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An MO-Theoretical Account of the Catalytic Decomposition of Alkyl Hydroperoxides by Transition-metal Ions

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Many chemical studies of the decomposition reactions of alkyl hydroperoxides with or without catalysts have been done during the last decade. The mechanism of the catalytic decomposition of the hydroperoxides by transition-metal ions has, however, been established on the basis of the Haber-Weiss mechanism,[1] and some aspects of the process of the reactions are still veiled. The present study has been undertaken in an attempt to elucidate the processes of the decomposition reactions, using the all-valence-electron ASMO SCF and extended Hückel (EHMO) methods involving metal *d*-orbitals of transition metals.

Method of Calculation

Three systems were investigated in this work: (a) the monomers and dimers of alkyl hydroperoxides (ROOH: R=H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, and t-C_4H_9), (b) the nucleophilic attack of the transition-metal ion (Cr(II), Co(II), or Fe(II)) on CH_3OOH, and (c) the electrophilic attack of Co(III) on CH_3OOH. The zero-differential overlap approximated ASMO SCF[2] and EHMO methods were used in this paper; the one-center and two-center Coulomb repulsion integrals were estimated by the Pariser[3] and the Ohno[4] approximations respectively. In the EHMO method, the resonance integrals were evaluated by

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[1] F. Haber and P. Weiss, *Proc. Roy. Soc.*, *Ser. A*, **147**, 233 (1939).

[2] The ionization energies (and electron affinities) of Cr, Co, and Fe are cited from Ref. 8 (Ref. 10), Ref. 8 (Ref. 10), and Ref. 9 (Ref. 10) respectively. The ASMO SCF method used was almost the same as the method reported by H. Kato, H. Konoshi, and T. Yonezawa (This Bulletin, **40**, 1017 (1967)).

[3] R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

[4] K. Ohno, *Theoret. Chim. Acta*, **2**, 568 (1953).

means of the Wolfsberg-Helmholtz approximation.[5]

Results and Discussion

First, we will interpret the unimolecular or the bimolecular decomposition[6] of ROOH in connection with the association of ROOH.[7] Figure 1 shows the changes in the total energies of ROOH dimers, together with those of monomers (R=H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, and t-C_4H_9), due to the stretching of the O–H bonds, which resulted from the EHMO calculations. The ROOH monomers are slightly less stable than the ROOH dimers. In addition, the reactivity of the former to nucleophiles such as low-valent metal ions is higher than that of the latter; notice, for example, the reactivity indices ($^1/_2 N^{LU}_{p\sigma}$), *i.e.*, the partial AO bond population in the lowest unoccupied (LU) MO, which is strongly localized in the O–O $p\sigma$-type orbital (see Table 1). Consequently, it is probable, at low concentrations of ROOH, that the unimolecular decomposition occurs predominantly either with or without catalysts.

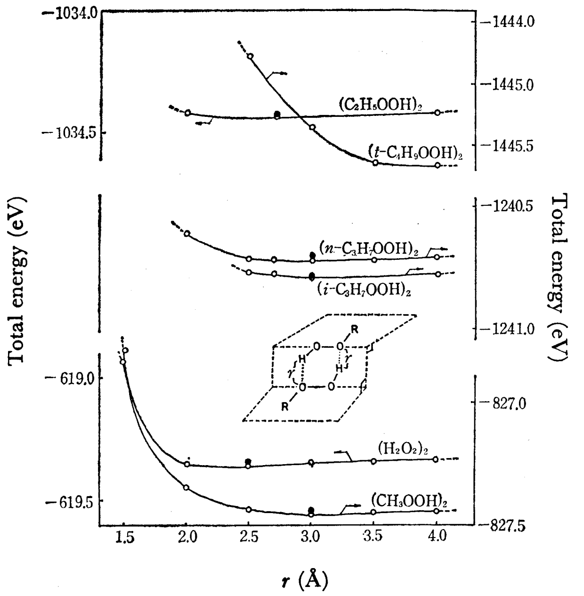

Fig. 1. Changes in the total energies of ROOH dimers as a function of the O–H distance (denoted by r), together with those of ROOH monomers.
(○: ROOH dimer; ●: ROOH monomer.)

