirane. We examine next the complementary case in which the hole lies lower than the HOMO of oxirane. The energy of the hole was tentatively assigned the same value as the Coulomb integral of the hydrogens of the three-membered ring. Resulting overlap populations are given in 5.



Except for the drastic change in oxygen and hole charges, a comparison with 4 reveals little effect on ring bond strengths. This is surprising. The wave function of the sys-

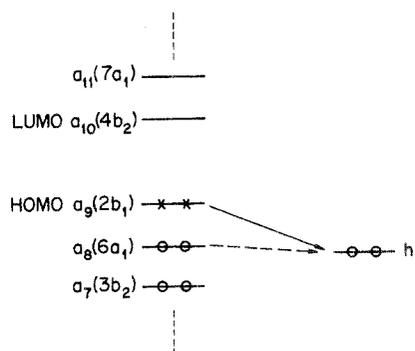


Figure 4. A schematic representation of direct electron shift from high-lying oxirane orbitals to a perturbing hole orbital.

tem may be decomposed as follows¹¹

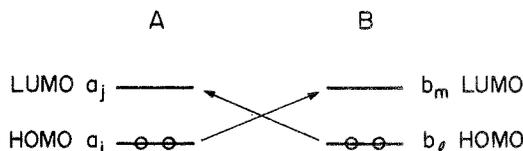
$$\Psi = 0.2079\Psi_0 + 0.2279\Psi_{8 \rightarrow h} + 0.4637\Psi_{9 \rightarrow h} + 0.1240\Psi_{8 \rightarrow h, 8 \rightarrow h} + 0.5046\Psi_{9 \rightarrow h, 9 \rightarrow h} + 0.3538\Psi_{8 \rightarrow h, 9 \rightarrow h} + \dots$$

where $\Psi_{8 \rightarrow h, 9 \rightarrow h}$ indicates the ditransferred state, one electron from a_8 and one electron from a_9 both moving into h . Thus in this case we have a direct transfer of electrons from a_9 (and/or a_8) to the hole orbital, as shown schematically in Figure 4. Since the HOMO is a symmetrical orbital, the removal of electrons from this orbital produces a decrease of the carbon-carbon overlap population. However, the decrease is small, because the HOMO is a lone-pair orbital almost completely localized at the oxygen atom. Our result should thus not be generalized to other systems. Strong charge transfer to or from a substrate is likely to cause large changes in electronic distributions.

Our discussion has treated separately the effects of a static field, orbital interaction with minimal charge transfer, and orbital interaction with strong charge transfer. Of course, in a real case all the effects will be operative, enhancing or compensating each other. A self-consistent field calculation will include all the effects, as well as the relaxation of electron density through the self-consistent process. A normal extended Hückel calculation does not include the field effect. In the case of oxirane an *ab initio* calculation gives somewhat greater carbon-carbon bond strengthening upon protonation than does an extended Hückel calculation.¹² This is consistent with our analysis of the field effect.

Intermolecular Interaction in the Presence of a Perturbing Field

It is clear that solvent polarity and catalysis play a key role in governing the chemical reactivity of molecules.¹³ We will now discuss the important features of a perturbation caused by an external field upon bimolecular reactions. Consider an interaction between two systems, which, for the sake of simplifying the discussion, are assumed each to possess two orbitals and two electrons. The orbitals of the two systems are labeled as indicated below.



The wave function which describes the thermal interac-

tion of the two systems is given by a linear combination of various electronic configurations¹⁴

$$\Psi = C_0\Psi_0 + C_{i \rightarrow m}\Psi_{i \rightarrow m} + C_{i \rightarrow j}\Psi_{i \rightarrow j} + C_{i \rightarrow j}\Psi_{i \rightarrow j} + C_{l \rightarrow m}\Psi_{l \rightarrow m} + \dots \quad (7)$$

