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A MO-THEORETICAL TREATMENT OF THE DECOMPOSITION OF HYDROPEROXIDES BY NUCLEOPHILES AND ELECTROPHILES

K. OHKUBO. T. NINOMIYA and H. KANAEDA

Department of Synthetic Chemistry. Kumamoto University. Kurokami- machi. Kumamoto. Japan

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Abstract—The mechanism of the decomposition of hydroperoxides (ROOH) by some nucleophiles (sulfides, phosphites, thiophene, sulfonium compounds, and transition metal ions) and electrophiles (transition metal ions) has been investigated using the extended Hückel method including d-orbitals, and the following results were obtained. ROOH is more stable energetically than $(ROOH)_2$. The reactivity of ROOH to nucleophiles and electrophiles has been explained by the partial AO population of the O—O pσ at the LU MO($\frac{1}{2}N_{p\sigma}^{LU}$) and that of the nonbonding O_β 2p at the HO MO($\frac{1}{2}N_{nbo}^{HO}$), respectively. Except for transition metal ions, the order of the ability of necleophiles to decompose ROOH is in good agreement with that of $\frac{1}{2}N_{nbo}^{HO}$ of the nonbonding orbital of the central atom, while the ability of transition metal ions is reflected in the ionization potentials of their d-orbitals. The process of decomposition is discussed giving regard to the electron-migrations between reactants: and the intramolecular reaction of RO radicals formed is treated by the extended Hückel method.

INTRODUCTION

HYDROPEROXIDES (ROOH) have often been postulated as intermediates in the oxidation of hydrocarbons. The thermal[1] and catalytic[2] decomposition of ROOH have been widely investigated, revealing the kinds of homolytic or heterotic decomposition products,[1-3] the dissociation energies of the O—O linkage in ROOH,[4,5] the association of ROOH,[6,7] etc. The decomposition mechanisms of ROOH have been widely discussed, especially those involving nucleophiles such as sulfides,[8] phosphites[9] and low valent transition metal ions,[10] or electrophiles such as high valent transition metal ions.[10] But the only theoretical treatment of the decomposition concerns the electronic structures of H_2O_2[11] and some alkyl hydroperoxides.[12]

The present study attempts to elucidate the decomposition of ROOH by some nucleophiles (sulfides, phosphites, thiophene, sulfonium compounds, and transition metal ions) and electrophiles (transition metal ions), using throughout the extended Hückel method including d-orbitals for thiophene, sulfonium compounds, and transition metal ions.

SYSTEMS INVESTIGATED

Decomposition reactions were studied

(a) Decompositions of hydroperoxides, ROOH (R=H, Me, Et, n-Pr, n-Bu, t-Bu, and $PhCMe_2$), and dimeric hydroperoxides, $(ROOH)_2$ (R=H, Me, and Me_3C), by the nucleophiles; Me_3S, Ph_2S, $\overline{CHMe_3S}$, $(MeO)_3P$, $(EtO)_3P$, and Me_3SCl.

(b) Decomposition reactions of AcOH by nucleophiles (Me_2S, $(MeO)_3P$, Me_3SCl, Co(II), Cr(II), and Fe(II)) and electrophiles (Co(III) and Cr(III)), CH_3OOH being used for simplicity of computation. Geometries used for the calculations are illustrated in the relevant figures in this paper.

Orbital exponents and Coulomb integrals ($H_{\mu\mu}$) used were mainly those reported by Clementi[13] and Jaffé,[14] respectively, while the values of $H_{\mu\mu}$ for O, Co, Cr, and Fe were obtained from Refs 15, 16, 16, 17, respectively. Resonance integrals ($H_{\mu\nu}$) were evaluated by the Wolfsberg–Helmholtz approximation:[18]

$$H_{\mu\nu} = K(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}/2$$

where K was taken to be 1·75[19] and $S_{\mu\nu}$ is the overlap integral between AO's.

RESULTS AND DISCUSSION

Calculated results for electronic structures of ROOH. As Table 1 indicates, there is a close resemblance in the bond populations of O—O and O—H linkages (M_{OO} and M_{OH}, respectively) for all ROOH's. The close identity of the values of M_{OO} is reflected in the almost identical dissociation energies of the O—O linkages of ROOH's, *i.e.* 38·5 kcal/mol on average.[4] The lowest unoccupied (LU) MO is strongly localized in the oxygen 2p AO lying on the O—O axis and is antibonding with respect to O—O, while the highest occupied (HO) MO is localized predominantly in the nonbonding oxygen 2p orbitals. The antibonding character of the O—O linkage is well projected on the orbital contour diagram of the LU MO of CH_3OOH (Fig 1).

