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MO Calculation for Interactions of Cu(II) and Co(III) with Hydroperoxides

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Synopsis. By means of MO calculation, cobalt(III) and copper(II) were considered to decompose primary and secondary hydroperoxides through the oxidative fission of their O–H bond. However, in basic solvents such as pyridine, copper(II) was found to promote the fission of their C–H bond of the α-position by the complex formation with them.

By the use of the extended Hückel and the simple Hückel MO method, Yonezawa *et al.* discussed the catalytic decomposition of *t*-butyl hydroperoxide (*t*-butyl HPO) by transition metals.1) The interaction of methyl HPO with lower-valent transition metals was also studied by MO calculation.2) However, no calculation has been carried out for the Cu(II)-HPO system, in which Cu(II) shows interesting catalytic activities.3)

Previously, we have ourselves studied the catalytic action of copper(II) chloride in the decomposition of primary and secondary HPOs (—1,2,3,4-tetrahydro-1-naphthyl, benzyl and cyclohexenyl HPOs—) in pyridine and suggested that the reaction proceeds through an ionic dehydration by the pyridine-Cu(II) system.4) The carbon-hydrogen bond of the α-position is considered to be weakened by the coordination of the HPOs to Cu(II) through the O lone-pair electron.

The present study has been undertaken in an attempt to obtain support for the mechanism of the ionic dehydration and also to elucidate the catalytic action of Cu(II) in the radical decomposition of HPO by the comparison with that of Co(III).

Method of Calculation

The semi-empirical SCF-MO method with the CNDO-type approximation was used. The reasonance integral, H_{rs}, was calculated by means of Wolfsberg-Helmholz approximation:6) $H_{rs}=-kS_{rs}(I_r+I_s)$ where k was taken as 0.5 for the atomic orbital (AO) pair including the d-orbital and as 0.4 for the AO pair including only s- and p-AOs. For an atom pair which do not form a bond, H_{rs} is taken as zero. Slater-type AOs were used for the s- and p-AOs, and the double-ζ type orbital was used for the d-orbital.7) The two-atomic part of the total energy, E_{AB}, proposed by Pople *et al.*,8) was used as a measure of the strength of the bond between A and B, atoms.5) The MO calculations were carried out for a closed-shell system, followed by the correction for an unpaired electron, because Cu(II)-HPO systems have odd numbers of electrons.

As model compounds for primary and secondary HPOs, methyl HPO (MHPO) and 1-methylallyl HPO(MAHPO) were employed. Square planar Cu(II)$(NH_3)Cl_2$ was used as a model catalyst in pyridine, and Co(III)$(OH)_5$ was employed as a cobalt catalyst in the non-basic solvent. The bond lenghts and bond angles of these compounds were estimated from the values in the literature;9) the distance between Cu(II) or Co(III) and the oxygen atom of HPO was taken as 1.95 or 2.22 Å respectively.

Results and Discussion

Cu(II) Catalyst. Cu(II) is considered to form a complex with HPOs, as is shown in Fig. 1. Calculations were carried out for both the O_1- and O_2-coordinations; the results are given in Tables 1 and 2.

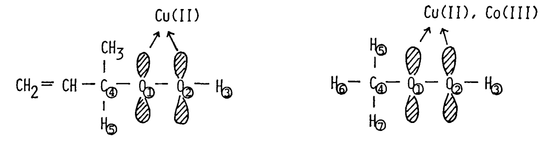
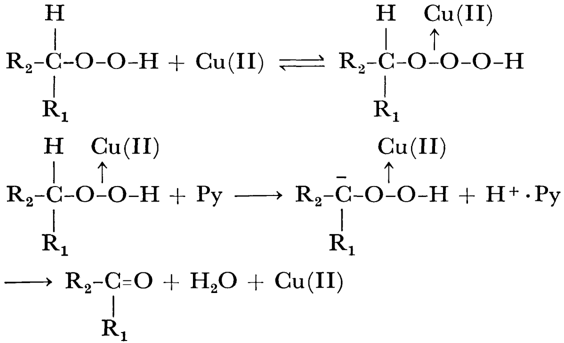


Fig. 1. Coordination position of MHPO and MAHPO.

The values of E_{total} and E_{Cu-O} show that, in both MHPO and MAHPO complexes, O_1 coordination is preferable to O_2 one. These results disagree with those of the previous study1) in which it was proposed, from the consideration of the orbital electron density of free HPO, that the metal ion forms a complex with HPO through the O_2 lone pair. However, it is more probable that the O_1 complex is a major species in the reaction, because the Cu(II)-HPO complex seems more suitable than free HPO for the discussion of the coordination position. As can be seen from the tables, the C–H bonds of the α-position are weakened by the coordination of the HPOs to Cu(II), since the absolute value of E_{C-H} is decreased by 0.09—0.16 eV. Therefore, these results support the reaction mechanism for the ionic dehydration of primary and secondary HPOs by the Cu(II)-pyridine system previously proposed:



$$R_2\text{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R_1}{|}}{C}}\text{-O-O-H} + \text{Cu(II)} \rightleftharpoons R_2\text{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R_1}{|}}{C}}\text{-}\overset{\overset{\displaystyle \text{Cu(II)}}{\uparrow}}{O}\text{-O-H}$$

$$R_2\text{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R_1}{|}}{C}}\text{-}\overset{\overset{\displaystyle \text{Cu(II)}}{\uparrow}}{O}\text{-O-H} + \text{Py} \longrightarrow R_2\text{-}\overset{-}{\underset{\underset{\displaystyle R_1}{|}}{C}}\text{-}\overset{\overset{\displaystyle \text{Cu(II)}}{\uparrow}}{O}\text{-O-H} + H^+\cdot\text{Py}$$

$$\longrightarrow R_2\text{-}\underset{\underset{\displaystyle R_1}{|}}{C}\text{=O} + H_2O + \text{Cu(II)} \qquad (1)$$

