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Electronic Structures of Dialkyl Peroxides

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Dialkyl peroxides (ROOR) have often been postulated as intermediates in hydrocarbon oxidations. The chemical properties of the said peroxides are closely akin to those of alkyl hydroperoxides (ROOH) in terms of the bond-dissociation energies[1] of their O–O linkages and their reactivities to nucleophiles[2] or electrophiles.[3] The bond character of the O–O linkage in ROOR, however, has not yet been established strictly. The present study intends to illuminate the electronic structures of ROOR in connection with those of ROOH by the use of the extended Hückel method.[4]

Calculation Method

The geometries of ROOR used for the calculations were set up similarly to those of ROOH,[5] as is indicated below:

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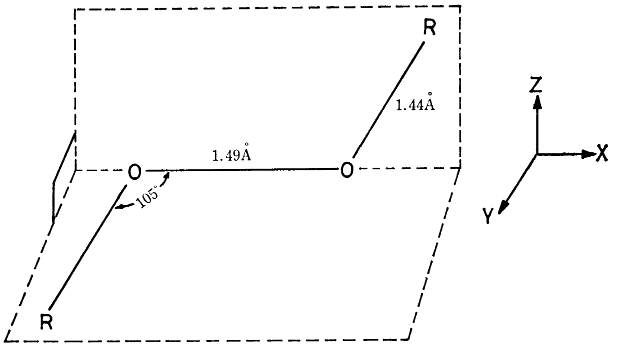
[1] A. D. Kirk and J. H. Knox, *Trans. Faraday Soc.*, **56**, 1296 (1960).

[2] For instance, L. S. Silbert, and D. Swern, *J. Amer. Chem. Soc.*, **81**, 2365 (1959); J. K. Kochi, *ibid.*, **85**, 1958 (1963).

[3] F. Haber and P. Weiss, *Proc. Roy. Soc.*, London, **A147**, 233 (1939); N. Uri, *Chem. Rev.*, **50**, 375 (1952).

[4] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964).



R=H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and t-C_4H_9

The orbital exponents and Coulomb intergrals ($H_{\mu\mu}$) were supplied by Clementi⁶⁾ and Jaffé⁷⁾ respectively. Especially, as the $H_{\mu\mu}$ values of the oxygen atom, the following values were taken:
$H_{\mu\mu}$(eV) = −36.07 (O 2s) and −15.85(O 2p).
The resonance integrals ($H_{\mu\nu}$) were evaluated by the Wolfsberg-Helmholtz approximation⁸⁾: $H_{\mu\nu}=0.875\,(H_{\mu\mu}+H_{\nu\nu})S_{\mu\nu}$, where $S_{\mu\nu}$ is the overlap intergral between AO's.

Results and Discussion

First, let us discuss the bond character of the O–O linkage in ROOR. As Table 1 indicates, the bond population of the O–O (M_{oo}) is relatively small, falling in the range, 0.353—0.369. This range of M_{oo} is the same as or slightly smaller than that of ROOH.⁵⁾ From this result, it can be deduced that the energy required for the homolytic scission of the O–O linkage (E_{dec}) in ROOR is much the same as that in ROOH; In fact, the observed values are 37.9± 0.4 kcal/mol for the former and 41.1 kcal/mol for the latter, on the average. A parallelism between M_{oo} and E_{dec} could be observed with some exceptions. This close resemblance in the bond character of the O–O linkage between ROOR and ROOH can also be observed in the orbital energy (see Table 1). The lowest unoccupied molecular orbitals (LU MO) of both peroxides are localized in O–O, as is illustrated by the following examples:⁹⁾

$$\begin{aligned}\varphi^{LU}(RO_\alpha O_\beta R) = {} & 0.823X_\alpha + 0.823X_\beta + 0.207S_\alpha \\ & - 0.207S_\beta - 0.132Y_\alpha + 0.016Y_\beta \\ & - 0.016Z_\alpha + 0.132Z_\beta + \cdots\end{aligned}$$

and

$$\begin{aligned}\varphi^{LU}(RO_\alpha O_\beta H) = {} & 0.833X_\alpha + 0.813X_\beta + 0.217S_\alpha \\ & - 0.201S_\beta - 0.139Y_\alpha + 0.017Y_\beta \\ & - 0.009Z_\alpha + 0.145Z_\beta + \cdots\end{aligned}$$

where R denotes CH_3. These wave functions show that the LU MO's are mainly the 2p AO's of oxygen atoms.

