NOTES

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Estimation of the Structures and Electronic States of Radicals Using the INDO-SCF MO Method. I. Alkoxyl Radicals

Katsutoshi OHKUBO and Futoshi KITAGAWA

Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860

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Synopsis. The most energetically stable alkoxyl radicals take the following configuration: r(C–O)=1.36 Å, r(C–H)=1.12 Å, and ∠OCH=109°28′ for $CH_3O\cdot$, and r(C–O)=1.36 Å, r(C–C)=1.47 Å, and ∠OCC=108° for $C_2H_5O\cdot$. The pseudo π orbital is observed in the C–O bond.

Alkoxyl radicals (referred to as RO·) have been postulated as momentarily-living intermediates participating in the oxidation and polymerization reactions. Recently, they have been considered to play an important role in the air-pollution cycle:

$$\underset{\text{H}}{\text{-C=C-C-}} + {}^1O_2 \longrightarrow \underset{\text{OOH}}{\text{-C-C=C-}}$$

$$\xrightarrow{\text{dec.}} \text{Radicals such as RO}\cdot$$

$$RO\cdot + {}^3O_2 \longrightarrow RO_3\cdot$$

$$\xrightarrow{\text{NO}} RO_2\cdot + NO_2 \text{ (or } RO_3NO)$$

$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2$$

The molecular structures and electronic states of RO radicals, however, seem to be open to question, although some rough estimates of the said aspects of the radicals have been established by the iterative extended Hückel[1] and CNDO/2[2] treatments of some lower molecules.

In the present study, we will estimate the molecular structures and electronic states of RO radicals by means of the INDO–SCF MO method,[3] taking methoxyl and ethoxyl radicals as examples.

Method of Calculation

The following two systems were investigated in this work: (a) the methoxyl radical, $CH_3O\cdot$ and (b) the ethoxyl radical, $CH_3CH_2O\cdot$. The geometric parameters of the above species are shown in Fig. 1. In $CH_3CH_2O\cdot$, the interatomic distance of C–H and the valence angle of H–C–H of the CH_3 group were uniformly taken to be 1.09 Å and 109°28′ for the sake of simplicity.

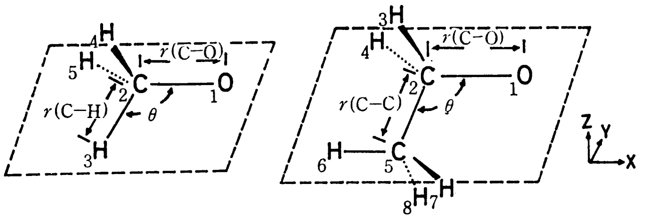


Fig. 1. Geometries used for calculations. (r(C–O), θ, r(C–H), and r(C–C) stand for geometric parameters.)

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

Results and Discussion

Methoxyl Radical. The INDO calculations were first performed on $CH_3O\cdot$ with two variables of the bond distances, r(C–O) and r(C–H), and one variable of the valence-bond angle, θ, by changing r(C–O), θ, and r(C–H) in turn.[4] As Table 1 indicates, the set of r(C–O)=1.36 Å, r(C–H)=1.12 Å, and θ=109°28′ give the lowest SCF total energy (E_{SCF}) of $CH_3O\cdot$. The bond angle of θ is in accordance with the usual sp^3 hybrid valence angle, while the bond lengths of r(C–O) and r(C–H) differ appreciably from those (r(C–O)≈1.44 Å[5] and r(C–O)≈1.09 Å[5]) of usual alcohols and carboxylic acids. In particular, the large estimated r(C–H) value of 1.12 Å is distinctive. It may also be seen in Table 1 that the formal charges (Q_A) of +0.240 for C and −0.178 for O give the dipole

TABLE 1. CHANGES IN TOTAL ENERGY AND ELECTRONIC STATE OF $CH_3O\cdot$ AS A FUNCTION OF THREE VARIABLES, r(C–O), θ, AND r(C–H)

r(C–O)/Å	θ	r(C–H)/Å	E_{SCF}/a.u.	Q_A C	Q_A O	Odd-electron density	μ/D
1.35	109°28′	1.09	−26.6063	+0.242	−0.180	1.037	1.80
1.36	109°28′	1.09	−26.6064	+0.240	−0.180	1.035	1.81
1.37	109°28′	1.09	−26.6060	+0.236	−0.180	1.034	1.82
1.36	109°	1.09	−26.6063	+0.239	−0.181	1.075	1.81
1.36	109°28′	1.09	−26.6064	+0.240	−0.180	1.035	1.81
1.36	110°	1.09	−26.6063	+0.240	−0.179	1.238	1.81
1.36	109°28′	1.11	−26.6101	+0.240	−0.179	1.058	1.79
1.36	109°28′	1.12	−26.6106	+0.240	−0.178	1.056	1.78
1.36	109°28′	1.13	−26.6103	+0.240	−0.177	1.101	1.77

moment (μ) of 1.78 D, working mainly in the direction of the C–O bond axis.

