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A Molecular Orbital Investigation of the Electronic Structures of Alkyl Peroxides. II.*1 Peracids and Peresters

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The electronic structures of several alkyl peroxides including the carbonyl group, *i. e.*, performic acid, peracetic acid and their methyl esters, are investigated by the extended Hückel method proposed by Hoffmann. The structure of the bond between peroxy oxygens, the intramolecular hydrogen bonding in peracid, the pyrolysis of peracid which is caused by the fact that the bond strength between peroxy oxygen atoms is weakened by an intramolecular hydrogen bonding, and the reaction mechanism of both the epoxidation of olefin by peracid and the ionic decomposition of peresters by basic catalysts can be successfully explained on the basis of the calculated results.

It is well known that organic peroxides have become important both in the studies of oxidation mechanisms and in connection with the polymerization processes. However, hardly no calculations of their electronic structures have been reported except for one with hydrogen peroxide,[1-3] and their reaction mechanisms have only been interpreted by the organic electronic theory.

In a previous paper,[4] we reported that the physicochemical properties and the reaction mechanisms of hydrogen peroxide and some lower alkyl hydroperoxides could be interpreted by the molecular orbital method. In the present paper, the electronic structures of several organic peroxides including the carbonyl group, *i. e.*, performic acid, peracetic acid, and their methyl esters, will be calculated by the extended Hückel method proposed by Hoffmann,[5] and the intramolecular hydrogen bonding in peracid, the epoxidation of olefin by peracid, and the ionic decomposition of peresters by a basic catalyst will be discussed.

Method of Calculation

The calculations are based upon the extended Hückel method proposed by Hoffmann.[5] As is shown in Eq. (1), the ith molecular orbital, φ_i, is represented by a linear combination of valence atomic orbitals (AO), χ_r:

$$\varphi_i = \sum C_r{}^i \chi_r, \tag{1}$$

where $C_r{}^i$ is a coefficient of the rth AO in the ith molecular orbital.

The secular determinant includes all the overlap integrals, S_{rs}, as in Eq. (2):

$$|H_{rs} - \varepsilon S_{rs}| = 0 \quad (r, s = 1, 2, \cdots, n), \tag{2}$$

The Coulomb integral, H_{rr}, of an atomic orbital is put equal to the negative value of an ionization potential of the valence state of neutral atom.[6] The values adopted are tabulated in Table 1.

TABLE 1. COULOMB INTEGRAL OF VARIOUS ATOMIC ORBITALS, H_{rr} (eV)[6]

Atom	Orbital		
	1s	2s	2p
Hydrogen	−13.60	—	—
Carbon	—	−21.43	−11.42
Nitrogen	—	−27.50	−14.49
Oxygen	—	−35.30	−17.76

The resonance integral, H_{rs}, between the rth and the sth AO's is given by Eq. (3):

$$H_{rs} = 0.875 \times (H_{rr} + H_{ss}) \times S_{rs}, \tag{3}$$

where S_{rs} is the overlap integral between the rth and sth AO's. The overlap integrals, S_{rs}, are calculated by using the bond distances[7] and the

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*1 Part I: T. Yonezawa, O. Yamamoto, H. Kato and K. Fukui, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 26 (1966).

1) W. G. Penney, G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

2) R. S. Mulliken, *ibid.*, **3**, 506 (1935).

3) Y. Amako, P. A. Giguère, *Can. J. Chem.*, **40**, 765 (1962).

4) T. Yonezawa, O. Yamamoto, H. Koto and K. Fukui, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 26 (1966).

5) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

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7) L. E. Sutton, "Interatomic Distances of Molecules and Ions," the Chemical Society, London (1958).

