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# An MO-Theoretical Study of the Electronic Structures of Formyloxyl and Acetoxyl Radicals

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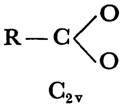
**Synopsis.** A semi-empirical NDDO MO method was applied to formyloxyl(HCOO) and acetoxyl($CH_3COO$) radicals in order to determine whether the ground-state electronic structure of the acyloxyl radical is of $\sigma$- or $\pi$-type. A $\sigma$-type state was found to be more stable than a $\pi$-type state over the entire range of values of the OCO angles of these radicals. This appears to be in agreement with the experimental facts which have been derived from the ESR spectra of several acyloxyl radicals.

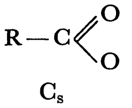
Acyloxyl radicals are important intermediates in the thermal decomposition of acyl peroxides, although only a few acyloxyl radicals have directly been detected.[1-2] An important problem related to the acyloxyl radicals is to determine whether their ground-state electronic structures are of $\sigma$- or $\pi$-type. This problem is a key point in clarifying the role of acyloxyl radicals in the decomposition processes of acyl peroxides and has already been investigated both experimentally and theoretically. The observed principal values and directions of the *g*-tensors[1,2] appear to support a $\sigma$-type ground state for the acyloxyl radicals, while theoretical calculations performed up to now using INDO[3] and STO-3G[4] methods support a $\pi$-type state. This note presents theoretical results which were obtained using a semi-empirical NDDO MO method and which support a $\sigma$-type electronic structure for the ground-state of the acyloxyl radical.

The restricted SCF procedure for open-shell electronic systems proposed by Pople *et al.*[5] was applied to the simple acyloxyl radicals, the formyloxyl and acetoxyl radicals. In the SCF procedure, the MO of an open-shell system are divided into three parts, doubly-occupied, singly-occupied, and empty MO. A variational method was successively applied to two of the three groups, and the MO for a given electron configuration were determined by SCF iteration. The $\sigma$- and $\pi$-type electronic structrues for a given conformation of the acyloxyl radicals were obtained by assigning the singly-occupied MO to $\sigma$- and $\pi$-orbitals, respectively. In the evaluation of the matrix elements, the NDDO approximation,[6] which gives well-balanced molecular geometries and excitation energies, was employed.

The energetic dependence of $\sigma$- and $\pi$-states of the formyloxyl and acetoxyl radicals on their molecular geometries was calculated in detail. In the calculation of formyloxyl, a planar conformation was assumed. $C_{2v}$ and $C_s$ symmetries are possible geometries for the planar formyloxyl radical:



$C_{2v}$



$C_s$

The expected lower electronic states of $C_{2v}$ symmetry are written as:

$$\cdots(b_2)^2(a_2)^2(a_1)^1;\ {}^2A_1(\Sigma)$$
$$\cdots(a_2)^2(a_1)^2(b_2)^1;\ {}^2B_2(\Sigma)$$
$$\cdots(a_1)^2(b_2)^2(a_2)^1;\ {}^2A_2(\Pi)$$

and those of $C_s$ symmetry as:

$$\cdots(a'')^2(a')^1;\ {}^2A'\ (\Sigma)$$
$$\cdots(a')^2(a'')^1;\ {}^2A''(\Pi)$$

The schematic shapes of the MO in the avove configurations are shown in Fig. 1. The energy variation of each electronic state on the OCO angle is shown in Fig. 2. The curves were obtained with CH and CO

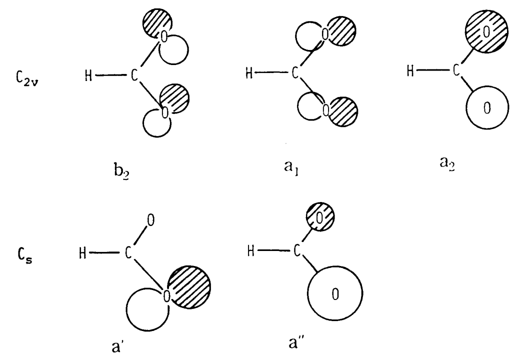


Fig. 1. Schematic representation of MO's which may be occupied by unpaired electron.