where

$$\Psi_0 = n_0 |a_i \bar{a}_i b_l \bar{b}_l| \quad n_0 = \left(\sqrt{4!} \begin{vmatrix} 1 & S_{il} \\ S_{il} & 1 \end{vmatrix} \right)^{-1} \quad (8)$$

$$\Psi_{i \rightarrow m} = \frac{1}{\sqrt{2}} n_{i \rightarrow m} [|a_i \bar{b}_m b_l \bar{b}_l| - | \bar{a}_i b_m b_l \bar{b}_l |] \quad (9)$$

$$n_{i \rightarrow m} = \left[\sqrt{4!} \left(\begin{vmatrix} 1 & S_{il} \\ S_{il} & 1 \end{vmatrix} \times \begin{vmatrix} 1 & S_{lm} \\ S_{lm} & 1 \end{vmatrix} + \begin{vmatrix} S_{im} S_{lm} \\ S_{il} & 1 \end{vmatrix}^2 \right)^{1/2} \right]^{-1}$$

$$\Psi_{i \rightarrow j} = \frac{1}{\sqrt{2}} n_{i \rightarrow j} [|a_i \bar{a}_j b_l \bar{b}_l| - | \bar{a}_i a_j b_l \bar{b}_l |] \quad (10)$$

$$n_{i \rightarrow j} = \left[\sqrt{4!} \left(\begin{vmatrix} 1 & S_{il} \\ S_{il} & 1 \end{vmatrix} \times \begin{vmatrix} 1 & S_{jl} \\ S_{jl} & 1 \end{vmatrix} + \begin{vmatrix} S_{ij} S_{jl} \\ S_{il} & 1 \end{vmatrix}^2 \right)^{1/2} \right]^{-1}$$

Our goal is to determine the coefficients in eq 7. For the electron density we have the following expressions¹⁵

$$4 \int \Psi_0^* \Psi_0' d\xi_1 d\tau_2 \dots d\tau_4 = 2(a_i^* a_i + b_l^* b_l) + 2[(a_i^* a_i + b_l^* b_l)(S_{il}^2 - S_{il}^4) - (a_i^* b_l + b_l^* a_i)(S_{il} - S_{il}^3)] / (1 - S_{il}^2)^2 \quad (11)$$

$$4 \int \Psi_0^* \Psi_{i \rightarrow m} d\xi_1 d\tau_2 \dots d\tau_4 = \sqrt{2}(a_i^* a_i + 2b_l^* b_l) S_{im} + \sqrt{2} a_i^* b_m + \dots \quad (12)$$

and

$$4 \int \Psi_0^* \Psi_{i \rightarrow j} d\xi_1 d\tau_2 \dots d\tau_4 = \sqrt{2} a_i^* a_j + \dots \quad (13)$$

by integrating over all the spin and space coordinates of electrons 2, . . . , 4 and over the spin coordinate of electron 1. It is clear that the original state gives a negative overlap population ($\sim 4S_{il}^2$) between A and B, which is characteristic of the interaction between two closed-shell systems.¹⁶ The mixing in of the charge-transferred state is important in bringing about intermolecular bond formation, through the overlapping of a_i and b_m by an electron donated from a_i . The mode of the mixing of $\Psi_{i \rightarrow m}$ with Ψ_0 is, of course, in phase in the ground state, so as to give a positive overlap population between A and B.¹⁷ As mentioned above, the mixing in of locally excited states is primarily responsible for the intermolecular reorganization of electron distribution. Therefore, the stabilization comes from the interaction between the HOMO of A and the LUMO of B and the converse. We are repeating here the basic conclusions of the theory of intermolecular interaction developed by Fukui¹⁸ and Salem.¹⁹

In photoinduced reactions, in which one of the two reactants is promoted to the lowest singlet excited state, the interaction between the HOMO and a singly occupied (SO) MO, and that between the LUMO and SOMO' give the main stabilizing terms, as shown below.^{18,19}



