Bond Nature of Peroxides and Related Compounds*

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Summary: Extended Hückel molecular orbital calculations were performed on various peroxides (hydroperoxides, peracids, and peresters), nitrites, nitrates, esters, ethers, and alcohols with particular reference to the bond nature of their O-O, O-N, C-O, and O-H linkages. We made several findings. Firstly, the order of the bond strengths of the above linkages in the compounds considered was: alcohol > ester > ether $\gg$ nitrate $\gg$ nitrite $\gg$ hydroperoxide $\geq$ peroxide $\geq$ perester $\geq$ peracid. Secondly, peroxide families or nitrite and nitrate families were characterized by the lowest unoccupied (or the $LU+1$), antibonding O-O or O-N linkages. Thirdly, a parallel between the overlap population of the above linkages (O-O or O-N) and their bond dissociation energies could be recognized, with certain irregularities. Fourthly, the monomer structures of alkyl hydroperoxides were more energetically stable and reactive to nucleophiles than dimer ones. Finally, the characteristic bond nature of the above linkages was discussed in connection with the wave function contours.

1 Introduction

Peroxides such as alkyl hydroperoxides, dialkyl peroxides, peracids, and peresters have been postulated as reaction intermediates in the oxidation of hydrocarbons. It is well established that the first and rate-determining step in the thermal decomposition of the above peroxides, together with those of nitrites and nitrates, is the fission of the oxygen-oxygen linkage, or the oxygen-nitrogen linkage respectively, generating free alkoxyl radicals. Although several experimental findings have been reported in regard to the bond properties of the O-O or O-N linkages in the above compounds (for instance, the enthalpy^{1)~4)}, the bond dissociation energy^{5)~11)}, the rate constant of the thermal O-O bond-scission¹²⁾, etc.), theoretical interpretations of the characteristic bond nature of the O-O or O-N linkage are still in an early stage. There exist only some studies regarding the electronic structures of H_2O_2 ¹³⁾ and of some alkyl peroxides¹⁴⁾. The bond nature of the O-O linkages in peracids and peresters, however, still remains obscure. This is due to the fact that the isolation of the above peroxides by the usual experimental techniques is even now very troublesome.

The objective of the present study is to elucidate the bond nature of the O-O linkage and the O-N linkage respectively in the compounds mentioned above, as related to the C-O or O-H linkage in ether, ester, and alcohol. Specifically, our interests were related to the following:

(a) the reactivities of alkyl hydroperoxides and dialkyl peroxides to nucleophilic decomposers, together with their bond properties of the O-O, (b) molecular structures of hydroperoxides in terms of the stabilities of their monomers and dimers, (c) estimation of the bond strengths of peracids and peresters, together with their electronic structures, and (d) the bond properties of the O-N linkages in nitrites and nitrates in view of the formation of alkoxyl radicals by their decompositions. The extended Hückel molecular orbital theory¹⁵⁾ was adopted for the investigation of these four items.

2 Method of Calculation

Five systems were investigated in this work: (a) alkyl hydroperoxides and dialkyl peroxides families, ROOH and ROOR ($R=H$, CH_3 , C_2H_5 , $n-C_3H_7$, $n-C_4H_9$, $t-C_4H_9$, $C_6H_5C(CH_3)_2$, etc.), (b) hydroperoxide dimers, $(ROOH)_2$ ($R=H$, CH_3 , $t-C_4H_9$, $C_6H_5C(CH_3)_2$, etc.), (c) peracids and peresters, (d) nitrites and nitrates, RONO and $RONO_2$, ($R=CH_3$, C_2H_5 , $n-C_3H_7$, $sec-C_3H_7$, $n-C_4H_9$, etc.), and (e) esters, ethers, and alcohols. The geometries of all five are illustrated in Fig. 1.

Orbital exponents and Coulomb integrals ($H_{\mu\mu}$) were supplied by Clementi¹⁶⁾ and Jaffé,¹⁷⁾ respectively. Especially, the following two different sets of values of $H_{\mu\mu}$ for the oxygen p -orbital were used in checking the charge of the oxygen atom: -18.53eV and -13.61eV . The calculations with the latter value gave more reasonable data and were listed in this paper.