Secondly, let us discuss the catalytic decomposition of ROOH by the transition-metal ions from the viewpoint of our experimental findings; about 95 mol% of the quantity of cumene hydroperoxide (the initial amount was 22.5 mmol) disappeared after 0.5 hr at 80°C in cumene (50 m*l*) containing Co(II) supplied by its stearate (0.33 mol/*l*), although, thermally, the hydroperoxide decomposed little even after 9.0 hr. Under the same reaction conditions, Ni(II), Fe(II), and Cr(III) lessened the quantity of the hydroperoxide by *ca.* 6, 4, and 17 mol% respectively. The order of the catalytic abilities of the low-valent transition metal ions for the hydroperoxide decomposition, *i.e.*, Co(II)>Ni(II)>Fe(II), can be well explained by the parallelism with that of the energy required for the electron-releasing from the metal ion to the antibonding O–O $p\sigma$ orbital, namely, with that of the orbital energies of the highest occupied (HO) AO of the metal ions (−7.84,[8] −9.24,[8] and −11.0 eV[9]) respectively).

Table 1. Electronic properties and reactivities of ROOH and their dimers

ROOH and $(ROOH)_2$	O–H (Å)	Bond population of the O–O	$\frac{1}{2}N^{LU}_{p\sigma}$	Total energy (eV)
H_2O_2		0.359	−0.309	−309.671
$(H_2O_2)_2$	2.5	0.358	−0.155	−619.359
CH_3OOH		0.360	−0.309	−413.716
$(CH_3OOH)_2$	3.0	0.361	−0.154	−827.455
C_2H_5OOH		0.358	−0.309	−517.211
$(C_2H_5OOH)_2$	2.7	0.358	−0.153	−1034.428
n-C_3H_7OOH		0.357	−0.308	−620.387
(n-$C_3H_7OOH)_2$	3.0	0.357	−0.154	−1240.791
i-C_3H_7OOH		0.356	−0.307	−620.356
(i-$C_3H_7OOH)_2$	3.0	0.356	−0.153	−1240.728
t-C_4H_9OOH		0.354	0.308	−722.831
(t-$C_4H_9OOH)_2$	(4.0)	0.354	−0.153	−1445.664

These results were obtained from the EHMO calculations.

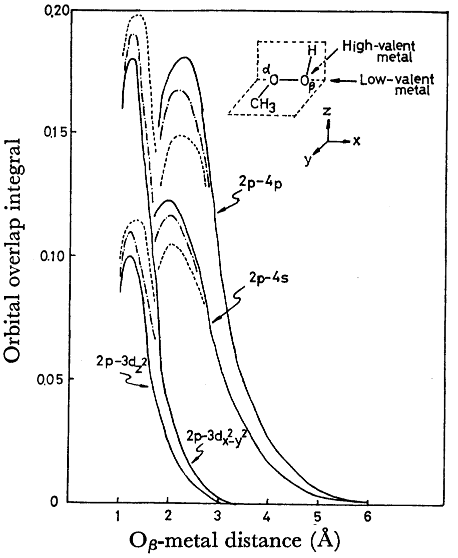

Fig. 2. Changes in orbital overlaps between oxygen p-orbitals and metal d-, s-, and p-orbital due to the variation of the O_β-metal distance. (——: Co; -·-·-: Cr; ------: Fe)

A more precise discussion should be made here with respect to the catalytic decomposition of ROOH by the metal ions. From the orbital overlaps between oxygen $2p$ and metal $3d$ AOs indicated in Fig. 2, the following two reactions can be expected in the O_β-metal region below 3.0 Å: the nucleophilic attack of a low-valent metal on the O–O $p\sigma$ orbital in the direction

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[5] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

[6] Bateman, *Quart. Rev.*, **8**, 147 (1954).

[7] C. Walling and H. Heaton, *J. Amer. Chem. Soc.*, **87**, 48 (1965).

[8] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 1004 (1964).