When there is a perturbation from an external field, we have a wave function similar to eq 7

$$\Psi' = C_0'\Psi_0' + C_{i \rightarrow m}'\Psi_{i \rightarrow m}' + C_{i \rightarrow j}'\Psi_{i \rightarrow j}' + \dots \quad (14)$$

where

$$\Psi_0' = n_0' |a_i \bar{a}_i b_l' \bar{b}_l'| \quad (15)$$

$$\Psi_{i \rightarrow m}' = \frac{1}{\sqrt{2}} n_{i \rightarrow m}' [|a_i \bar{b}_m' b_l' \bar{b}_l'| - | \bar{a}_i b_m' b_l' \bar{b}_l'|] \quad (16)$$

The perturbed MO's a' and b' will be given by

$$a_i' = k_{ii} a_i + k_{ij} a_j$$

$$b_l' = k_{ll} b_l + k_{lm} b_m \quad \text{etc.} \quad (17)$$

k_{ij} and k_{lm} are small in comparison with k_{ii} and k_{ll} , respectively, as long as the perturbation is small. Then we have

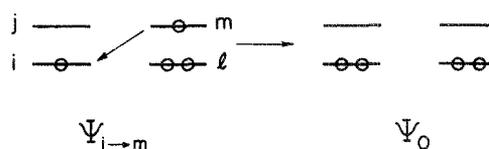
$$\Psi_0' = k_{ii}^2 k_{ll}^2 \Psi_0 + \sqrt{2} k_{ii} k_{ij} k_{ll}^2 \Psi_{i \rightarrow j} + \sqrt{2} k_{ii}^2 k_{ll} k_{lm} \Psi_{i \rightarrow m} + k_{ij}^2 k_{ll}^2 \Psi_{i \rightarrow j, i \rightarrow j} + k_{ii}^2 k_{lm}^2 \Psi_{i \rightarrow m, l \rightarrow m} + \dots \quad (18)$$

$$\Psi_{i \rightarrow m}' = - (k_{ii} k_{ll}^2 k_{mm} + k_{ii} k_{ll} k_{lm} k_{ml}) \Psi_{i \rightarrow m} - (k_{ii} k_{ll} k_{lm} k_{mm} + k_{ii} k_{lm}^2 k_{ml}) \Psi_{i \rightarrow m, l \rightarrow m} - (k_{ij} k_{ll}^2 k_{mm} + k_{ij} k_{ll} k_{lm} k_{ml}) \Psi_{i \rightarrow j, i \rightarrow m} + \dots \quad (19)$$

We have thus derived in explicit form the expansion coefficients. In the above expressions the straightforward, but algebraically complicated, correction due to the normalization factors has been dropped. It is easy to calculate the overlap integrals between these electron configurations

$$\int \Psi_0^* \Psi_{i \rightarrow m} d\tau = \sqrt{2} S_{im} + O(S_{ab}^3)$$

The contributions to this integral are shown diagrammatically below.



and



and

$$\int \Psi_{i \rightarrow m}^* \Psi_{i \rightarrow m} d\tau = -S_{il} + O(S_{ab}^3)$$

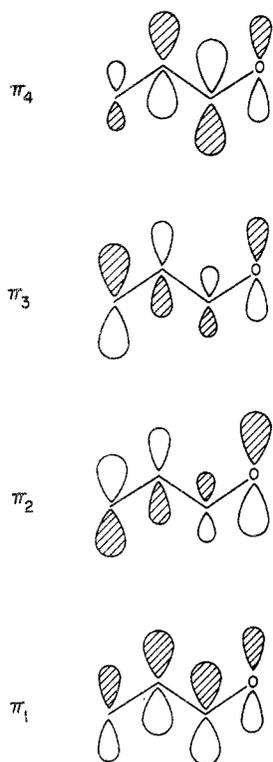
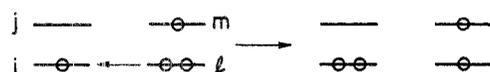


Figure 5. The π orbitals of acrolein.