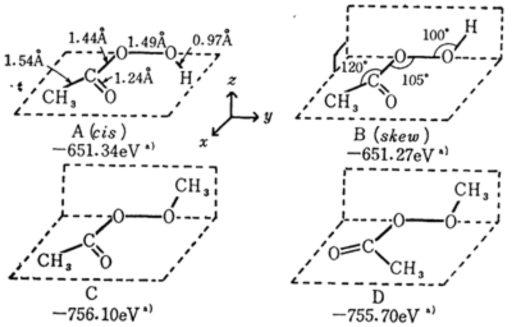


Fig. 1. Configurations of peracid and perester for calculation of S_{rs}.
a) calculated total energy

TABLE 2. POPULATION ANALYSIS

AO population	$N_r = \sum_i^{\text{occ}} \nu_i [(C_r{}^i)^2 + \sum_{s \neq r} C_r{}^i C_s{}^i S_{rs}]$
Partial AO population	$n_r{}^i = \nu_i [(C_r{}^i)^2 + \sum_{s \neq r} C_r{}^i C_s{}^i S_{rs}]$
Atom population	$M_{\text{A}} = \sum_r^{\text{on A}} N_r$
AO bond population	$N_{rs} = 2 \sum_i^{\text{occ}} \nu_i C_r{}^i C_s{}^i S_{rs}$
Atom bond population	$M_{\text{AB}} = \sum_r^{\text{on A}} \sum_s^{\text{on B}} N_{rs}$

bond angles⁷⁾ in Figs. 1A and 1B. The values which have not yet been measured are estimated on the assumptions that a carbon atom in the alkyl group is tetrahedral with C–H=1.09 Å, that $CH_3C(=O)OO$ is coplanar with a bond angle of 120° for the carbonyl carbon atom, and that the dihedral angle is 90°. The various populations calculated are defined as in Table 2,⁸⁾ where ν_i is the number of electrons occupying the ith molecular orbital.

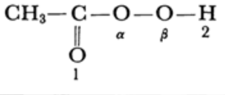
Results and Discussion

The Structures of Peracids and Peresters. Giguère *et al.*⁹⁾ and Swern *et al.*¹⁰⁾ have made clear, by the study of infrared spectra, that the aliphatic peracids have intramolecular hydrogen bonding, and Giguère proposed a "two-dimensional structure" (cis-form) for performic and peracetic acid (Fig. 1A). On the other hand, Swern proposed a structure of a skew-form with a dihedral angle of 72° (Fig. 1B) from the observed dipole moment values for higher aliphatic peracids. For peresters, two kinds of structures are possible, *i. e.*, where the carbonyl group is oriented either inward or outward (toward the O–O group) (Fig. 1C and Fig. 1D).

A typical perester is *t*-butyl ester, but in the present paper, for the sake of simplification, we will treat methyl esters, *i. e.*, methylperoxy formate and acetate, on the assumption that their structures are of a skew-form with a dihedral angle of 90°. Figure 1 gives the total electronic energy of each configuration of peracetic acid and methylperoxy acetate. For peracetic acid, the cis-form is shown to be more stable, by about 1.8 kcal/mole, than the skew-form; this difference may be regarded as a delocalization energy⁸⁾ due to hydrogen bonding, and it almost agrees with the experimental heat of formation for hydrogen bonding. For methylperoxy acetate, the C structure, in which the carbonyl group is oriented inward, is more stable. These results are in accordance with the conclusion of Silbert *et al.*¹¹⁾ pointing out that the carbonyl group of diacyl peroxide is oriented inward from the observed values of dipole moment.

Table 3 gives the formal charge, Q_{A}, and the atom bond population, M_{AB}, of peracetic acid and methylperoxy acetate. For a cis-form of peracetic acid, the M_{AB} value between H_2 and O_1 (M_{H2-O1}) is positive; this intramolecular hydrogen bonding may contribute to the lowering of the total electronic energy. Moreover, $M_{H2-O\beta}$ decreases in a cis-form, and the negative charge of O_1 in peracetic acid in the cis-form is less than that in the skew-form, while the negative charge of O_β increases in the cis-form. All of these facts indicate that the electron of the carbonyl group of the cis-form is transfered toward O_β and that a bond strength of O_β–H_2 is weakened by an intramolecular hydrogen bonding. Further, a comparison of the formal charges, Q_{A}, of α- and β-oxygen ($Q_{O\alpha}$ and $Q_{O\beta}$) indicates that in both peracetic acid and methylperoxy acetate O_β is more negative than O_α. In the following discussions we will adopt a cis-form for peracids and the structure shown in