TABLE 1. ELECTRONIC STRUCTURES OF HYDROPEROXIDES

$RO_\alpha O_\beta H$ (R)	$M_{O\alpha}$	$M_{O\beta}$	M_{OO}	M_{OH}	Orbital energy (eV) HO	LU
H	6·593	6·593	0·359	0·511	−15·12	−9·19
Me	6·544	6·607	0·361	0·508	−14·03	−9·10
Et	6·551	6·609	0·358	0·508	−13·60	−10·89
n-Pr	6·563	6·611	0·357	0·508	−13·18	−9·10
n-Bu	6·563	6·611	0·357	0·508	−12·97	−10·85
t-Bu	6·570	6·628	0·354	0·503	−12·72	−9·09
$PhCMe_2$	6·658	6·709	0·350	0·489	−11·81	−10·67

These LU and HO MO's play important roles in the weakening of the O—O linkage by interaction with nucleophiles (N-reagents) and electrophiles (E-reagents), respectively. In view of the larger electron density and delocalizability[12] of O_β in $RO_\alpha O_\beta H$ compared with those of O_α, N-reagents should attack ROOH from the β-oxygen side, in the direction of the O—O axis, while E-reagents should approach O_β in the direction of the O_β nonbonding orbital expansion, *i.e.* from the side opposite to R.

It is of interest here to discuss the reactivity of ROOH to N- and E-reagents. When the value of the partial AO bond population of the antibonding pσ-orbital of O—O in the LU MO, $\frac{1}{2}N^{LU}_{p\sigma}$, is employed as an index of reactivity to N-reagents, a larger alkyl group attached to O_α lessens the reactivity, giving the following order:

H_2O_2 (−0·310) > CH_3OOH (−0·309) > n-C_3H_7OOH (−0·307) > t-C_4H_9OOH (−0·305) > $C_6H_5C(CH_3)_2OOH$ (−0·285), where the values in the parentheses stand for $\frac{1}{2}N^{LU}_{p\sigma}$. On the other hand, the value of the partial AO population of the O_β non-bonding orbital in the HO MO, $\frac{1}{2}N^{HO}_{nbo}$, can be used as an index of reactivity to E-reagents. The value of $\frac{1}{2}N^{HO}_{nbo}$ suggests that the larger the R group the less reactive is ROOH to E-reagents; for instance, H_2O_2 (0·321) > n-C_3H_7OOH (0·006) > $C_6H_5C(CH_3)_2OOH$ (0·0023).

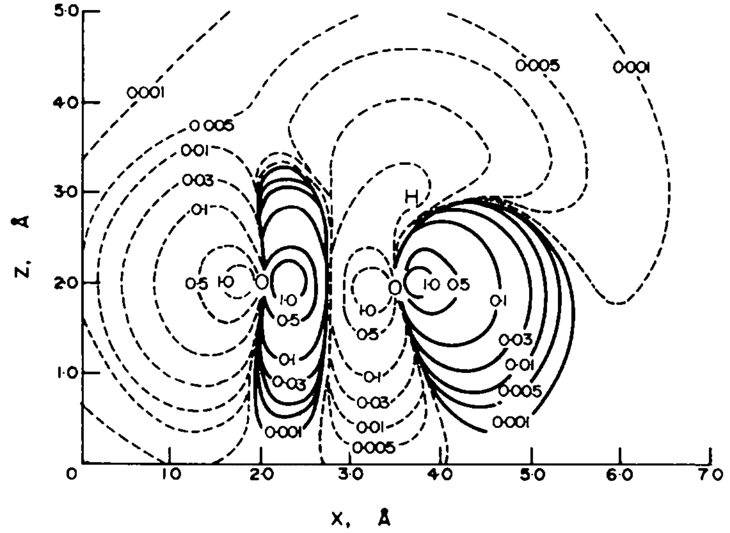


FIG 1. Orbital contour diagram of the LU MO of CH_3OOH. (Solid and dotted curves indicate positive and negative MO-signs respectively)

Next let us consider the dimeric hydroperoxides. The stabilities of the dimers, $(H_2O_2)_2$, $(CH_3OOH)_2$, and $((CH_3)_3COOH)_2$, were investigated from an energetic point of view. As can be seen from the total energy values (E_{EH}) recorded in Fig 2; H_2O_2, CH_3OOH, and $(CH_3)_3COOH$ are more stable than their dimers by 0·021 eV, 0·164 eV, and 1·73 eV in the units of H_2O_2, CH_3OOH, and $(CH_3)_3COOH$ respectively. Moreover, the monomer of ROOH is considered to be more reactive than the dimer to N-reagents, because the absolute value of $\frac{1}{2}N^{LU}_{p\sigma}$ in ROOH is larger than that in $(ROOH)_2$. From this, it can be seen that only the monomer structure of ROOH need be considered in the reaction between N- or E-reagents and hydroperoxides.