[9] L. L. Lohr, Jr., and W. N. Lipscomb, *ibid.*, **3**, 22 (1964).

Table 2. Changes in the electronic states of transition metal ions and CH_3OOH attacked by low-valent metal ions

O_β-Metal ion distance (Å)	Atom population of metal	AO populations					
		Transition metal			CH_3OOH		
		$d_{x^2-y^2}$	d_{z^2}	d_{xy}	$O_\beta-p_y$	$O_\beta-p_x$	$O_\alpha-p_x$
	4.000(6.000)				1.996(1.996)	1.050(1.050)	0.983(0.983)
1.6	3.243(6.0)	0.327(1.615)	0.109(1.855)	0.038(0.037)	1.869(1.885)	1.558(1.189)	1.388(1.149)
1.5	(5.323)	(1.111)	(1.697)	(0.076)	(1.870)	(1.378)	(1.613)
1.4	3.218	0.315	0.135	0.089	1.813	1.639	1.490

These results were obtained from the ASMO SCF calculations.
Values and those in parentheses indicate the cases of Cr(II) and Fe(II) respectively.

of the O–O axis from the O_β side[10] and the electrophilic attack of a high-valent metal on the nonbonding lone-pair O_β $2p_y$-orbital (note the larger population and delocalizability to nucleophiles[11] of O_β as compared with those of O_α). In these attacks, the wholly unoccupied $4s$ and $4p$ orbitals situated at high-energy levels may not play an important direct role in the interaction of the metal ion with ROOH.

Thirdly, it is of interest to notice the changes in the electronic states of the transition-metal ions and ROOH by the interaction, which predominantly occurs near the maximum overlaps between oxygen $2p$ orbitals and metal d-orbitals, *i.e.*, near 1.5 Å (see Fig. 2). The orbital symmetry allows two pairs of overlaps: the dp-σ overlap between the O–O $p\sigma$ and $d_{x^2-y^2}$ and/or d_{z^2} and that between the nonbonding lone-pair O_β, p_y, and d_{xy}. In both attacks we recognized an electron-inflowing from the $d_{x^2-y^2}$ metal to the O–O $p\sigma$ and an electron-backdonation from the lone-pair, O_β p_y, to the d_{xy} metal, as can be seen from Table 2. It is necessary to mention here that the negative value of the bond population of the O–O in ROOH attacked by the metal ion within the O_β-metal distance of 2.0 Å indicates a scission of the O–O linkage, while, even at the O_β–S distance of 1.47 Å, the bond population of the O–O is positive in the case of the nucleophilic interaction of $(CH_3)_2S$ with CH_3OOH.[12] The remarkable ability of the transition-metal ions for the hydroperoxide decomposition was, for instance, thus reflected in the change in the electronic state of ROOH attacked by the metal ion.

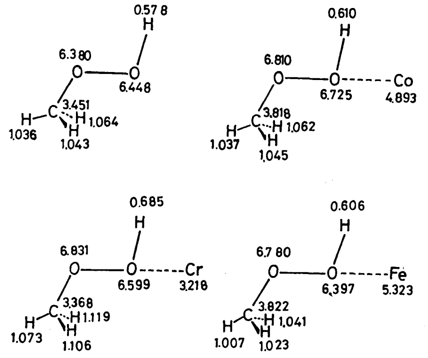

Fig. 3. Valence electron distributions of the systems of CH_3OOH–transition metal ion. (O_β–Co or Cr=1.5 Å; O_β–Fe=1.4 Å)

Finally, the valence-electron distributions of the CH_3OOH-metal ion systems are indicated in Fig. 3.

The calculations were carried out on the FACOM 230-60 computer at the Computer Center of Kyushu University.

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[10] J. Hinze and H. H. Jaffé, *Can. J. Chem.*, **41**, 1315 (1963).

[11] T. Yonezawa, O. Yamamoto, H. Kato, and K. Fukui, *Nippon Kagaku Zasshi*, **87**, 26 (1966).

[12] K. Ohkubo, T. Ninomiya, and H. Kanaeda, *Tetrahedron*, **28**, 2969 (1972).