Tetrahedron Letters No. 28, pp 2421 - 2424, 1977. Pergamon Press. Printed in Great Britain.

THEORETICAL ASSIGNMENT OF THE ELECTRONIC GROUND STATE OF THE FORMYLOXYL RADICAL

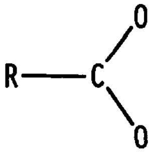
O. Kikuchi
Department of Chemistry, The University of Tsukuba
Sakura-mura, Ibaraki 300-31, Japan

(Received in Japan 7 May 1977; received in UK for publication 27 May 1977)

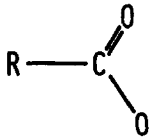
"Σ or Π ?" is a recent point in dispute for the electronic ground state of acyloxyl radicals which are very important intermediates in thermal and photochemical decomposition of acyl peroxides. Both ESR-experimental[1,2] and MO-theoretical[2-4] investigations have been reported on the electronic structure of acyloxyl radicals. The observed g-tensors[1,2] appear to support the Σ-ground state for the acyloxyl radical. Recent semi-empirical NDDO calculations[4] also predict the Σ-ground state. On the other hand, the INDO calculations[2,3] and ^{13}C CIDNP[2] support the Π-type ground state, and the question has not been solved whether the electronic ground state of the acyloxyl radical is Σ- or Π-type. This paper intends to solve this problem by means of *ab initio* spin-restricted open-shell SCF calculations.

C_{2v} and C_s are possible symmetries for the planar RCOO radical.

C_{2v}



C_s



The lower electronic states expected for C_{2v} HCOO are $^2A_1(\Sigma)$, $^2B_2(\Sigma)$, and $^2A_2(\Pi)$, and those for C_s HCOO are $^2A'(\Sigma)$ and $^2A''(\Pi)$. The qualitative pictures of the unpaired-electron orbitals for these five states are shown in Fig. 1. In order to determine these five electronic states, *ab initio* calculations of HCOO were performed in a minimal basis set at the STO-3G level, the GTO expansion of STO

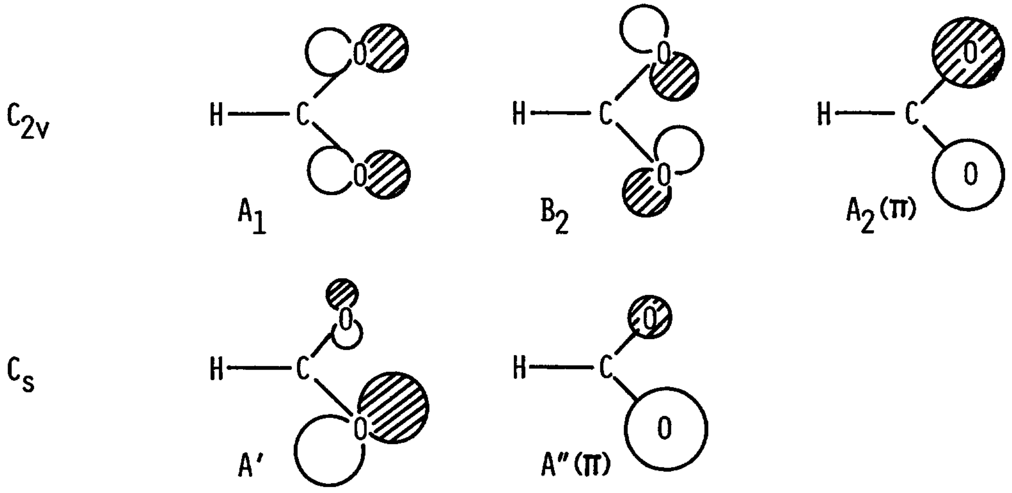


Fig. 1. Qualitative pictures of the unpaired-electron orbitals for the lower-lying five electronic states of HCOO.

being chosen from the work of Stewart.[5] The orbital exponents of STO employed are the standard molecular exponents given by Hehre et al.[6] Bond lengths used are; C-H and C-O bond lengths of 1.08 and 1.25 Å for C_{2v} HCOO; two different C-O bond lengths of 1.23 and 1.27 Å for C_s HCOO. These values were estimated from the semi-empirical work on HCOO,[4] which indicates that the total energy of HCOO is more sensitive to the OCO angle than the bond lengths. The OCO angle was thus varied from 100° to 130° in steps of 10° to obtain the lowest energy for each electronic state.

The self-consistency was achieved by repeated diagonalization of the correct general SCF operator given by Hirao and Nakatsuji.[7] It is expected that the iterative diagonalization of the general SCF operator leads satisfactorily to the correct converged solutions even when the usual Roothaan open-shell treatment diverges.[7] The total energies of four states, $^2A_1$, $^2B_2$, $^2A_2$, and $^2A''$, were obtained satisfactorily by this procedure, while the convergence difficulty was found for the $^2A'$ state even if the MO's were correctly selected in each iteration process. The conjugate gradient method[8] was thus employed to obtain the MO's of the $^2A'$ state, the gradient of the electronic energy with respect to each MO being evaluated by the orthogonality-constrained variation method.[9]

The lowest energies obtained for the five different electronic states are listed in Table 1. When the HCOO radical is constrained to the C_{2v} symmetry, $^2A_2(\Pi)$ was the lowest state for the OCO angle of 100°∿130°. It is, however, expected that the distorted $^2A'(\Sigma)$ state is much lower in energy than the Σ-states of the C_{2v} symmetry reflecting the favourable mixing of Σ-configurations caused by anti-symmetric stretching of the OCO group. The calculated total energy of the $^2A'(\Sigma)$ state with OCO=120° was 15 kcal/mol lower than the C_{2v} $^2A_2(\Pi)$ state and 7 kcal/mol lower than the C_s $^2A''(\Pi)$ state. These results support the $^2A'(\Sigma)$ ground state for the HCOO radical.