Decomposition of cumene hydroperoxide by N- *or* E-*reagents.* In Table 2 are listed the experimental data obtained on this decomposition reaction. The distribution of the decomposition products (*viz.* the ratio of CA/AP) is different between $(CH_3)_3SCl$ and $\overline{CH(CH)_3S}$, and the other compounds. This may be attributed to the fact that $(CH_3)_3SCl$ and $\overline{CH(CH)_3S}$ act as decomposers in a different way from the other

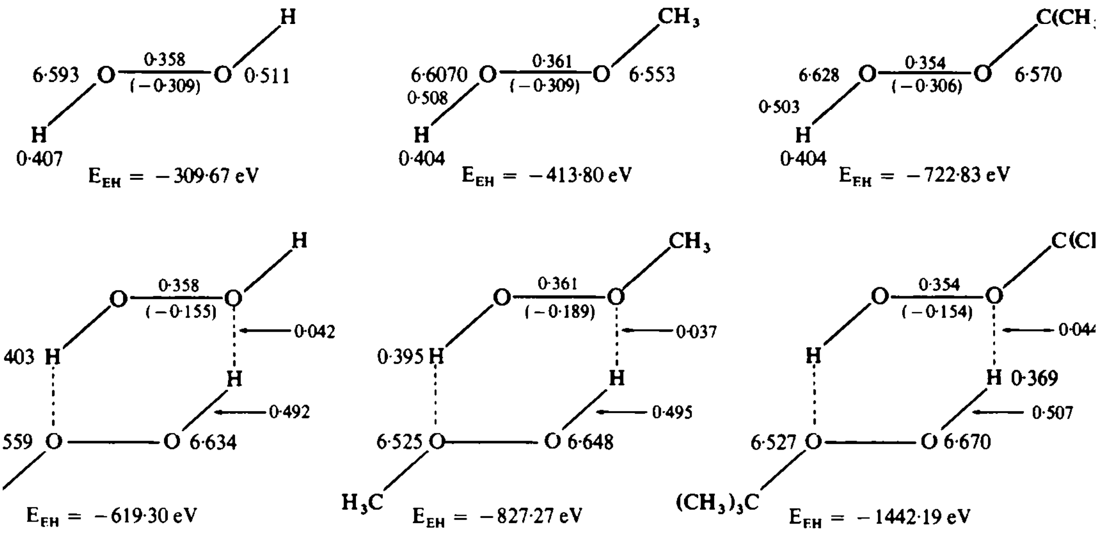


FIG 2. Electronic structures of some alkyl hydroperoxides and their dimers. (The figures in parentheses indicate $\frac{1}{2}N_{p\sigma}^{I,U}$)

TABLE 2. ABILITY OF SULFONIUM COMPOUNDS AND SOME NUCLEOPHILES FOR THE DECOMPOSITION OF CUMENE HYDROPEROXIDE (22·5 mmol)
(reaction temp: 80°, reaction time: 4 hr)

Compound	Concentration (mol/l)	CHP dec (mmol)	R(initial)[h] (mol/lsec × 10^4)	Products[a] (mmol) AP	DCP	CA
None		1·0	0·014	0·24	trace	0·76
$(C_6H_5)_2S$	0·148	20·0	0·392	1·64	2·2	13·8
$(C_6H_5)_2S$	0·216	trace[b]				
$CH(CH)_3S$	0·12	4·6[c]	0·188	4·0	trace	0·6
$CH(CH)_3S$	0·476	15·6	0·278	13·6		
$(C_6H_5)_3SCl$	0·141	21·80	0·417	10·63	4·16	1·91
$(C_6H_5)_3SCl$	0·670	5·50[d]	0·187	2·29	1·12	0·45
$(C_6H_5)_3SCl$	0·424	22·39[e]	0·667	13·28	2·77	3·56
$(CH_3O)_3P$	0·148	8·8	0·222	0·88	trace	7·3
$(C_2H_5O)_3P$	0·148	6·4	0·190	1·03	0·34	4·70
$(C_6H_5O)_3P$	0·148	9·5	0·311	1·10	trace	8·25
Ni(II)[f]	0·006	6·2	0·167	1·38	trace	4·81
Co(II)[f]	0·006	22·5	2·722	4·73	trace	19·1
Fe(II)[g]	0·006	5·7	0·111	1·23	trace	4·42

[a] Other decomposition products such as methane, phenol, etc. were neglected in this table for the sake of simplicity. In CHP decomposition by $(C_6H_5)_3SCl$ (0·141 mol/l) at 80° for 4 hr, for instance, CH_3OH (2·88 mmol), C_6H_5OH (0·33 mmol) and gaseous products such as CH_4 (6·63 mmol) were detected.