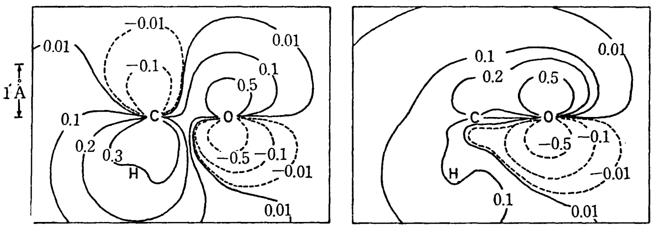
The odd-electron (its density=1.056) is predominantly localized in the following occupied MO, ψ^{odd}_{occ}:

$$\psi^{odd}_{occ} = 0.734Y_O + 0.112Z_O - 0.358Y_C + 0.456S_{3H} - 0.287S_{4H} - 0.167S_{5H}{}^{6)}$$

while the lowest unoccupied MO, ψ^{odd}_{unocc}, is also occupied strongly by the oxygen $2p_y$-orbital as:

$$\psi^{odd}_{unocc} = 0.849Y_O + 0.129Z_O + 0.174Y_O + 0.386S_{3H} - 0.248S_{4H} - 0.146S_{5H}{}^{6)}$$

Here, let us illustrate the orbital contour maps of both MOs in Fig. 2 in order to aid understanding of the MOs.



ψ^{odd}_{occ} ψ^{odd}_{unocc}

Fig. 2. Orbital Contour Maps of ψ^{odd}_{occ} and ψ^{odd}_{unocc} of $CH_3O\cdot$.
(x-y cross-section; solid and dotted curves are positive and negative MO signs respectively.)

Ethoxyl Radical. The INDO calculations were performed further on $CH_3CH_2O\cdot$ with three variables (r(C–O), θ, and r(C–C) in Fig. 1). The computation results with respect to the most energetically stable $CH_3CH_2O\cdot$ are shown in Table 2, together with the results from the CNDO/2 calculations. The bond angle of θ differs by 1°28′ from the sp^3 hybrid valence angle, and the r(C–C) of 1.47 Å is shorter than the usual single C–C bond (~1.54 Å). Moreover, the Q_A values of 2C and O atoms are more positively or negatively charged than those of $CH_3O\cdot$, although the magnitude of the odd-electron density (1.045) is weak in comparison with $CH_3O\cdot$.

With regard to the ionization energies (I_p), the INDO evaluations are relatively large, as we expected, for such open-shell molecules as the $CH_3O\cdot$ and $CH_3CH_2O\cdot$ radicals as well as for the closed-shell molecules. The I_p values[7] of 0.526 a.u. for $CH_3O\cdot$ and 0.509 a.u. for $CH_3CH_2O\cdot$ differ considerably from those derived from experiments (0.339 a.u.[8] for the former and 0.337 a.u.[9] for the latter).

Finally, it is worthy of emphasis that, in the INDO calculations, the pseudo π orbital consisting of the $2p_z$-orbitals of the C and O atoms is observed in the

Table 2. Molecular structure and electronic state of $CH_3CH_2O\cdot$

Minimum E_{SCF}/a.u.		−35.056	(−36.385)
r(C–O)/Å		1.36	(1.36)
r(C–C)/Å		1.47	(1.54[a)])
θ/deg.		108	(109°28′ [a)])
Dipole moment μ/D		1.94	(1.95)
Q_A	O	−0.200	(−0.162)
	2C	+0.262	(+0.158)
	5C	+0.039	(−0.019)
N_O[b)]	p_x	1.369	(1.355)
	p_y	1.045	(1.044)
	p_z	1.961	(1.968)
N_C[b)]	p_x	−0.8246	(−0.8769)
	p_y	1.001	(1.022)
	p_z	0.9139	(0.9524)
P_{C-O}[c)]	p_x–p_x	−0.7504	(−0.7463)
	p_y–p_y	0.2335	(0.2426)
	p_z–p_z	0.2052	(0.1834)

a) Fixed values in the CNDO/2 calculations.
b) AO populations of O and C. c) Bond-orders of C–O. Values in parentheses denote those resulted from the CNDO/2 calculations.

C–O bond (for instance, see AO populations of the C and O and the bond-orders of the C–O bond in Table 2), as well as that in the iterative extended Hückel calculations.[1]

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

References

1) O. Yamamoto, H. Kato, and T. Yonezawa, *Nippon Kagaku Zasshi*, **91**, 907 (1970).

2) K. Ohkubo and F. Kitagawa, *Nippon Kagaku Kaishi*, **1973**, 2147.

3) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).

4) Strictly speaking, a molecule involving three variables requires 3^2 SCF evaluations for estimating its minimum SCF energy, but the present study did not follow this procedure for the simplicity of computations.

5) L. E. Sutton, editor, "Interatomic Distances," The Chemical Society, London (1958).

6) The notations of Y_O, Y_C, S_{3H}, *etc.* stand for the $2p_y$ of O the $2p_y$ of C, the s of 3H, *etc.* respectively. The eigenvectors below 0.09 were neglected for simplicity.

7) Estimated from the orbital energy of the highest occupied MO.

8) M. S. B. Munson and J. L. Franlkin, *J. Phys. Chem.*, **68**, 3191 (1964).

9) R. R. Bernecker and F. A. Long, *ibid.*, **65**, 1565 (1961).