TABLE 3. CALCULATED VALUES OF M_{AB} AND Q_{A} OF PERACETIC ACID AND METHYLPEROXY ACETATE



$$\underset{\underset{1}{\text{O}}}{\overset{}{CH_3-\underset{\|}{C}}}-\underset{\alpha}{O}-\underset{\beta}{O}-\underset{2}{H}$$

		$CH_3C(=O)OOH$		$CH_3C(=O)OOCH_3$
		A(*Cis*)	B(Skew)	C
M_{AB}	O_1–H_2	0.032	−0.001	—
	O_β–H_2	0.468	0.480	—
Q_{A}	O_α	−0.520	−0.521	−0.547
	O_β	−0.667	−0.636	−0.600
	O_1	−1.326	−1.351	−1.351

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8) K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin **38**, 1263 (1965).

9) P. A. Giguère and A. W. Olmos, *Can. J. Chem.*, **30**, 821 (1952).

10) D. Swern and L. S. Silbert, *Anal. Chem.*, **35**, 880 (1963).

11) L. S. Silbert, L. P. Witnauer, D. Swern and C. Ricciuti, *J. Am. Chem. Soc.*, **81**, 3244 (1959).

TABLE 4. CALCULATED VALUES OF N_{rs} OF OXYGEN-OXYGEN BOND IN PERACETIC ACID (*Cis*)

	$S_{O\alpha}$	$X_{O\alpha}$	$Y_{O\alpha}$	$Z_{O\alpha}$
$S_{O\beta}$	−0.023	−0.001	0.044	0
$X_{O\beta}$	0.005	−0.012	0.017	0
$Y_{O\beta}$	0.119	0.031	0.284	0
$Z_{O\beta}$	0	0	0	−0.018

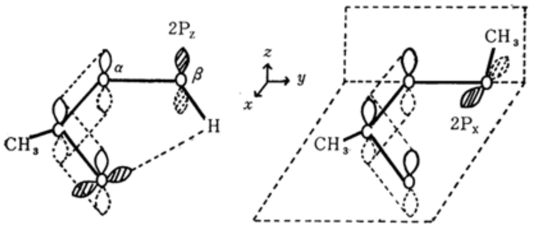


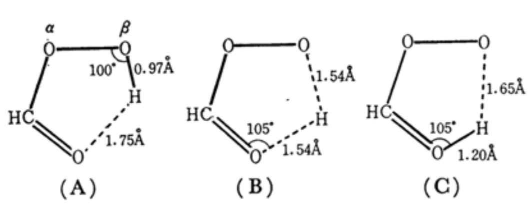
Fig. 2. π-orbitals and lone pair of peracetic acid and methylperoxy acetate.

Fig. 1C, in which the carbonyl group is oriented inward, for peresters.

Next, let us consider the characteristics of each bond. Table 4 gives the AO bond population, N_{rs}, of an oxygen-oxygen bond in peracetic acid (cis), where $S_{O\alpha}$ and $X_{O\alpha}$ represent the 2S and $2P_X$ orbitals of α-oxygen. As is shown in Fig. 2, the bond axis between oxygen atoms is taken for the Y-direction, while the π-orbitals are taken for the Z-direction. In view of the calculated values of N_{rs}, it is obvious that the nature of the oxygen-oxygen bonding is predominantly of the Pσ-character ($Y_{O\alpha}$–$Y_{O\beta}$) and that it shows little π-character ($Z_{O\alpha}$–$Z_{O\beta}$). On the other hand, the N_{rs} value between π-orbitals is 0.134 for the C=O bond and 0.059 for the C–O bond. Consequently, as Fig. 2 shows, the C=O and C–O bonds have the π-character. Methylperoxy acetate also shows the same results. In β-oxygen, the N_r of the $2P_z$ orbital of peracetic acid is 1.999 and the N_r of the $2P_x$ orbital of methylperoxy acetate is 1.937. These orbitals are considered to have no interaction with other orbitals and to be lone pairs.