Resonance integrals ($H_{\mu\nu}$) were evaluated by the Wolfsberg-Helmholtz approximation¹⁸⁾:

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Fig. 1 Geometries Used for Calculations

$$H_{\mu\nu} = 0.875(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}$$

where $S_{\mu\nu}$ is the overlap integral between AOs. The wave function contours were portrayed by means of Slater's AO functions¹⁹⁾.

3 Results and Discussion

3.1 Bond Nature of the O-O Linkages in Alkyl Hydroperoxides and Dialkyl Peroxides

Alkyl hydroperoxides (ROOH) and dialkyl peroxides (ROOR) are characterized by their lowest unoccupied (LU), antibonding O-O linkages and by their relatively low bond dissociation energies, which fall in the range 30 to 40 kcal/mol. There exists a close resemblance of the bond nature of the O-O linkage between ROOH and ROOR (see **Table 1** and **2**). This is reflected in their analogous wave functions in the LU MO, as given by the following ϕ^{LU} *1):

$$\begin{aligned}\phi^{\text{LU}}(\text{RO}_\alpha\text{O}_\beta\text{H}) &= 0.833X_\alpha + 0.813X_\beta + 0.217S_\alpha \\ &\quad - 0.201S_\beta - 0.139Y_\alpha + 0.017Y_\beta \\ &\quad - 0.009Z_\alpha + 0.145Z_\beta + \dots\end{aligned}$$

and

$$\begin{aligned}\phi^{\text{LU}}(\text{RO}_\alpha\text{O}_\beta\text{R}) &= 0.823X_\alpha + 0.823X_\beta + 0.207S_\alpha \\ &\quad - 0.207S_\beta - 0.132Y_\alpha + 0.016Y_\beta \\ &\quad - 0.016Z_\alpha + 0.132Z_\beta + \dots\end{aligned}$$

where R denotes CH_3 .

The above LU MO functions indicate that the oxygen 2p AO lying on the O-O axis occupies strongly the LU MO of both peroxides. This close resemblance between ROOH and ROOR should be also projected on the wave function contours illustrated in **Fig. 2** and **3**.

In regard to the bond strength of the O-O linkage in ROOH or ROOR, the strength, which can be estimated by the overlap population of the O-O (M_{oo}), lessens with attaching of the larger alkyl group (R) to the O-O in both peroxides, and there is a parallelism between the value of M_{oo} and the bond dissociation energy of the O-O linkage, as can be seen in

*1) Notations of X_α , X_β , S_α , Y_α etc. denote p_x -orbitals of O_α and O_β , s -orbital of O_α , p_y -orbital of O_α , etc., respectively. The following notations expressed hereafter stand for the same meanings.

Table 1 O-O Bond Nature of Alkyl Hydroperoxides

ROOH (R)	O-O		Orbital Energies (eV)		$\frac{1}{2}N_{p\sigma}^{LU}$	ΔH_f^a (kcal/mol)	E_{dec} (kcal/mol)
	$p\sigma$	total	HO	LU			
H	0.349	0.359	-15.12	-9.19	-0.310	—	48.0 (5)
CH ₃	0.346	0.361	-14.03	-9.10	-0.309	—	—
C ₂ H ₅	0.345	0.358	-13.33	-9.10	-0.308	—	37.7 ± 0.7 (5)
<i>n</i> -C ₃ H ₇	0.345	0.357	-13.18	-9.10	-0.308	—	—
<i>n</i> -C ₄ H ₉	0.345	0.356	-12.97	-9.10	-0.308	—	—
<i>t</i> -C ₄ H ₉	0.343	0.354	-12.72	-9.09	-0.306	-52.3 (2)	37.8 (5)

a) Enthalpy of formation.

Values in parentheses indicate the reference-numbers.