[b] Reaction temperature was 25°.

[c] Reaction time was 3 hr.

[d] Reaction temperature was 55°.

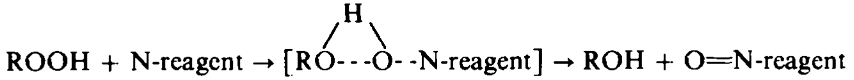
[e] Reaction time was 5 hr.

[f] Stearates.

[g] A naphthenate.

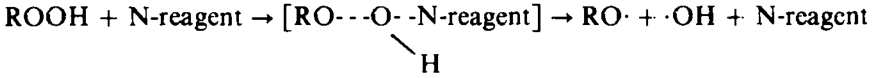
[h] Reaction rates of the initial stage.

compounds. Namely, with the sulfonium compound and thiophene the contribution of the sulfur d-orbitals to the interaction with ROOH must be taken into consideration. Discussion of this in detail will be presented later. With regard to the decomposition of ROOH by N-reagents, three representative processes can be considered:



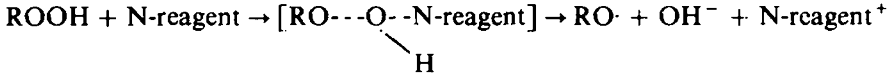
$$\text{ROOH} + \text{N-reagent} \rightarrow [\text{R}\overset{\diagup\text{H}\diagdown}{\text{O}\cdots\text{O}}\cdots\text{N-reagent}] \rightarrow \text{ROH} + \text{O}{=}\text{N-reagent} \qquad (1)$$

where the N-reagent is a sulfide or a phosphite,



$$\text{ROOH} + \text{N-reagent} \rightarrow [\text{RO}\cdots\underset{\diagdown\text{H}}{\text{O}}\cdots\text{N-reagent}] \rightarrow \text{RO}\cdot + \cdot\text{OH} + \text{N-reagent} \qquad (2)$$

where the N-reagent is a sulfonium compound or thiophene, and



$$\text{ROOH} + \text{N-reagent} \rightarrow [\text{RO}\cdots\underset{\diagdown\text{H}}{\text{O}}\cdots\text{N-reagent}] \rightarrow \text{RO}\cdot + \text{OH}^- + \text{N-reagent}^+ \qquad (3)$$

where the N-reagent is a low valent transition metal ion. With the exception of transition metal ions, the order of the ability of N-reagents to decompose cumene hydroperoxide, estimated from the amount of the hydroperoxide decomposed, was as follows: triphenylsulfonium chloride $\gg$ diphenylsulfide $>$ triphenylphosphite $>$ trimethylphosphite $>$ triethylphosphite $\simeq$ thiophene. Considering that the ability should reflect the AO populations of the nonbonding orbital (N_{nbo}) of the central sulfur or phosphorus, and in particular those of $\frac{1}{2}N_{nbo}^{HO}$ listed in Table 3 are in good agreement with the order of decomposing ability found.

The order of the ability of the low valent transition metal ions to decompose ROOH was as follows: Co(II) $>$ Ni(II) $>$ Fe(II). This order is well in agreement with the energy required for electron-release from the d-orbitals of the transition metal ion to the O—O pσ-orbital:

Co(II) (7·84 eV) $>$ Ni(II) (9·24 eV) $>$ Fe(II) (11·00 eV).

ROOH *Decomposition by the* N-*reagents* $(CH_3)_2S$, $(CH_3O)_3P$, and $(CH_3)_3SCl$. Methyl derivatives were taken for convenience of computations. In Fig 3 are indicated

TABLE 3. AO POPULATIONS OF THE NONBONDING ORBITALS OF NUCLEOPHILES

Nucleophile	N_{nbo}	$\frac{1}{2}N_{nbo}$	HO (nonbonding orbital) (eV)
$(CH_3)_2S$	1·993	0·729	−11·98
$(C_6H_5)_2S$	1·845	0·312	−11·74
$\overline{CH(CH)_3S}$	1·579 (0·064)		−12·49
$(CH_3)_3SCl$	1·981 (0·068)	0·701	−11·42
$(CH_3O)_3P$	1·298	0·197	−12·28
$(C_2H_5O)_3P$	1·231	0·156	−12·06

