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Estimation of Structures and Electronic States of Radicals Using INDO-SCFMO Method. II. Alkylperoxyl Radicals

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Synopsis. The energetically most stable CH_3OO and CH_3CH_2OO radicals have been found to have the following geometric values: $r(O_\alpha–O_\beta)=1.12$ Å, $r(O_\alpha–C)=1.38$ Å for the former and 1.39 Å for the latter, $\angle CO_\alpha O_\beta=112°$ for the former and 115° for the latter, and $r(C–C)=1.47$ Å for the latter.

Alkylperoxyl radicals (referred to as ROO·) have been postulated as reactive intermediates participating in the oxidation and polymerization reactions. The said radicals are recently believed to play an important role in the air-pollution cycle:

Hydrocarbons such as olefin$+{}^1O_2 \rightarrow$ Hydroperoxide $\xrightarrow{\text{dec.}}$ Radicals such as RO·

$$RO\cdot + {}^3O_2 \rightarrow (RO_3\cdot) \xrightarrow{NO_2} ROO\cdot + NO_2$$

$$ROO\cdot + NO \rightarrow RO\cdot + NO_2$$

The molecular structures and electronic states of ROO·, however, are yet open to question, although aspects of HOO· have been investigated by INDO[1] and *ab initio* SCF[2] methods. There are, therefore, good reasons for embarking on an MO-study of ROO· with a view of estimating how their structures and electronic properties. We wish now to report our results on ROO· ($R=CH_3$ and CH_3CH_2).

Method of Calculation

The following two systems were investigated in this work: (a) the methylperoxyl radical, $CH_3OO\cdot$ and (b) the ethylperoxyl radical, $CH_3CH_2OO\cdot$. The geometric parameters of the above species are shown in Fig. 1. All the valence-bond angles except those denoted by θ were uniformly taken to be 109°28′ for the sake of simplicity.

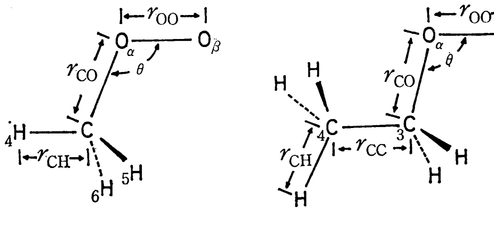

Fig. 1. Geometries used for calculations. ($r(O_\alpha–O_\beta)$, $r(O_\alpha–C)$, $r(C–C)$, $r(C–H)$, and θ denote geometric parameters.)

The method of calculation is a semiempirical INDO, using the integrals and parametrization in Ref. 3.

Results and Discussion

Methylperoxyl Radical. The INDO calculations were first performed on $CH_3OO\cdot$ with three variables of the bond distances ($r(O_\alpha–O_\beta)$, $r(O_\alpha–C)$, and $r(C–H)$) and one variable of the valence bond angle (θ) by changing $r(O_\alpha–O_\beta)$, θ, $r(O_\alpha–C)$, and $r(C–H)$ in turn.[4] As can be seen from Table 1, the set of $r(O_\alpha–O_\beta)=1.20$ Å, $r(O_\alpha–C)=1.38$ Å, $r(C–H)=1.12$ Å, and $\theta=112$ ° gives the lowest SCF total energy (E_{SCF}) for $CH_3OO\cdot$.[5] The estimated bond length of $O_\alpha–O_\beta$ (1.20 Å) is very close to that of O_2 (exptl.=1.207 Å[7]), but appreciably shorter than that of HOO·[8] (exptl.=1.30 Å[9]), while the $O_\alpha–C$ length (1.38 Å) is fairly short as compared with the single C–O bonds (1.43 Å). The C–H bond

Table 1. Changes in total energy and electronic state of $CH_3OO\cdot$ as a function of four variables, $r(O_\alpha–O_\beta)$, θ, $r(O_\alpha–C)$, and $r(C–H)$

$r(O_\alpha–O_\beta)$/Å	θ	$r(O_\alpha–C)$/Å	$r(C–H)$/Å	E_{SCF}/a.u.	Q_A O_α	Q_A O_β	Odd-electron density	μ/D
1.19	112°	1.44	1.09	−44.3438	−0.036	−0.125	1.218	2.18
1.20	112°	1.44	1.09	−44.3439	−0.043	−0.120	1.207	2.16
1.21	112°	1.44	1.09	−44.3430	−0.048	−0.116	1.200	2.16
1.20	111°	1.44	1.09	−44.3438	−0.042	−0.121	1.208	2.15
1.20	112°	1.44	1.09	−44.3439	−0.043	−0.120	1.207	2.16
1.20	113°	1.44	1.09	−44.3438	−0·043	−0.120	1.208	2.18
1.20	112°	1.37	1.09	−44·3498	−0.039	−0.120	1.205	2.04
1.20	112°	1.38	1.09	−44.350295	−0.040	−0.120	1.206	2.06
1.20	112°	1.39	1.09	−44.350290	−0.040	−0.120	1.207	2.09
1.20	112°	1.38	1.11	−44.3539	−0.039	−0.119	1.205	2.03
1.20	112°	1.38	1.12	−44.3543	−0.038	−0.119	1.208	2.03
1.20	112°	1.38	1.13	−44.3540	−0.038	−0.118	1.205	2.01