$$\Psi_{i \rightarrow m} \quad \Psi_{l \rightarrow j}$$

$$\int \Psi_{i \rightarrow m}^* \Psi_{i \rightarrow m, l \rightarrow m} d\tau = S_{im} + O(S_{ab}^3)$$

$$\int \Psi_{i \rightarrow j}^* \Psi_{i \rightarrow m} d\tau = S_{jm} + O(S_{ab}^3)$$

$$\int \Psi_{i \rightarrow j}^* \Psi_{i \rightarrow j, i \rightarrow m} d\tau = S_{im} + O(S_{ab}^3)$$

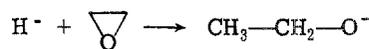
$$\int \Psi_0^* \Psi_{i \rightarrow m, i \rightarrow m} d\tau = O(S_{ab}^3) \text{ etc.}$$

Therefore, neglecting small terms, and assuming all the overlap integrals to have similar magnitudes, we have

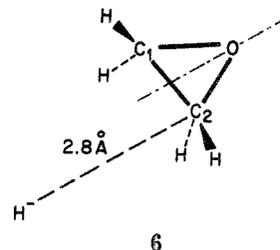
$$\int \Psi_0^* \Psi_{i \rightarrow m'} d\tau \cong -\sqrt{2}(k_{ii}^3 k_{il}^4 k_{mm} S_{im} - k_{ii}^3 k_{il}^3 k_{im} k_{mm} S_{il} + k_{ii}^2 k_{ij} k_{il}^4 k_{mm} S_{jm}) \quad (20)$$

The first term corresponds to interaction between the HOMO of A and the LUMO of B in the charge transfer from A to B. The second and third terms come from the interaction between the HOMO of A and the HOMO of B and from the interaction between the LUMO of A and the LUMO of B, respectively. It is clear that the interaction partially acquires the characteristics of an excited state reaction. Thus we may interpret the role of such perturbing agents as chemically inducing the equivalent of local electronic excitation by mixing the unoccupied levels into the occupied levels. However, far more important is that the ground-state-type and excited-state-type interactions commingle as shown in eq 20. They may have a positive effect, reinforcing each other, or a negative effect, canceling each other, depending on the nature of the perturbation.

Here we consider, as an example, the attack of hydride ion on oxirane²⁰



Hydride ion was placed 2.8 Å from one of the carbon atoms in the molecular plane, as shown in 6.²¹ The energy level of



the hydride ion was taken as -7 eV, 1.1 eV lower than the LUMO of unperturbed oxirane. The wave function of the system is given by

$$\Psi = 0.9786\Psi_0 + 0.1794\Psi_{h^- \rightarrow 10} + 0.0252\Psi_{h^- \rightarrow 11} + \dots$$

where h^- is the hydride orbital. It can be seen that the charge transfer from the hydride ion to the LUMO of the three-membered ring plays a dominant role in chemical bond formation between the two species. By placing oxirane under the influence of the point charge, the initially doubly occupied MO a_7 comes to mix with a_{10} , as was illustrated in Figure 2, in such a way as to enlarge the coefficient of the p_z AO's of the carbons. A calculation shows that the overlap integral between the hydride orbital and the LUMO of perturbed oxirane is greater than the corresponding integral in the unperturbed state. The doubly occupied MO a_7 of the isolated molecule comes to lose a fraction of its electron pair by mixing unoccupied levels into itself. Correspondingly, the overlap population between the hydride orbital and a_7 , which is negative (-0.0006) due to the electron exchange interaction, becomes less negative (-0.0002) upon introduction of the electrostatic field. The absolute value of the overlap population is small, because a_7 is antisymmetric and the hydride-carbon separation large.

The mixing of a_7 and a_{10} yields new MO's a_7' and a_{10}' . The LUMO a_{10}' of the perturbed system has a greater frontier electron density at the carbons than it had in the unperturbed molecule. This facilitates charge transfer, and therefore bond formation, between hydride and oxirane. The occupied MO a_7' has less density in the C_2 AO's than a_7 , thus decreasing the antibonding effects between hydride and oxirane. Thus there are two cooperative effects of the mixing of a_7 and a_{10} , both facilitating bond formation between oxirane and hydride.