The Pyrolysis of Peracids. In the pyrolysis of peracids,[12–14] there occurs not only a radical decomposition, as is shown in Eq. (4), but also the decomposition shown in Eq. (5), in which the bond strength between oxygen atoms is weakened by an intramolecular hydrogen bonding, resulting in the elimination of β-oxygen.

$$\mathrm{RC({=}O)OOH} - \mathrm{RC({=}O)O\cdot} + \mathrm{\cdot OH} \qquad (4)$$



(A) $M_{O\alpha-O\beta}=0.367$ (B) $M_{O\alpha-O\beta}=0.354$ (C) $M_{O\alpha-O\beta}=0.350$

Fig. 3. Calculated values of $M_{O\alpha-O\beta}$ of performic acid in various configurations.

$$\mathrm{RC({=}O)OOH} - \mathrm{RC({=}O)OH} + (1/2)\mathrm{O_2} \qquad (5)$$

To examine the effect of the intramolecular hydrogen bonding on the bonding between oxygen atoms, we calculated the electronic structures of performic acid at various O–H bond distances. Their configurations are given in Fig. 3.

The atom bond population between oxygen atoms, $M_{O\alpha-O\beta}$, are given in Fig. 3 (under each configuration). With the increase in the bond distance between O_β–H, the value of $M_{O\alpha-O\beta}$ decreases; this means that, as the distance of O_β–H increases, the bond strength between oxygen atoms becomes weak and β-oxygen tends to be eliminated. This agrees with the experimental observations of Eq. (5).

The Nature of the Lowest Vacant Orbital. Peroxides easily react with the nucleophilic reagents, as will be described later. Therefore, we will now consider the lowest vacant orbitals (LV). Table 5 shows that the energy of LV in both peracids and peresters is lower than with other compounds, such as ethane, and that they are apt to accept an electron. This agrees with the tendency of the half-wave potential[15] in polarography. It is known from the partial AO population, n_r, in Table 5 that LV is an anti-bonding orbital which is localized in Pσ orbitals between two oxygen atoms*2 (for example, the partial AO bond population for the Pσ (O_α–O_β) of performic acid is −0.243, and the n_r^{LV} value of both peracids and peresters become largest in the Pσ orbital). Accordingly, the nucleophilic reagents will react with the Pσ orbital of β-oxygen.[4]

The Epoxidation of Olefin. Waters *et al.*[16] proposed a mechanism of the epoxidation of olefin by peracid in which the π-electron in C_2 of olefin nucleophilically attacks the β-oxygen of peracid, and in which a heterolytic breakage of the oxygen-oxygen bond of peracid takes place, consequently forming epoxide and acid.

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[12] C. Schmidt, A. H. Sehon, *Can. J. Chem.*, **41**, 1819 (1963).

[13] W. E. Parker, L. P. Witnauer and D. Swern, *J. Am. Chem. Soc.*, **80**, 323 (1958).

[14] T. Suzuki, I. Iwamoto and S. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 1212 (1962).

[15] a) W. E. Parker, C. Ricciuti, C. l. Ogg and D. Swern, *J. Am. Chem. Soc.*, **77**, 4037 (1958); b) L. S. Silbert, L. P. Witnauer, D. Swern and C. Ricciuti, *J. Am. Chem. Soc.*, **81**, 3244 (1959).