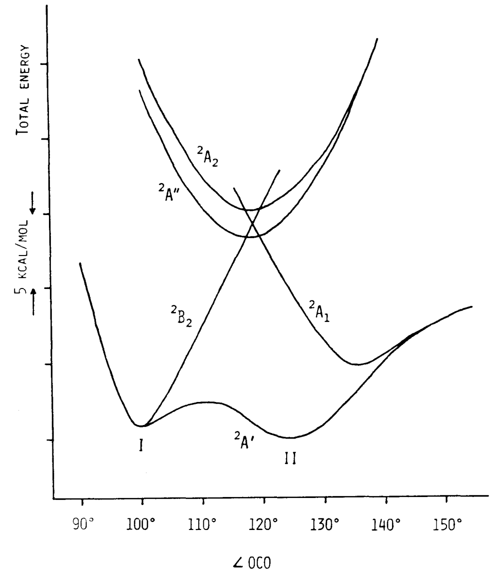


Fig. 2. Dependence of electronic states of formyloxyl radical upon the OCO angle. ${}^2B_2$, ${}^2A_1$, and ${}^2A'$ states correspond to the "$\sigma$-radical" and ${}^2A_2$ and ${}^2A''$ to the "$\pi$-radical".

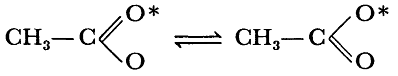
bond lengths which were optimized for each OCO angle and each state.

A $\sigma$-type electronic structure is more stable than a $\pi$-type structure over the entire range of OCO angles. The most stable $\pi$-type radical lies 13 kcal/mol above the most stable $\sigma$-radical. This is contrary to the theoretical results obtained up to the resent[2-4] and agrees with the experimental results which were derived from the $g$-tensors of several acyloxyl radicals.[1,2] Two stable conformations are expected for the ground state of formyloxyl: one is of $C_{2v}$ symmetry (I: $^2B_2$ with $\angle OCO=100°$) and the other is of $C_s$ symmetry (II: $^2A'$ with $\angle OCO=125°$). Although the energy difference between I and II is very small, their electronic structures differ greatly. In radical I, more than 98% of the unpaired electrons are equally shared on two equivalent oxygen atoms, while about 90% of the unpaired electrons localized on oxygen atom in radical II. The geometrical changes of formyloxyl along the lowest curve are listed in Table 1.

TABLE 1. GEOMETRY OF THE $^2\Sigma$-TYPE FORMYLOXYL RADICAL

| Total energy | ∠OCO | C-O(1) | C-O(2) | C-H |
|---|---|---|---|---|
| −772.04 eV | 90° | 1.315 Å | 1.375 Å | 1.065 Å |
| −772.51 | 100 | 1.250 | 1.250 | 1.075 |
| −772.43 | 110 | 1.210 | 1.290 | 1.085 |
| −772.52 | 120 | 1.245 | 1.300 | 1.075 |
| −772.50 | 130 | 1.240 | 1.290 | 1.148 |
| −772.31 | 140 | 1.230 | 1.255 | 1.225 |
| −772.20 | 150 | 1.220 | 1.220 | 1.320 |
| −772.15 | 160 | 1.190 | 1.190 | 1.420 |

The results for the acetoxyl radical were almost identical to those of the formyloxyl radical. In the acetoxyl radical, as for the formyloxyl radical, the energy difference between the two $\sigma$-radicals corresponding to I and II of formyloxyl is very small (<2 kcal/mol) and the barrier for the conversion between them is also very small (<2 kcal/mol). This indicates that the conversion



$$CH_3-C\begin{matrix}O^*\\O\end{matrix} \rightleftharpoons CH_3-C\begin{matrix}O^*\\O\end{matrix}$$

is very fast. In fact, the very fast scrambling between the two oxygen atoms, and the equivalence of the two oxygen atoms before the successive reactions involving the acetoxyl radical, have been confirmed experimentally.[7] A slight difference between formyloxyl and acetoxyl is the unpaired-electron distribution in radical II; 13% of the unpaired electrons delocalizes on the methyl-carbon atom in acetoxyl.

The question remains whether conventional MO methods can correctly predict the small energy difference between two closely adjacent electronic states. However, the present results are the first theoretical support for a $\sigma$-type ground state of the formyloxyl and acetoxyl radicals which appear to agree with the experimental facts derived from ESR spectra of several acyloxyl radicals.

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