Newton[10] calculated the HCOO radical by *ab initio* STO-3G *un*restricted SCF version and found that the C_{2v} Π-state gave an energy lower than that of the distorted Σ-configuration. Dispite the unrestricted wavefunction includes the spin-polarization effect, it is not an eigen-function of the spin-squared operator, S^2. According to the communication addressed to McBride from Newton, the spin-unrestricted eigen states of HCOO showed an unusually large admixture of states of higher multiplicity.[10] The disagreement between the unrestricted and restricted calculations can not be elucidated here, because detailed results for the unrestricted calculations have not been published. The CI calculations or extended-basis calculations will improve the total energies obtained here. These more reliable calculations, however, were not performed in this paper.

The unpaired-electron of the $^2A'(\Sigma)$ state is more than 95% localized on the 2p AO of the O^1 atom (Fig. 2). This 2p AO is in a direction perpendicular to

Table 1. Lowest energies(a.u.) of five electronic states of HCOO.

States		OCO[a)]	Total energy
C_{2v}	$^2A_1(\Sigma)$	130°	-185.48829
	$^2B_2(\Sigma)$	110°	-185.51140
	$^2A_2(\Pi)$	120°	-185.54552
C_s	$^2A'(\Sigma)$	120°	-185.56996
	$^2A''(\Pi)$	120°	-185.55832

a) The OCO angle which gave the lowest energy for each state.

the C-O^1 bond. Recently, we[11] examined the direction of the experimental g-tensor of benzoyloxyl radical, and calculated the g-tensors in various possible ground states. These two considerations supported the assignment of the $^2A'(\Sigma)$ ground state for the benzoyloxyl radical.[11] Since the feature of the unpaired-electron distribution of $^2A'(\Sigma)$ in Fig. 2 is completely self-consistent with that analysis, it is concluded that the ground state of HCOO is the distorted C_s $^2A'(\Sigma)$ state.

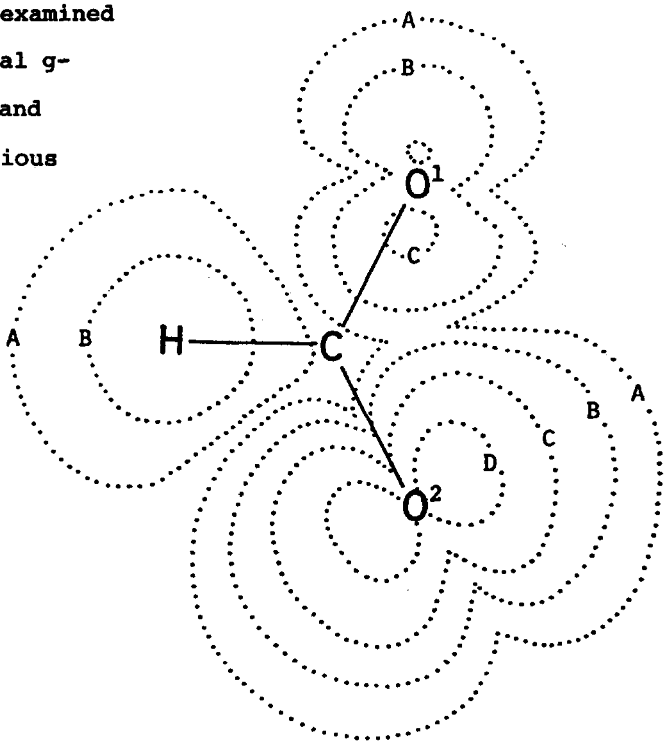


Fig.2. Calculated unpaired-electron density map for the lowest $^2A'(\Sigma)$ state. Contour values are A=0.0001, B=0.001, C=0.01 and D=0.1 electrons.

The author wishes to thank Dr. S. Kato for his kind advices in programing.

References

1) M. Iwasaki. B. Eda and K. Toriyama, J. Am. Chem. Soc., 92, 3211(1970); H.C. Box, H.G.Freund, K.T.Lilga and E.E.Budzinski, J. Phys. Chem., 74, 40(1970); K. Minakata and M. Iwasaki, J. Chem. Phys., 57, 4758(1972); E.E. Budzinski and H.C. Box, ibid., 63, 4927(1975).
2) N.J. Karch, E.T. Koh, B.L. Whitsel and J.M. McBride, J. Am. Chem. Soc., 97, 6729(1975).
3) T. Koenig, R.A.Wielesek and J.G.Huntington, Tetrahedron Lett., 1974, 2283.
4) O. Kikuchi, K. Utsumi and K. Suzuki, Bull. Chem. Soc. Japan, 50, 1339(1977).
5) R.F. Stewart, J. Chem. Phys., 52, 431(1970).
6) W.J. Hehre, R.Ditchfield, R.F.Stewart and J.A.Pople, ibid., 52, 2769(1970).
7) K. Hirao and H. Nakatsuji, ibid., 59, 1457(1973).
8) R. Fletcher and C.M. Reeves, Computer J., 7, 149(1964).
9) T. Morikawa, Chem. Phys. Lett., 32, 521(1975).
10) M.D. Newton, c.f. Ref. 37 cited in Ref. (2).
11) M.B. Yim, O. Kikuchi and D.E. Wood, to be published.