The wave function of the system composed of oxirane and hydride, with a point charge of 0.3e, is given by

$$\Psi' = 0.8995\Psi_0' + 0.4038\Psi_{h^- \rightarrow 10}' + 0.0258\Psi_{h^- \rightarrow 11}' + \dots$$

$$= 0.8984\Psi_0 + 0.4034\Psi_{h^- \rightarrow 10} + 0.0258\Psi_{h^- \rightarrow 11} + 0.0320\Psi_{7 \rightarrow 10} + \dots$$

Here the energy level of hydride was tentatively taken as -7.0 eV, the same as in the unperturbed case. The greater mixing of the charge-transferred state $\Psi_{h^- \rightarrow 10}$ in Ψ' than in the unperturbed wave function Ψ is due to the somewhat artificial way of choosing the energy of the hydride orbital.

The LUMO of ethylene oxide was lowered in the presence of a potential field.²² Such a lowering of the LUMO and an elevation of the HOMO may represent another way in which static and dipolar fields can influence the course of chemical reactions.

The overlap integral between an MO of A and an MO of B can be decomposed into intermolecular AO pair overlaps. For instance, we have

$$\int \Psi_0'^* \Psi_{i..m}' d\tau = \sum_r^A \sum_s^B k_{rs}' S_{rs} \quad (21)$$

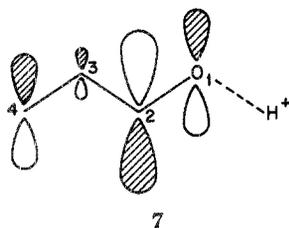
$$k_{rs}' \cong -\sqrt{2}(k_{ii}^3 k_{ii}^4 k_{mm} c_{ir} c_{ms} - k_{ii}^3 k_{ii}^3 k_{ii}^3 k_{mm} c_{ir} c_{is} + k_{ii}^2 k_{ij} k_{ii}^4 k_{mm} c_{jr} c_{ms})$$

The terms on the right-hand side of eq 21 reinforce each other by having the same sign for certain intermolecular AO pairs r and s , and weaken each other by possessing different signs for other AO pairs. In the above example, the overlap between the hydride orbital and the $2p_z$ AO of the carbon of oxirane was strengthened. The effect of the perturbation is very selective and specific. This, of course, is the most interesting point of the influence of an external field.

In summary thermal intermolecular interaction in a perturbing field is characterized by the acquisition of some features of what in the isolated, unperturbed system would be excited-state interaction. The precise mode of mixing in of such excited states is of key importance in activating or deactivating specific sites in a molecule.

Orbital Interchange and Degeneracy

Finally we must add another possible effect of external perturbation. In a recent paper Houk and Strozier pointed out the LUMO of acrolein is greatly modified, both in energy and in shape, by the presence of a proton.²³ We carried out a similar calculation by the CNDO/2 method.²⁴ The unperturbed π MO's of acrolein and the LUMO of the protonated acrolein with the proton 2.0 Å from oxygen are shown in Figure 5 and in 7, respectively. The change in the



LUMO, as noted by Houk and Strozier, is remarkable. The perturbation is also much greater than in the corresponding oxirane case discussed in the preceding sections.

The LUMO of unperturbed acrolein has maximum frontier electron density at C_4 , while protonated acrolein has it at C_2 . By expanding the perturbed LUMO in terms of unperturbed MO's we have

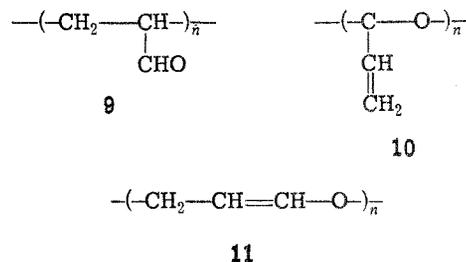
$$\pi_3' = -0.0046\pi_1 - 0.2285\pi_2 + 0.8097\pi_3 + 0.5404\pi_4$$