Table 2 O-O Bond Nature of Dialkyl Peroxides

ROOR	O-O		Orbital Energies (eV)		$\frac{1}{2}N_{p\sigma}^{LU}$	ΔH_f^a (kcal/mol)	E_{dec} (kcal/mol)
	$p\sigma$	total	HO	LU			
CH ₃ OOCH ₃	0.344	0.360	-13.59	-9.00	-0.309	—	36.9 (6)
C ₂ H ₅ OOC ₂ H ₅	0.342	0.355	-12.89	-8.99	-0.307	-54.6 (1)	34.1 (5)
<i>n</i> -C ₃ H ₇ OO <i>n</i> -C ₃ H ₇	0.341	0.353	-12.82	-8.99	-0.306	—	36.5 (8)
<i>n</i> -C ₄ H ₉ OO <i>n</i> -C ₄ H ₉	0.341	0.353	-12.82	-8.99	-0.306	—	—
<i>t</i> -C ₄ H ₉ OO <i>t</i> -C ₄ H ₉	0.329	0.354	-11.78	-9.05	-0.292	-94.3 (2)	34 ± 2 (7)
<i>t</i> -C ₄ H ₉ OOC(CH ₃) ₂ C ₂ H ₅	0.338	0.343	-10.91	-9.07	—	—	33.5 (25)

a) Enthalpy of formation.

Values in parentheses stand for the reference-numbers.

Fig. 2 Wave Function Contour of CH₃OOH at the LU MO. (Solid and broken lines indicate the MO signs. The values of the contour in this map and the following ones are those of the wave functions.) Fig. 3 Wave Function Contour of CH₃OOCH₃ at the LU MO**Table 1 and 2.**

It is of interest here to discuss the reactivity of ROOH or ROOR to nucleophiles. The partial AO bond population of the O-O $p\sigma$ -orbital in the LU MO ($\frac{1}{2}N_{p\sigma}^{LU}$) can be employed as the reactivity index for the decomposition of the O-O linkage by nucleophilic attack, in view of the substantial contribution of the $p\sigma$ -orbital to the O-O linkage formation. From the reactivity index, an assumption can be made that the larger alkyl group attaches to the O-O linkage, the lower becomes the reactivity of ROOH or ROOR to nucleophiles.

3.2 Alkyl Hydroperoxide Dimer, (ROOH)₂

Recently, the dimer structures of hydroperoxides, (ROOH)₂, have come to the attention of some authors^{20,21}, and kinetic²⁰ or spectroscopic^{20,21} study has suggested dimer structures of (ROOH)₂. We will discuss here the dimeric hydroperoxides in terms of their energetic stabilities. As **Fig. 4** indicates, the total energies (E_{EH} in eV) of ROOH (R=H, CH₃, and *t*-C₄H₉) are found to be lower than those of (ROOH)₂. A monomer structure of ROOH, therefore, is more plausible for the molecular structures of alkyl hydroperoxides. In addition, the

Fig. 4 Valence Electron Distributions and Total Energies of Some Hydroperoxide Dimers. (Values in parentheses stand for $1/2N_{p\sigma}^{LU}$.)

Fig. 5 Valence Electron Distributions of Peracids and Peresters

reactivity of $(\text{ROOH})_2$ to nucleophilic reagents is also diminished in comparison with ROOH in view of the smaller value of $1/2N_{p\sigma}^{LU}$ of $(\text{ROOH})_2$.

3.3 Bond Nature of the O-O Linkages in Peracids and Peresters

The thermal stabilities of peracids (RCOOOH) and peresters (RCOOOR') are relatively akin to those of ROOH ¹². The bond nature of their O-O linkages, however, still remains obscure. As **Fig. 5** indicates, the bond strength of the O-O linkage in RCOOOH or RCOOOR' is somewhat weak in comparison with ROOH or ROOR , and, strictly speaking, that of RCOOOR' is found to be somewhat stronger than that of RCOOOH (for instance, compare CH_3COOOH with $\text{CH}_3\text{COOOCH}_3$).

It is of interest that *t*-butyl peracid or perester has a very feeble O-O linkage and that the larger the alkyl group (R in RCOOOH and R' in RCOOOR') that is attached to oxygen atom, the weaker becomes the bond strength of the O-O linkage. The antibonding $p\sigma$ -type orbital of the O-O linkage also characterizes the electronic structures of RCOOOH and RCOOOR' . This antibonding O-O orbital occupies strongly the $\text{LU}+1$ MO and is expressed by the following wave functions.