(1.12 Å) is also estimated to be longer than the normal C–H distance (1.09 Å). The angle of θ (112 °) also differs by 4° from that of HOO· (exptl. = 180°[9]). Moreover, the estimated dipole moment (2.03 D) of $CH_3OO\cdot$, which possesses the slightly negative formal charges (Q_A) of two oxygen atoms, may be close to those of CH_3OH (exptl. = 1.69 D[10]; calcd. by INDO = 1.94 D[3]) and H_2O (exptl. = 1.846 D[11]; calcd. by INDO = 2.10 D[3]).

With regard to the g value of the CH_3OO radical, it was evaluated to be 2.003 by means of the Stone equation.[12] The g value is found to be in good agreement with the experimental value of 2.015.[13]

The odd-electron (its density = 1.208) is predominantly localized in the following half-occupied MO (−0.5005 a.u.), $\phi^{\text{occ}}_{\text{odd}}$:

$$\phi^{\text{odd}}_{\text{occ}} = 0.592Z_{O_\alpha} - 0.729Z_{O_\beta} + 0.150Z_C + 0.223S_{5H} - 0.223S_{6H},$$

while the lowest unoccupied MO (0.1608 a.u), $\phi^{\text{odd}}_{\text{unocc}}$, comes mainly from the following AOs:

$$\phi^{\text{odd}}_{\text{unocc}} = 0.873Z_{O_\beta} - 0.416Z_{O_\alpha} - 0.147Z_C + 0.148S_{5H} - 0.148S_{6H}$$

where Z_{O_α}, Z_C, S_{5H}, *etc.* stand for the p_z of O_α, the p_z of C, the s of 5H, *etc.* respectively.

It is observed that the O_β p_z-orbital contributes distinctly to the formation of both MOs.

Ethylperoxyl Radical. As Fig. 1 indicates, the ethylperoxyl radical, $CH_3CH_2OO\cdot$, has four geometric parameters ($r(O_\alpha–O_\beta)$, $r(O_\alpha–C)$, $r(C–C)$, and θ) in the present INDO calculations. The calculated results with respect to the most energetically stable $CH_3CH_2OO\cdot$ are summarized in Table 2. The angle of θ (115°) is larger than that of $CH_3OO\cdot$, though the $O_\alpha–O_\beta$ and $O_\alpha–C$ lengths are just (or nearly) the same as those of $CH_3OO\cdot$. The r(C–C) of 1.47 Å is shorter than the usual single C–C bond (1.54 Å). The INDO calculations, however, sometimes estimate the C–C bond length of hydrocarbons too short; for example, the C–C bond lengths of C_2H_6 (1.46 Å) and C_2F_6 (1.49 Å) are reasonably shorter than those of the experiments (1.536 and 1.51 Å respectively). Moreover, the two oxygen atoms of $CH_3CH_2OO\cdot$ were found to be more positively charged than those of $CH_3OO\cdot$, although the magnitude of the odd-electron density (1.204) is small in comparison with $CH_3OO\cdot$.

TABLE 2. MOLECULAR STRUCTURE AND ELECTRONIC STATE OF $CH_3CH_2OO\cdot$

Minimum E_{SCF}/a.u.		−52.803
$r(O_\alpha$-$O_\beta)$/Å		1.20
$r(O_\alpha$-C)/Å		1.39
r(C-C)/Å		1.47
θ/deg		115
μ/D		1.94
g value		2.010
Q_A	O_β	−0.124
	O_α	−0.053
	3C	+0.237
	4C	+0.025
N_{O_β}[a]	s	1.867
	p_x	1.066
	p_y	1.987
	p_z	1.204
N_{O_α}[a]	s	1.661
	p_x	1.154
	p_y	1.470
	p_z	1.769
$P_{O_\alpha-O_\beta}$[b]	p_x-p_x	−0.836
	p_y-p_y	+0.076
	p_z-p_z	+0.399

a) AO population. b) Bond-order.

Finally, it is worthy of emphasis that, in the INDO calculations, a π-conjugation consisting of the lone-pair p_z-orbital of O_α and the half-occupied p_z-orbital of O_β was recognized in both the radicals (for instance, see the bond-orders of the $O_\alpha–O_\beta$ bond of $CH_3CH_2OO\cdot$ in Table 2).

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

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4) A molecule involving N geometric parameters requires at least N^2 SCF evaluations for estimating its minimum SCF energy (for instance, see MINDO/2p program, QCPE program No. 228). The present calculations, however, did not follow this procedure for the simplicity of computations, and the minimum energy of a molecule was determined by changing the parameters in turn until the values of the parameters come to be identical.

5) CNDO/2 calculations[6] gave the best set of $r(O_\alpha–O_\beta) = 1.19$ Å and $\theta = 111°$ at the fixed bond distances of $r(O_\alpha–C) = 1.44$ Å and $r(C–H) = 1.09$ Å.

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