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Restricted SCF and MC-SCF Study of the Σ and Π States of the Formyloxyl and Formylaminyl Radicals

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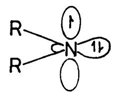
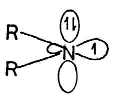
Open-shell restricted SCF and MC-SCF methods with the semi-empirical MINDO/3 approximation have been applied to the Σ and Π states of the formyloxyl and formylaminyl radicals. In the MC-SCF formalism, the $\pi \rightarrow \pi^*$ singly- and doubly-excited configurations are included. The optimized molecular structures and spin distributions predicted by the SCF and MC-SCF methods are compared. For the Π state of formyloxyl, the restricted SCF method gives a distorted C_s structure as the most stable Π structure, while the MC-SCF gives a symmetric C_{2v} structure. The use of the MC wavefunctions is recommended for the evaluation of the molecular and electronic structures of these radicals, in which a doublet instability of the restricted SCF solution is expected to occur.

Aminyl radicals[1)] are unique in that the central nitrogen atom possesses both an unpaired electron and a lone pair of electrons in its pure $2p_z$ AO and hybrid σ AO; they are, therefore, capable of existing in either a Π or Σ ground electronic state. Since the σ hybrid AO is lower in energy than the pure $2p_z$ AO, the Π state is the ground state of alkylaminyl radicals.[1)]



Π



Σ

When one of the alkyl groups is replaced by a carbonyl group, an electron-withdrawing group, the $2p_z$ AO is stabilized by the carbonyl π^* orbital. Thus, the Π and Σ states of the acylaminyl radicals[2)] may be expected to lie very close to each other, and their ground state can not easily be predicted. The same Σ-Π problem occurs in the acyloxyl radicals,[3,4)] which are important intermediates in the thermal and photochemical decompositions of acyl peroxides.

Several semi-empirical and *ab initio* calculations have been reported for solving the Σ-Π problem for the acylaminyl[5,6)] and acyloxyl[7–9)] radicals. One theoretical problem involved in these radicals is the doublet instability expected in the RHF wavefunction for the three-electron π system. It has been pointed out[10–12)] for the allyl radical that the doublet instability occurs in its π system for some region of its geometrical space, and this instability does not depend upon the approximation employed in the semi-empirical or *ab initio* RHF methods.[12)] In this study, a multi-configuration(MC)-SCF formalism for the doublet states is applied to the formylaminyl and formyloxyl radicals in the hope of obtaining molecular and electronic structures which are not disturbed by the doublet instability of three-electron π system. The Π and Σ states of these radicals are calculated by a three-configuration MC-SCF equation with the semi-empirical MINDO/3 approximation.[13)] Since the energy difference between the Π and Σ states of these radicals is expected to be very small,[5–9)] it is difficult to derive any ultimate conclusion about the Σ-Π problem of these radicals by the present semi-empirical approximation. Attention is paid especially to the molecular and electronic structures of these radicals, obtained by both the open-shell restricted SCF and the MC-SCF methods.

Procedure

The distortion of the nuclear framework of the allyl radical leads to a further lowering of the RHF energy,[11,14)] which is inconsistent with the ESR experimental evidence.[15)] This instability of the RHF solution seems to be general in three-electron π systems.[12)] The instability problem which appears in the three-electron system has been examined in detail for the H_3 system by Yamaguchi and Fukutome.[16)] They showed that the RHF solution is stable in only a small region of the geometrical space of the H_3 system. The CCC angle of the allyl radical, and also the corresponding angles of formylaminyl and formyloxyl, are expected to be $\approx 120°$. The UHF solution of the H_3 system[16)] indicates that the correct wavefunction of this region has the ASDW configuration, which is expressed in terms of the RHF orbitals by a mixture of three electron configurations. In the present formylaminyl and formyloxyl systems, these three configurations correspond to the ground configuration and the $\pi \rightarrow \pi^*$ singly- and doubly-excited configurations. Thus, the following four configuration functions are taken into account in the present MC-SCF formalism:

$$^2\Psi_g = |\cdots i\bar{i}\cdots m|$$

$$^2\Psi_i^k(1) = \frac{1}{\sqrt{2}}\{|\cdots i\bar{k}\cdots m| + |\cdots k\bar{i}\cdots m|\}$$

$$^2\Psi_i^k(2) = \frac{1}{\sqrt{6}}\{|\cdots i\bar{k}\cdots m| - |\cdots k\bar{i}\cdots m| - 2|\cdots ik\cdots \bar{m}|\}$$

$$^2\Psi_{i\,i}^{k\,k} = |\cdots k\bar{k}\cdots m|,$$

and the wavefunction is expressed by:

$$^2\Phi = C_0\Psi_g + C_1\Psi_i^k(1) + C_2\Psi_i^k(2) + C_3\Psi_{i\,i}^{k\,k}. \tag{1}$$