Fig. 6 Wave Function Contour of CH_3COOOH at the $\text{LU}+1$ MO

Table 3 O-N Bond Nature of Nitrites and Nitrates

Compound	O-N			Orbital Energies (eV)		$\Delta H_f^{(a)}$ (kcal/mol)	E_{dec} (kcal/mol)
	σ	π	total	HO	LU+1		
CH ₃ ONO	0.547	0.129	0.676	-12.39	-1.61	-20.33 (9)	36.4 (9)
C ₂ H ₅ ONO	0.546	0.129	0.675	-12.39	-1.52	-30.50 (9)	37.7 (22)
<i>n</i> -C ₃ H ₇ ONO	0.546	0.129	0.675	-12.39	-1.58	-38.01 (9)	37.7 (9)
<i>sec</i> -C ₃ H ₇ ONO	0.547	0.132	0.679	-12.39	-1.50	—	37.0 (9)
<i>n</i> -C ₄ H ₉ ONO	0.546	0.129	0.675	-12.39	-1.58	—	37.0 (9)
CH ₃ ONO ₂			0.662	-12.86	-0.87	-37.2 (9)	38.4 (9)
C ₂ H ₅ ONO ₂			0.662	-12.68	-0.79	-45.51	36.4 (9)
<i>n</i> -C ₃ H ₇ ONO ₂			0.662	-12.68	-0.85	-51.27 (9)	37.6 (9)

a) Enthalpy of formation.

Values in parentheses indicate the reference-numbers.

Fig. 7 Wave Function Contour of CH₃COOOCH₃ at the LU+1 MO

$$\begin{aligned} \phi^{LU+1}(\text{CH}_3\text{COO}_\alpha\text{O}_\beta\text{H}) = & 0.821X_\alpha + 0.824X_\beta \\ & + 0.210S_\alpha - 0.183S_\beta \\ & + 0.147Y_\alpha - 0.011Y_\beta \\ & - 0.016Z_\alpha + 0.160Z_\beta + \dots \end{aligned}$$

or

$$\begin{aligned} \phi^{LU+1}(\text{CH}_3\text{COO}_\alpha\text{O}_\beta\text{CH}_3) = & 0.811X_\alpha + 0.836X_\beta \\ & + 0.202S_\alpha - 0.186S_\beta \\ & + 0.143Y_\alpha - 0.014Y_\beta \\ & - 0.024Z_\alpha + 0.155Z_\beta + \dots \end{aligned}$$

The features of these wave functions is immediately reflected in their contour maps, as illustrated in Fig. 6 and 7.

3.4 Bond Nature of the O-N Linkages in Nitrites and Nitrates

We will discuss further the bond nature of the O-N linkages in nitrites (RONO) and nitrates (RONO₂). The O-N linkages of these compounds are somewhat stronger than the O-O linkages in peroxide families, and are characterized by the antibonding 2*p* AOs of oxygen and nitrogen atoms lying on the O-N axis. Moreover, the effects of the difference between alkyl groups (R) on the bond strength of the

O-N linkage can scarcely be recognized, in view of the substantially similar overlap populations of the O-N (see Table 3). This is directly related to the almost identical bond dissociation energies of the O-N linkages. In regard to the antibonding O-N linkage, the above 2*p* AOs occupy strongly the LU+1 MO, as is seen from the following wave functions*2).

$$\begin{aligned} \phi^{LU+1}(\text{RO-NO}) = & 0.824X_\text{O} + 0.772X_\text{N} + 0.058S_\text{O} \\ & - 0.294S_\text{N} + 0.368Y_\text{O} \\ & + 0.215Y_\text{N} + \dots \end{aligned}$$

and

$$\begin{aligned} \phi^{LU+1}(\text{RO-NO}_2) = & 0.759X_\text{O} + 0.804X_\text{N} + 0.012S_\text{O} \\ & - 0.242S_\text{N} + 0.458Y_\text{O} \\ & - 0.003Y_\text{N} + \dots \end{aligned}$$

where R stands for CH₃.

The striking resemblance in the bond nature of the O-N linkages in nitrite and nitrate families would be projected on the wave function contours portrayed in Fig. 8 and 9.

Fig. 8 Wave Function Contour of CH₃ONO at the LU+1 MO. (Solid and broken lines indicate the MO signs.)

*2) Notations of X_O, X_N, etc. indicates the *p_x*-orbitals of O and N in the O-N linkage, etc., respectively.