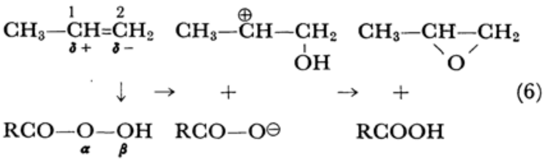
*2 In the present treatment, the next lowest vacant orbital is a α-orbital which is localized in the carbonyl group. This orbital lies in close proximity to LV.

[16] W. A. Waters, H. Gilman "Organic Chemistry," Vol. IV (1953).

TABLE 5. NATURE OF THE LOWEST VACANT ORBITAL (LV)

Compound	n_r^{LV}		Energy of LV, eV (Calc.)	$E_{1/2}$[a] V (Obs.)
	$P\sigma(O_\alpha)$	$P\sigma(O_\beta)$		
HC(=O)OOH	0.804	0.960	−11.03	0−−0.06
$CH_3C(=O)OOH$	0.801	0.866	−11.05	
$HC(=O)OOCH_3$	0.896	0.940	−10.95	−0.82−−0.96
$CH_3C(=O)OOCH_3$	0.774	0.869	−10.94	
C_2H_6	—	—	3.13	—

a) Half-wave potential[15] for long-chain aliphatic peracids (C_8-C_{16}) and *t*-butyl peresters.



(6)

We will consider the mechanism of the first step in epoxidation by the molecular orbital method. The highest occupied orbital (HO) of ethylene and propylene is a π-orbital. Moreover, the n_r^{HO} of the $2P_\pi$-atomic orbital of propylene is 0.685 for C_1 and 1.069 for C_2. Consequently, the $2P_\pi$-atomic orbital of C_2 may take part in an electrophilic attack. As has been previously stated, the LV of peracid is an anti-bonding Pσ orbital which shows a strongly repulsive nature in the oxygen-oxygen bond, and the Pσ-orbital*[3] of β-oxygen is the active position for a nucleophilic reaction. These active positions agree with the Waters mechanism.[16] Therefore, we assumed the transition state of epoxidation to be as shown in Fig. 4A. The performic acid - propylene system,*[4] in which the $O_\beta \cdots C_2$ distance is 1.5 Å, was chosen as a model for examining the electronic structure of the assumed transition state.

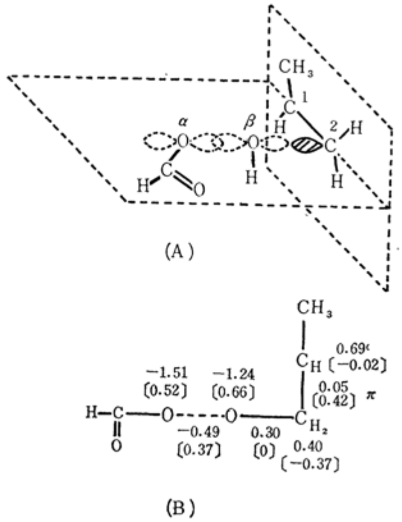


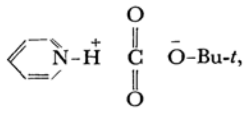
Fig. 4. (A) Model of transition state of epoxydation $O_\beta-C_2=1.5$Å
(B) Calculated values of M_{AB}, N_{rs}, and Q_A at transition state
Bracket shows the values of free molecules before the formation of the " complex ".

The calculated values of the Q_A, M_{AB} and N_{rs} of carbon and oxygen atoms are given in Fig. 4B. The bracket shows the values of free molecules before the formation of the complex. Before the formation of the complex, the N_{rs} of the $2P_\pi$-atomic orbital of propylene is 0.42, with a strong π-bonding, but after the complex formation it decreases to 0.05, indicating that the π-bonding has disappeared. The M_{AB} between C_2 in propylene O_β in performic acid ($C_2 \cdots O_\beta$) shows a plus value of 0.30, while the M_{AB} between oxygen atoms of performic acid shows a minus value of −0.49. Therefore, we can find that the O_β–C_2 bond becomes relatively stable and that, at the same time, the O_α–O_β bond becomes weak. From the calculated values of Q_A's in the "complex," it is obvious that the electrons are transferred from propylene to performic acid, and that as a result the C_1 of propylene has a large positive charge and the O_α of performic acid has a large negative charge. These results also agree with the Waters mechanism.