π_2 and π_3 mix in such a way as to increase the frontier electron density both at C_2 and C_4 . However, the dominant effect is brought about by mixing in of π_4 , increasing further the density at C_2 , and decreasing the density at C_4 . One

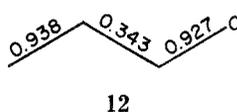
reason why π_3 mixes better with π_4 than with π_2 may be the greater energy separation between π_3 and π_2 than that between π_3 and π_4 . However this calculation suggests another important phenomenon. The π_4 orbital has greater electron density in the carbonyl bond region, while π_3 is more localized in the vinyl bond region. Therefore π_4 will be more stabilized by the presence of a proton than π_3 . The separation between π_3 and π_4 is about 4.8 eV in the isolated state, but it is about 3.3 eV in the field of a proton.

Higher unoccupied MO's may be more perturbed by an external perturbation than the LUMO and come closer to the LUMO. In the extreme case these higher lying vacant levels may even come lower than the original LUMO. In other circumstances lower lying occupied MO's may be more destabilized by an external field than the HOMO. In such a case we can expect the frontier electron density distribution to be quite different from that in an unperturbed state.²⁵

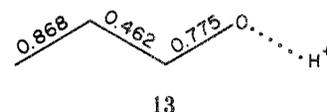
Acrolein provides an example of this kind of perturbation. The Diels-Alder reaction of methylacrylate with diene in the presence of Lewis acid gave a different mixture of products from that obtained without catalysis.²⁶ Polymerization of acrolein can take place through the opening of a vinylic bond, 9, through the opening of the carbonyl bond, 10, or through the migration of a double bond, 11. The polyacetal, 10, is obtained only when the polymerization is initiated by a strong anionic catalyst, *e.g.*, sodium naphthalene, in a polar solvent, *e.g.*, tetrahydrofuran, and at low temperatures.²⁷ In this case the counterion, *e.g.*, Na^+ , in cooperation with solvent molecule(s), will presumably influence the acrolein, activating the carbonyl group.



The π bond orders of unperturbed and perturbed acrolein are shown in 12 and 13. Bond alternation takes place in such a manner as to strengthen the C_2-C_3 bond and weaken the O_1-C_2 and C_3-C_4 bonds.²⁸ The stretching of a given bond causes the elevation of the MO's having no node and the lowering of the MO's possessing a node in that bond region.²⁹ The shortening of a bond has an opposite effect. In the case of acrolein the stretching of C_2-O_1 and C_3-C_4 bonds and shortening of the C_2-C_3 bond will lower the energy of the LUMO, because that orbital has a node between O_1 and C_2 .



12



13

An analysis similar to that of this section has been independently carried out by Imamura and Hirano.³⁰

In this paper we have discussed several possible modes by which a reagent could affect the reactivity of an organic molecule. Field effects, orbital overlap, charge transfer, and polarization may operate independently or cooperatively, depending on the system in question. No doubt the influ-

ence of solvents or catalysts upon chemical reactions is not so simple that it can be treated fully by the approximate MO methods that we have applied. We have also not examined all possible interactions.³¹ Our work suggests, however, that appropriately modified frontier electron densities calculated by idealizing the external perturbation may be helpful in understanding and predicting the chemical reactivity of organic molecules. Also it is anticipated that in the near future accurate MO calculations will become available for chemically interacting systems explicitly including solvent molecules and catalytic species. The methodology developed here can be easily applied to other modes of calculation, with, it is hoped, further insight into the nature of chemical reactivity resulting therefrom.

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$$h_{ij} = 0.875S_{ij}(h_{ii} + h_{jj})$$

A similar result was obtained by the use of

$$h_{ij} = 0.875S_{ij}(h_{ii}^0 + h_{jj}^0) + 0.5S_{ij}(\Delta_{ii} + \Delta_{jj})$$