Values in parentheses stand for the AO population of d_{z^2}-orbital overalapping with the O—O pσ-orbital of ROOH.

the changes in the values of M_{OO} and M_{OH} of CH_3OOH caused by attack of the N-reagents. $(CH_3)_3SCl$ shows a much greater ability for the catalytic decomposition of the hydroperoxide than sulfide or phosphite, both of which exhibit almost the same activity (strictly speaking, the sulfide is a little more active than the phosphite). It is necessary here to notice the change in the value of M_{OH} caused by the approach of $(CH_3)_3SCl$ to the hydroperoxide. Reduction in the distance between O_β and S (denoted as r) is not accompanied by a marked decrease in the value of M_{OH}. This implies that bond scission of the O—H linkage can not be expected in the interaction between the sulfonium compound and the hydroperoxide. The long range-interaction between the partially occupied sulfur d-orbitals, in particular the sulfur d_{z^2}-orbital, and the antibonding pσ-orbital brings about only the gradual weakening of the O—O bond. The nonbonding 3p AO on the central sulfur participates in the interaction with the hydroperoxide below 2·0 Å. On the other hand, the nucleophilic attack of sulfide or phosphite gives rise to a weakening of the O—H bond, which would support the mode of the interaction presented in Eq (1). The atom population of the central sulfur and phosphorus, M_N, also lessen gradually with the decrease in value of r. These diminutions in the values of M_N and M_{OO} are brought about by the

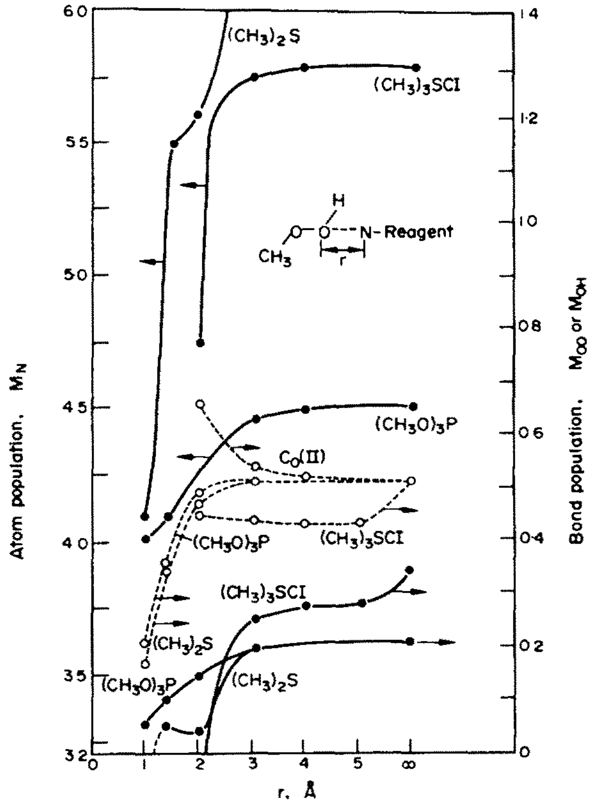


FIG 3. Changes in the values of M_{OO} and M_{OH} of CH_3OOH, and M_N of some nucleophiles on variation of r. (The solid curves indicate M_{OO} or M_N; The dotted curves stand for M_{OH})

TABLE 4. CHANGES IN THE N_{nbo} OF SOME NUCLEOPHILES AND THE $N_{p\sigma}$ OF CH_3OOH OF VARIATION OF THE O_β-N DISTANCE

O_β - N (Å)	N_{nbo}			$N_{p\sigma}$		
	$(CH_3)_2S$	$(CH_3O)_3P$	$(CH_3)_3SCl$	$(CH_3)_2S$	$(CH_3O)_3P$	$(CH_3)_3SCl$
	1·993	1·298	1·981 (0·0683)		0·346	
5·0			1·981 (0·0681)			0·283
4·0			1·981 (0·0663)			0·282
3·0	1·987	1·287	1·955 (0·0519)	0·346	0·346	0·272
2·0	0·622	1·129	0·985 (0·1099)	0·307	0·332	−0·004
1·5		1·061			0·320	
1·47	0·639			0·295		
1·0	0·979	1·140		0·270	0·318	

Values in parentheses indicate those of the $d_z{}^2$.

electron-outflowing from the nonbonding orbital (and/or from the sulfur $d_z{}^2$-orbital in the cases of $(CH_3)_3SCl$ and $\overline{CH(CH)_3S}$) to the O—O pσ-orbital. This concept is supported by the decrease in N_{nbo} values as the reaction proceeds (Table 4). The contour diagram for the interaction between CH_3OOH and $(CH_3)_2S$ or $(CH_3)_3SCl$ indicates the more tangible circumstances of the hydroperoxide decomposition (Figs 4, 5, and 6).