Table 1. Bond character of the O–O linkage and orbital energies in dialkyl peroxides (ROOR)

ROOR (R)	M_{oo}	N_{oo} ($p\sigma$)	Orbital energy (eV) HO	LU	E_{dec} [a] (kcal/mol)
H	0.369	0.359	−15.12	−9.19	48.0[b]
CH_3	0.360	0.344	−13.58	−9.00	36.9[c]
	(0.361)	(0.346)	(−14.03)	(−9.10)	(——)
C_2H_5	0.355	0.342	−12.89	−8.99	34.1[b]
	(0.358)	(0.345)	(−13.60)	(−9.10)	(37.7[b])
n-C_3H_7	0.353	0.341	−12.82	−8.99	36.5[d]
	(0.357)	(0.345)	(−13.18)	(−9.10)	(——)
n-C_4H_9	0.353	0.341	−12.82	−8.99	——
	(0.357)	(0.345)	(−12.97)	(−10.85)	(——)
t-C_4H_9	0.354	0.329	−11.78	−9.05	34±2[e]
	(0.354)	(0.343)	(−12.72)	(−9.09)	(37.8[b])

a) Activation energies of decomposition.
b) Cited from Ref. 1.
c) Cited from Y. Takezaki and C. Takeuchi, *J. Chem. Phys.*, **9**, 1527 (1954).
d) Cited from E. J. Harris, *Proc. Roy. Soc.* (London), **A173**, 126 (1939).
e) Cited from J. Murawski, J. S. Roberts, and M. Szwarc, *J. Chem. Phys.*, **19**, 698 (1951).
Values in parentheses stand for those in ROOH.

Next, let us examine the reactivity of ROOR to nucleophiles or electrophiles. The LU MO and the HO MO play an important role in weakening the O–O linkage by means of interaction with nucleophiles and electrophiles respectively. The LU MO is strongly localized in the O–O linkage, as has been mentioned before, and has an antibonding character with respect to the O–O bond, whereas the HO MO is occupied predominantly by the nonbonding oxygen orbitals. Consequently, nucleophiles attack ROOR in the direction of the O–O axis, while electrophiles approach the nonbonding oxygen orbital expansion from the opposite side of R.

As the reactivity indices we employed the value of

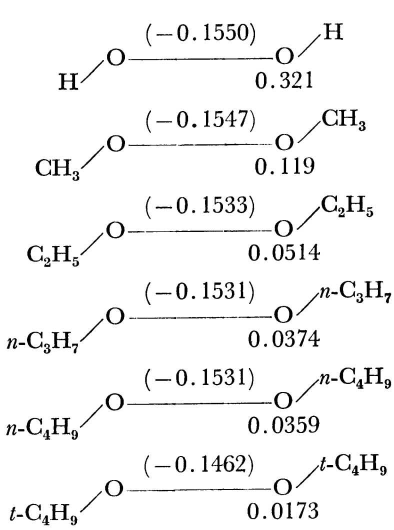


Fig. 1. Reactivity indices in ROOR.
(The figures without parentheses stand for $1/2N_{nbo}^{HO}$; th figures with parentheses indicate $1/4N_{p\sigma}^{LU}$.)

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

6) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

7) J. Hinze and H. H. Jaffè, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

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

9) The notations of X_α, X_β, S_α, *etc.* denote $O_\alpha px$, $O_\beta px$, $O_\alpha s$ orbitals *etc.* respectively.

the partial AO bond population of the antibonding $p\sigma$-orbital of the O–O in the LU MO, ¼$N_{P\sigma}^{LU}$, and that of the partial AO population of the nonbonding oxygen orbital in the HO MO, ½N_{nbo}^{HO}, both of which are given in Fig. 1. A presumption can be made that the reactivity of ROOR to nucleophiles or electrophiles lessens with the bonding of the larger alkyl groups to the O–O.

Finally, it is of interest to compare the reactivity indices to nucleophiles in ROOR with those in ROOH. Three alkyl hydroperoxides selected for the sake of comparison, CH_3OOH, *n*-C_3H_7OOH, and *t*-C_4H_9OOH, have the following values of $-N_{P\sigma}^{LU}$: −0.1547, −0.1539, and −0.1528 respectively. On the basis of the facts derived above, we may conclude that ROOH is more reactive than ROOR to the nucleophilic attack.