1,1- or 1,3-Addition Mechanism of Olefin Epoxidation with Organic Peroxy Acids. A Molecular Orbital Study

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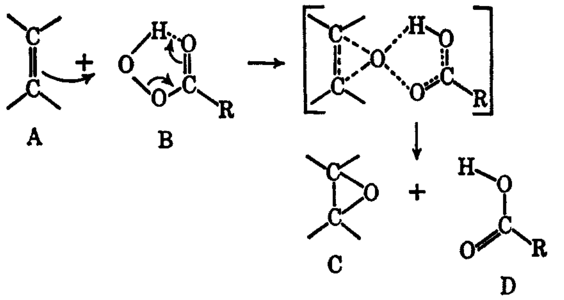
The electronic structure of the peroxy acid molecule in its intramolecularly hydrogen bonded (B) and dipolar (B^+) form has been investigated using the semiempirical Pariser–Parr–Pople SCF-MO method. On the basis of the π-electron distribution and the observed relatively small difference between the total energies of both molecular species ($E_{B^+} - E_B = 0.03$ eV), it was concluded that both proposed mechanisms, namely 1,1 and 1,3 addition, are theoretically possible, the first mechanism being more probable in nonpolar and the second in polar media.

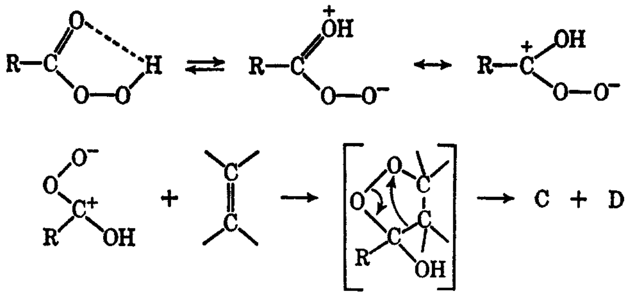
While there are several studies of epoxidation with peroxy acids to be found in the literature,[2–5] the question of the mechanism of this interesting reaction is still open. Bartlett[6] was the first to propose the nucleophilic attack of olefin on electrophilic peroxy acid molecule, *i.e.*, the molecular 1,1-addition mechanism of epoxidation reaction, according to Scheme I.

SCHEME I



The small negative value of the Hammett ρ constant,[3] the absence of general acid and neutral salt effect, and the rather high negative entropy of activation,[4] as well as the established evidence of strong intramolecular hydrogen bonding in aliphatic[7] and aromatic[8] peroxy acids, have been taken as a support to the proposed mechanism. Recently, Kwart and Hoffman[9] proposed the possibility of epoxidation mechanism involving 1,3-dipolar addition of a hydroxycarbonyl oxide (derived from intramolecularly hydrogen-bonded peroxy acid molecule) to the olefinic dipolarophile as shown in Scheme II. Strong parallelism between general kinetic characteristics and reactivity parameters of epoxidation on one, and 1,3-dipolar addition[10] on the other hand, has been taken as a support to this presumption.

SCHEME II



Bingham, Meakins and Whitham[11] have investigated kinetically epoxidation of cyclohexene and norbornene with peroxylauric acid in methylene chloride at 25°. They presumed that, if 1,3-dipolar addition is really involved in epoxidation reaction, norbornene should react much more readily than cyclohexene. On the basis of approximately the same second-order rate constants for epoxidation of both olefins they concluded that dipolar addition mechanism is not the rate-determining step in the norbornene–peroxylauric acid reaction.

It is our intention to present in this paper the results of quantum mechanical evaluation of both proposed mechanisms.

Method of Calculation.—The calculations were made to show which atom in the molecule of peroxy acid is the most reactive. For this purpose the semiempirical Pariser–Parr–Pople SCF-MO method[12,13] and the following reactivity indexes were used: charge density, localization energy, and frontier electron density.