In the catalytic decomposition of ROOH by transition metal ions, it is seen from the orbital overlappings between oxygen 2p AO and 3d AO that the nucleophilic attack

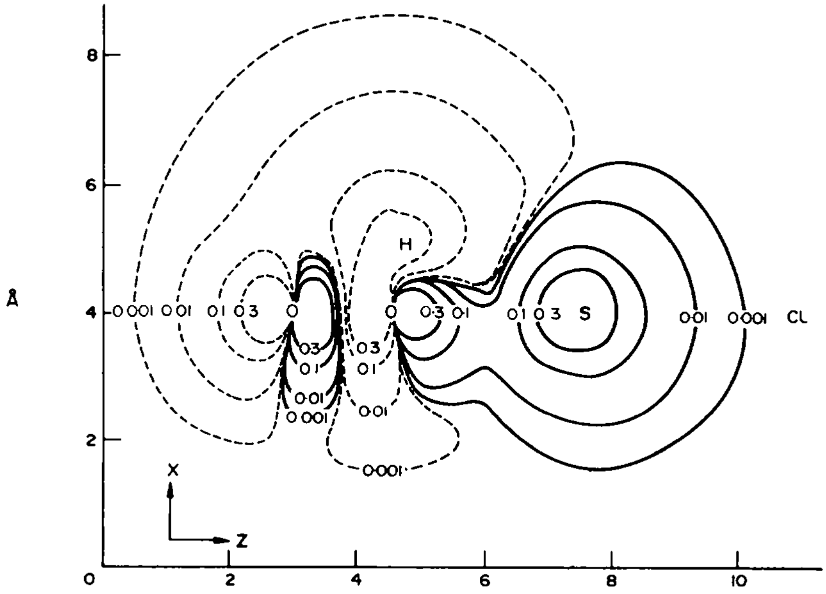


FIG 4. Contour diagram for the LU MO of the interacting system comprising CH_3OOH and $(CH_3)_3SCl$ (S—O = 3·0 Å). (Solid and dotted curves indicate positive and negative MO-signs respectively)

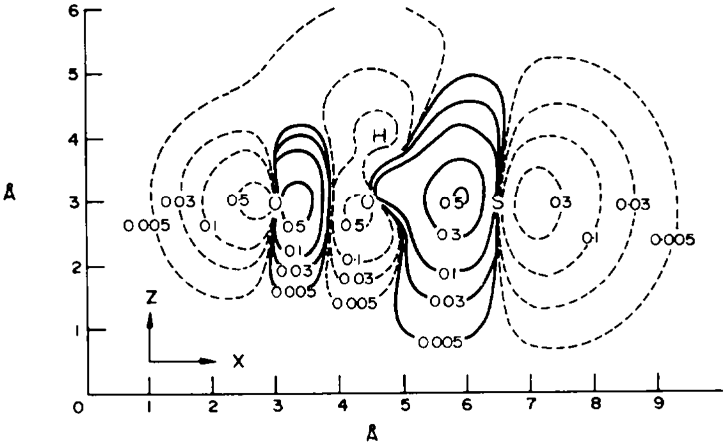


Fig 5. Contour diagram for the LU MO of the interacting system comprising CH_3OOH and $(CH_3)_2S$ (S--O = 2·0 Å). (Solid and dotted curves indicate positive and negative MO-signs respectively)

of Co(II) to the O—O pσ-orbital occurs at a O_β-Co distance of within 4·0 Å (Fig 7). In this situation, the wholly unoccupied 4s and 4p orbitals situated at high energy levels do not play an important role directly in the interaction with ROOH. The orbital symmetry allows two pairs of overlapping: the dp-σ overlap between the pσ and $d_{x^2-y^2}$ and/or d_{z^2}, and overlap between the nonbonding 2p of O_β and these d-orbitals. As Fig 7 also indicates, electron-inflowing from the $d_{x^2-y^2}$ to ROOH and electron-backdonation to d_{z^2} from ROOH can be expected in the nucleophilic or electrophilic attack of transition metal ions. Moreover, the energy diagram for the interaction between ROOH and Co(II), together with the changes in energy of the