Base-Catalyzed Decomposition of the Perester. Pincock[17] pointed out that *t*-butylperoxy formate (TBF) undergoes a bimolecular ionic decomposition, with the formation of *t*-butyl alcohol and carbon dioxide, when catalyzed by low concentrations of the base (pyridine, triethyl amine, solid sodium carbonate) (Eq. (7)):

$$\text{H-C(=O)-O-O-Bu-}t \xrightarrow{\text{base}} CO_2 + t\text{-BuOH}. \quad (7)$$

As the mechanism, he proposed the concerted ionic decomposition, in which pyridine attacks formate hydrogen nucleophilically.



(8)

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*[3] The direction of the oxygen-oxygen bond axis.

*[4] For the sake of simplification, this system will be called the "complex."

17) R. E. Pincock, *J. Am. Chem. Soc.*, **86**, 1820 (1964).

TABLE 6. CALCULATED VALUES OF Q_A AND M_{AB} OF METHYLPEROXY FORMATE, AMMONIA, AND ASSUMED TRANSITION STATES

		NH_3	HCO_3CH_3	Case I	Case II	Case III
Q_A	H_1	—	0.112	0.415	0.192	0.155
	O_α	—	−0.544	−0.978	−0.720	−0.648
	O_β	—	−0.596	−1.259	−1.390	−0.594
	C_2	—	1.748	1.796	1.698	1.311
	N	−1.198	—	−0.450	−0.293	−0.604
M_{AB}	H_1-C_2	—	0.811	0.467	0.906	0.791
	O_α-O_β	—	0.356	−0.188	−0.210	0.352
	C_2-O_α	—	0.530	0.669	0.544	0.439

Therefore, we will now treat the electronic distributions in three kinds of "complexes," when ammonia interacts with the formate hydrogen (case I), peroxide oxygen (case II), and carbonyl carbon (case III) of methylperoxy formate (MPF), as is shown in Fig. 5. The calculated values of the formal charge, Q_A, and the atom bond population, M_{AB} are given in Table 6. In all these cases, I, II and III, the negative charge of the nitrogen atom in ammonia decreases. Case III shows that the positive charge of carbonyl carbon, Q_{C2} and $M_{C2-O\alpha}$ decrease, while the $Q_{O\alpha}$, $Q_{O\beta}$ and $M_{O\alpha-O\beta}$ of peroxide oxygen undergo no change. On the other hand, cases I and II show that the negative charge of O_β, $Q_{O\beta}$, increases and $M_{O\alpha-O\beta}$ becomes negative and the O_α–O_β bond becomes weak. Consequently, in cases I and II we can find that the electron of ammonia transfers to the LV of MPF. In case I, moreover, M_{H1-C2} greatly decreases and the H_1–C_2 bond becomes weak. Hence, our theoretical results as to case I may support the proposition by Pincock, in which the basic catalyst attacks formate hydrogen nucleophilically and the decomposition proceeds in a concerted mechanism (Eq. (8)).

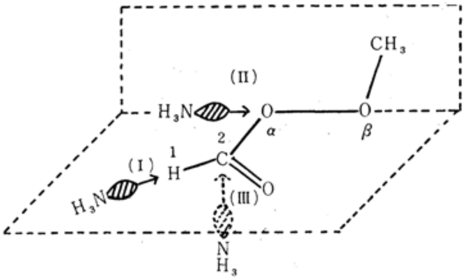

Fig. 5. Assumed transition state of ionic decomposition of methylperoxy formate by basic catalyst.
case I: $H—NH_3=1.1Å$
case II: $O—NH_3=1.6Å$
case III: $C—NH_3=1.4Å$

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