The parameters were chosen in the semiempirical manner. The evaluation of γ_{AA} was made from the equation

$$\gamma_{AA} = I_{AA} - A_{AA}$$

(one-center integrals)

where I_{AA} is the valence-state ionization potential and A_{AA} is the valence-state electron affinity of atom A. The required values were taken from the paper by Hinze and Jaffé.[14] Two-center integrals were evaluated with Mataga–Nishimoto formula.[15] In the calculation on the intramolecularly hydrogen-bonded molecule the influence of the H atom was introduced and the values of the ionization potentials of the atoms O_2 and O_3 were changed from their normal values. The resonance

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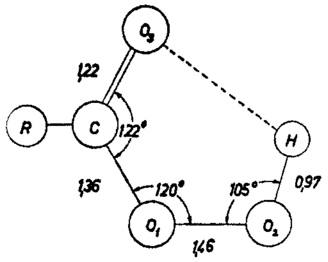

Figure 1.—The geometry of intramolecularly hydrogen-bonded peroxy acid molecule. Bond lengths are in angstroms.

integral was introduced between O_2 and O_3 for the same purpose.[16] In the dipolar form of the peroxy acid molecule the ionization potential of O_2^- was approximated as affinity of the atom O and the affinity, as the energy required to bring electron from the infinity to the distance of van der Waals radii. For the ionization potential of O_3^+ the value of the second ionization potential was used and the affinity was approximated as the first ionization of atom O. The geometry of the peroxy acid molecule in Figure 1 was taken from the literature.[7,17,18] Resonance integrals were obtained by using the method proposed by I'Haya.[19] Tables I and II summarize all the used parameters.

Table I

Atom	One- and two-center integrals			
	O_1	O_2	O_3	C
O_1	13.1			
O_2	7.9	13.1		
O_3	5.8	5.0	13.1	
C	7.9	5.3	8.4	10.5

Table II

Atom	Resonance integrals, eV
C − O_1	−1.70
C − O_3	−2.00
O_1 − O_2	−0.90
O_2 − O_3	−0.20[a]

[a] On account of the hydrogen bonding.

Results and Discussion

Charges and bond orders of intramolecularly hydrogen bonded and dipolar form of peroxy acid molecule are in Figure 2. The localization energy on the atoms O_1 and O_2 are 0.5 and 0.1 eV, respectively, and the frontier electron densities are 0.16 and 0.02. The total energy of π electrons, and the core in molecule B and B^+ were calculated. The difference is $E_{B^+} - E_B = 0.03$ eV.

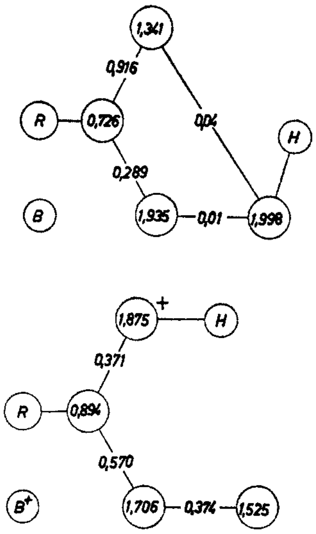

Figure 2.—Charges and bond orders in intramolecularly hydrogen bonded (B) and dipolar (B^+) form of the peroxy acid molecule.

On the basis of the above-mentioned results, it can be concluded that the oxygen atom next to hydrogen in the peroxycarboxyl group is most likely the place where a nucleophile, in our case the olefin molecule, attacks the peroxy acid molecule. This is quite in keeping with the proposed 1,1-addition mechanism. The π-electron distribution in the dipolar form of peroxy acid molecule, on the other hand, is also in agreement with 1,3-dipolar addition mechanism. The relatively small difference between the total energies of intramolecularly hydrogen bonded and dipolar form of peroxy acid molecule allows the conclusion that both proposed mechanisms are theoretically possible. It is reasonable to assume that 1,1-addition mechanism is more probable in nonpolar and 1,3-dipolar addition mechanism in polar media.

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