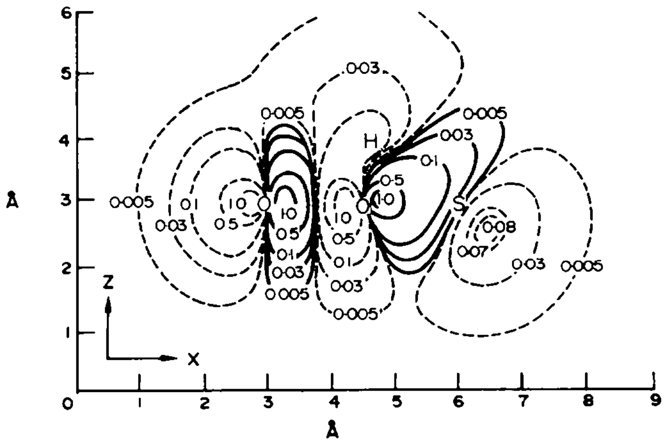


Fig 6. Contour diagram for the LU MO of the interacting system comprising CH_3OOH and $(CH_3)_2S$ (S—O = 1·47 Å). (Solid and dotted curves indicate positive and negative MO-signs respectively)

antibonding pσ-orbital caused by attack of Cr(II) and Fe(II), indicate the site of the decomposition process, as is shown in Fig 8. The reduction in orbital energy of pσ due to electron-inflowing from the transition metal ion shows the high activity of Co(II) and Cr(II) compared with Fe(II). With regard to the bond population of O—O (M_{OO}), the negative value of M_{OO}, even at the distance (r) = 3·0 Å, indicates scission of the O—O bond, although the value of M_{OO} is positive (M_{OO} = 0·255) in

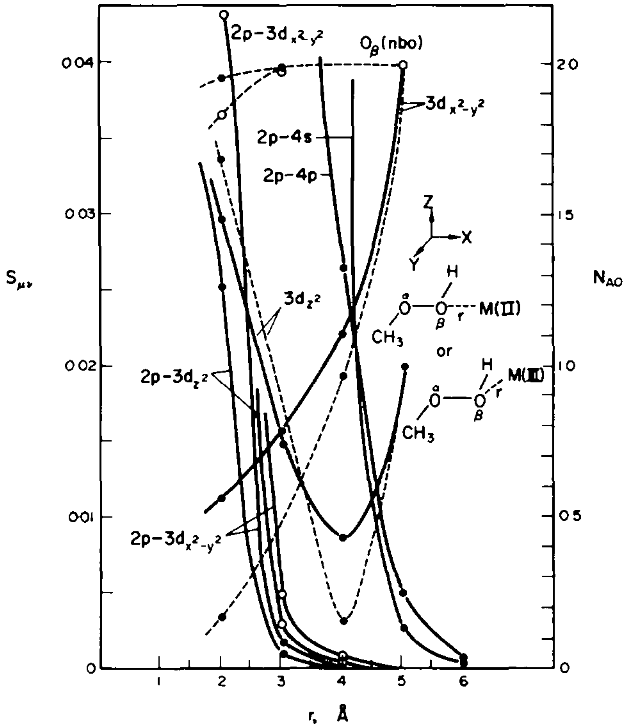


FIG 7. Changes in the orbital overlap ($S_{\mu\nu}$) and the AO population (N_{AO}) of M (Co or Cr) on variation of r. (The broken lines indicate the electrophilic attack of M (III): ●: Co, ○: Cr)

the reaction between $(CH_3)_2S$ and CH_3OOH at the distance of O_β-S = 1·47 Å (Fig 9). Thus high ability of the transition metal ions for hydroperoxide decomposition was reflected in O—O bond population in the ROOH being attacked.

Finally, we investigated the behaviour of the RO radicals formed on decomposition. We chose to study their intramolecular reaction, this being of more interest than, for example, their intermolecular reaction with hydrocarbons and their radical coupling reactions. The total energy (E_{EH}) shown in Fig 10 indicates the ease of the intramolecular reaction. The calculations show therefore that the transformation of cumyloxy radical to acetophenone has remarkably low activation energy, though Godin[1] has pointed out that the activation energy (*ca* 7·3 kcal/mol) is higher than that required for the formation of α-cumyl alcohol.

The calculations were carried out on FACOM 230·60 computer.