Py: pyridine

Co(III) Catalyst. Higher-valent transition metals are known to decompose HPO by the one-electron oxidation of a peroxidic bond to produce the peroxy radical and proton:

Table 1. MHPO and Cu(II)-MHPO complex

		MHPO	Cu-MHPO comp'ex	
			Cu-O_1	Cu-O_2
E_{total}/eV			-3073.68	-3073.48
Atom population	O_1	6.340	6.321	6.239
	O_2	6.373	6.281	6.365
	H_3	0.642	0.570	0.614
	$H_{5,6,7}$	1.023	0.970	0.970
	Cu		11.241	11.249
$E_{O_1-O_2}$		-14.81	-14.69	-14.23
$E_{O_2-H_3}$		-23.69	-22.94	-22.63
$E_{C_4-H5,6,7}$	av./eV.	-20.37	-20.21	-20.23
$E_{Cu-O_1 \text{ or } O_2}$			-12.13	-12.06

Table 2. MAHPO and Cu(II)-MAHPO complex

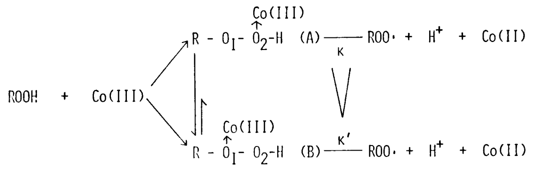
		MAHPO	Cu-MAHPO complex	
			Cu-O_1	Cu-O_2
E_{total}/eV			-3612.50	-3610.26
Atom population	O_1	6.333	6.310	6.283
	O_2	6.396	6.317	6.417
	H_3	0.647	0.583	0.636
	H_5	0.953	1.035	0.981
	Cu		11.229	11.088
$E_{O_1-O_2}$		-14.69	-14.64	-13.61
$E_{O_2-H_3}$		-23.77	-23.19	-22.76
$E_{C_4-H_5}$	vs./eV.	-20.19	-20.10	-20.18
$E_{Cu-O_1 \text{ or } O_2}$			-12.40	-12.30

Table 3. MHPO and Co(III)-MHPO complex

		MHPO	Co-MHPO complex	
			Cu-O_1	Cu-O_2
E_{total}/eV.			-3750.28	-3749.78
Atom population	O_1	6.340	6.283	6.233
	O_2	6.373	6.290	6.297
	H_3	0.642	0.701	0.613
	$H_{5,6,7}$	1.023	0.997	1.050
	Co		8.043	8.049
$E_{O_1-O_2}$		-14.81	-14.87	-14.94
$E_{O_2-H_3}$		-23.67	-23.51	-22.60
$E_{C_4-H5,6,7}$	av./eV.	-20.37	-20.19	-20.38
$E_{Co-O_1 \text{ or } O_2}$			-10.03	-9.73

$$\mathrm{ROOH} + \mathrm{M}^{+(n+1)} \longrightarrow \mathrm{ROO}\cdot + \mathrm{H}^+ + \mathrm{M}^{n+} \qquad (2)$$

When MHPO coordinates to Co(III) through the O_1 or O_2 lone-pair, it may be seen from Table 3 that the absolute value of $E_{O_1-O_2}$ is increased, but that of $E_{O_2-H_3}$ is decreased: this is in good agreement with the experimental result (Eq. (2)). The decrease in the absolute value of E_{02-H3} is larger in the O_2 coordination (about 1.1 eV) than that in the O_1 coordination (about 0.16 eV), suggesting that Reaction (2) proceeds more easily from the O_2 coordination than from the O_1 coordination. On the other hand, the O_1 coordination seems more favorable than O_2 coordination from the consideration of E_{total} and E_{Co-O}. Therefore, it is plausible that Co(III) forms two complexes with HPO in equilibrium with one another (see A and B below) and that the B complex, in high concentration, cannot contribute to Reaction (2) so much as the A complex. That is, the rate of the decomposition of the B complex in a higher concentration is small compared with that of the A complex in a low concentration. In this way, the decomposition of HPO seems to be catalyzed by Co(III).



Cu(II), though effective in the decomposition of HPO, is considered not to promote the fission of the O_2–H_3 bond of HPO (Eq. (2)).[3] However, it can be seen from Tables 1 and 2 that the absolute value of $E_{O_2-H_3}$ is decreased by 0.7 eV (O_1 coordination)—1.1 eV (O_2 coordination), which suggests that Cu(II) can promote Reaction (2) as well as Co(III). Therefore, it can be expected that, in a non-basic solvent, Cu(II) promotes the direct decomposition of HPO (Eq. (2)) at the initial stage of the reaction (induction period), where the transformation of Cu(II) to Cu(I) occurs, and that, at the later stages of the reaction, the rapid oxidation of the alkyl radical by Cu(II) (Eq. 3) would predominate over Reaction (2):[3,10]

$$\mathrm{R}\cdot + \mathrm{Cu(II)} \longrightarrow \mathrm{R}^+ + \mathrm{Cu(I)} \qquad (3)$$

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