Fig. 9 Wave Function Contour of CH_3ONO_2 at the LU+1 MO

3.5 Bond Nature of the C-O Linkages in Esters and Ethers, and of the O-H Linkages in Alcohols

Esters (RCOOR'), ethers (ROR') and alcohols (ROH) are thermally stable compounds, compared with the compounds mentioned before. The bond dissociation energies of their C-O or O-H linkages are relatively high, and that of the latter linkage almost corresponds to that of the C-H bond of the usual hydrocarbons. The order of their thermal stabilities, alcohol > ester > ether, is given by that of the bond dissociation energies, which bear a rough parallel to the overlap population of the C-O or O-H linkage (in ROR' or ROH respectively) with some irregularities (see **Table**

Table 4 C-O Bond Nature of Esters^{a)}

RCOOR'	C-O			E_{dec} (kcal/mol)
	σ	π	total	
$\text{CH}_3\text{COOCH}_3$	0.584	0.133	0.717	87.7 (9)
$\text{CH}_3\text{COOC}_2\text{H}_5$	0.581	0.134	0.715	87.1 (9)
$\text{CH}_3\text{OOC}n\text{-C}_3\text{H}_7$	0.582	0.134	0.716	88.1 (9)
$\text{CH}_3\text{COO}i\text{-C}_3\text{H}_7$	0.582	0.134	0.716	86.9 (9)
$\text{CH}_3\text{COO}n\text{-C}_4\text{H}_9$	0.582	0.134	0.716	90.9 (9)
$\text{CH}_3\text{COO}i\text{-C}_4\text{H}_9$	0.582	0.134	0.716	92.1 (9)
HCOOCH_3	0.564	0.143	0.707	82.7 (9)
$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$	0.582	0.133	0.715	85.6 (9)

a) C-O bond does not stand for carbonyl group.
Values in parentheses indicate the reference-numbers.

Table 5 C-O Bond Nature of Ethers

ROR'	C-O			E_{dec} (kcal/mol)
	σ	π	total	
CH_3OCH_3	0.542	-0.018	0.524	77
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	0.541	-0.016	0.525	77
$i\text{-C}_3\text{H}_7\text{OCH}_3$	0.541	-0.015	0.526	53
$n\text{-C}_3\text{H}_7\text{OC}_3\text{H}_7$	0.540	-0.016	0.524	78.4
$\text{C}_6\text{H}_5\text{OCH}_3$	0.583	0.037	0.620	85.9
$\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	0.581	0.038	0.619	85.3
$\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$	0.559	0.035	0.594	90.0

4, 5, and 6). Particularly in ester, the difference in the bond dissociation energies of the C-O linkage does not correspond to the almost

Table 6 O-H Bond Nature of Alcohols

ROH	O-H			ΔH_f^{a} (kcal/mol)	E_{dec} (kcal/mol)
	$ss\sigma$	$sp\sigma$	total		
HOH	0.162	0.378	0.540	—	120 (9)
CH_3OH	0.192	0.362	0.553	-57.02 (23)	100 (9)
$\text{C}_2\text{H}_5\text{OH}$	0.190	0.361	0.551	-66.36 (23)	99 (9)
$n\text{-C}_3\text{H}_7\text{OH}$	0.189	0.361	0.551	-73.25 (23)	101 (9)
$n\text{-C}_4\text{H}_9\text{OH}$	0.190	0.361	0.551	-79.7 (23)	103 (9)
$t\text{-C}_4\text{H}_9\text{OH}$	0.190	0.354	0.545	-87.9 (2)	104 (9)

a) Enthalpy of formation.

Values in parentheses indicate the reference-numbers.

Fig. 10 Wave Function Contour of $\text{CH}_3\text{COOCH}_3$ at the LU+1 MO. (Solid and broken lines implies opposite signs of MO.)

Fig. 11 Wave Function Contour of CH_3OH at the LU MO

constant overlap population of the C–O linkage; this may be due to observational and calculation errors. In regard to the above order, it is worthy of mention that the large bond strength of the O–H in ROH is ascribed to the large contribution of $sp\sigma$ -overlapping of the O–H, and that the π bond nature brings about a stronger C–O linkage in ester than the C–O in ether (in which the π character is not to be expected).

The wave function contours illustrated in **Fig. 10** and **11** indicate the bond nature discussed above.

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

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