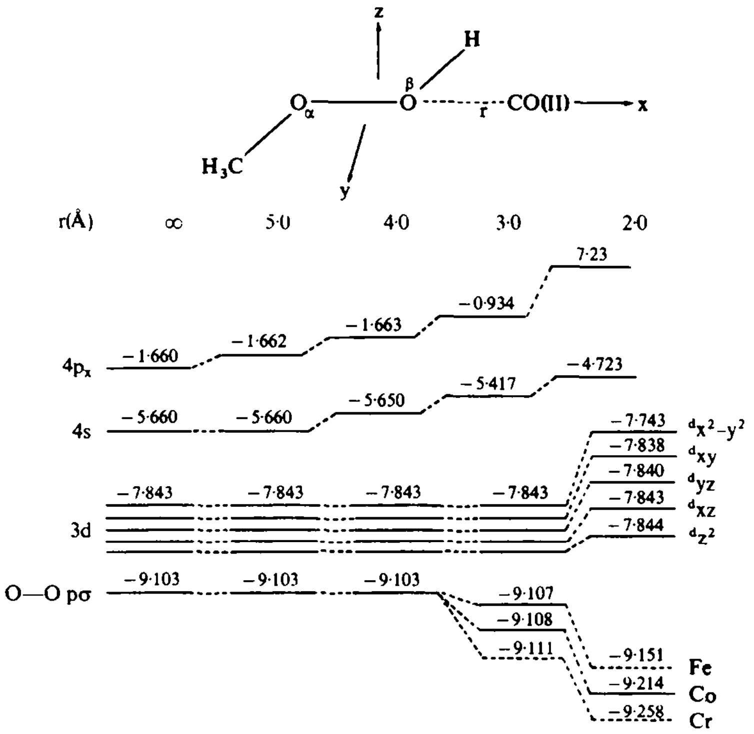


FIG 8. Energy diagram in the interaction between CH_3OOH and transition metal ions

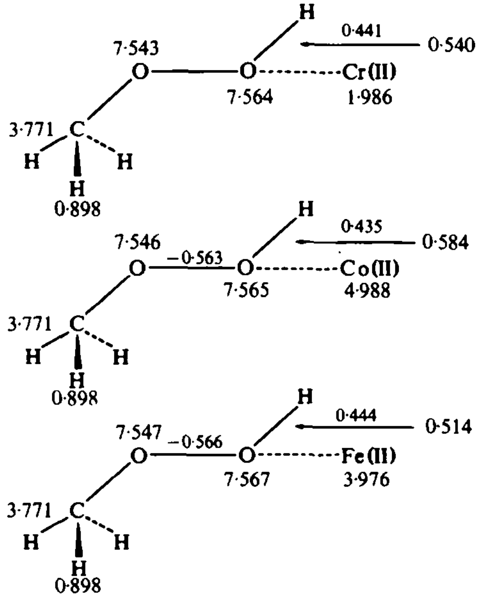


FIG 9. Atom and bond populations in the interaction between CH_3OOH and transition metal ions. (The distance of O-transition metal ion was 3·0 Å)

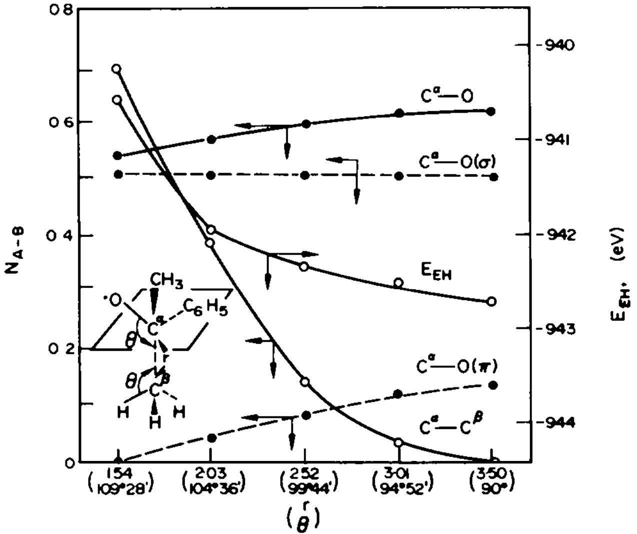


FIG 10. Changes in the values of E_{EH} and N_{A-B} along the intramolecular reaction path from $C_6H_5(CH_3)_2CO\cdot$ to $C_6H_5(CH_3)_2C{=}O + CH_3$

EXPERIMENTAL

Decomposition reaction of cumene hydroperoxide. Cumene hydroperoxide (22·5 mmol) in cumene (50 ml) was vigorously stirred in the presence of decomposer (viz. nucleophile or electrophile) at 80° for 4 hr. The mixture was then analyzed for decomposition products, acetophenone (AP), dicumyl peroxide (DCP), α-cumyl alcohol (CA), and residual cumene hydroperoxide (CHP). Analysis was carried out in accordance with a previously reported method.[20]

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