The electronic energy of Eq. 1 is written as:

$$E_{\text{elec}} = E_g + \sum_{p,q} A_{pq}L_{pq} + \sum_{p,q,r,s} B_{pqrs}\langle pq|rs\rangle, \tag{2}$$

where p, q, r, and s run over the i, m, and k orbitals, and where A_{pq} and B_{pqrs} are expressed by the configuration expansion coefficients (they are given in the Appendix). Also,

$$E_g = \sum_{p=1}^{m-1} 2H_{pp} + \sum_{p,q}^{m-1} (2J_{pq} - K_{pq}) + H_{mm} + \sum_{p}^{m-1} (2J_{pm} - K_{pm})$$

$$L_{pq} = H_{pq} + \sum_{r}^{m-1} \{2\langle rr|pq\rangle - \langle rq|pr\rangle\}$$
$$+ \frac{1}{2}\{2\langle mm|pq\rangle - \langle mq|pm\rangle\},$$
$$I_{pq} = \int \phi_p^*(1) H_{\mathrm{core}}(1) \phi_q(1) d\tau$$
$$\langle rs|tu\rangle = \int \phi_r^*(1)\phi_s(1)\frac{1}{r_{12}}\phi_t^*(2)\phi_u^*(2)d\tau_1 d\tau_2.$$

A troublesome aspect of implementing the MC-SCF formalism involves the handling of the off-diagonal Lagrangian multipliers, which insure orthonormality between open- and closed-shell orbitals of the same symmetry.[17] Segal[18] has put forward the "partitioning basis-set" technique, which simplifies the calculation of the wavefunctions of the excited states of molecules. His method corresponds to a partial variation method, in which the variations of open-shell orbitals are expanded by virtual orbitals. Thus, the MO's obtained by this method are not optimum ones. However, its simplicity makes it possible to obtain many types of MC-SCF wavefunctions easily. This technique, which has been applied to the calculation of MC-SCF wavefunctions by Basch[19] and also by the present author,[20] was used in the present study. After treatment the same as that described previously,[20] Fock-type eigenvalue equations are obtained:

$$\left.\begin{aligned} F_\lambda|\phi_\lambda\rangle &= \varepsilon_\lambda|\phi_\lambda\rangle \qquad (\lambda=1,2,\cdots,\ m-1;\ \neq i) \\ F_i|\phi_i\rangle &= \varepsilon_i|\phi_i\rangle \\ F_m|\phi_m\rangle &= \varepsilon_m|\phi_m\rangle \\ F_k|\phi_k\rangle &= \varepsilon_k|\phi_k\rangle. \end{aligned}\right\} \tag{3}$$

The operators, F_λ F_i, F_m, and F_k, are given by:

$$F_\lambda = F_c + \sum_{r,s}^{i,k} \frac{1}{2} A_{rs}(2f_{rs} - g_{rs})$$
$$F_c = H_{\mathrm{core}} + \sum_{p=1}^{m-1}(2J_p - K_p) + \frac{1}{2}(2J_m - K_m)$$
$$F_m = \frac{1}{2}F_\lambda - \frac{1}{4}(2J_m - K_m) + B_{miim}g_{ii} + B_{mkkm}g_{kk}$$
$$+ \frac{1}{2}B_{mikm}(g_{ik} + g_{ki})$$
$$F_i = F_{ii} + F_{ik}|\phi_k\rangle\langle\phi_i| + |\phi_i\rangle\langle\phi_k|F_{ki}$$
$$F_k = F_{kk} + F_{ki}|\phi_i\rangle\langle\phi_k| + |\phi_k\rangle\langle\phi_i|F_{ik}$$
$$F_{ii} = F_\lambda + \frac{1}{2}A_{ii}F_c + B_{iiii}f_{ii} + \frac{1}{2}B_{iikk}f_{kk}$$
$$+ \frac{1}{2}B_{ikii}(f_{ik} + f_{ki}) + \frac{1}{2}B_{ikki}g_{kk} + B_{miim}g_{mm}$$
$$F_{kk} = \frac{1}{2}A_{kk}F_c + B_{kkkk}f_{kk} + \frac{1}{2}B_{iikk}f_{ii}$$
$$+ \frac{1}{2}B_{ikkk}(f_{ik} + f_{ki}) + \frac{1}{2}B_{ikki}g_{ii} + B_{mkkm}g_{mm}$$
$$F_{ik} = \frac{1}{2}A_{ik}F_c + \frac{1}{2}B_{mikm}g_{mm} + \frac{1}{2}B_{ikii}f_{ii}$$
$$+ \frac{1}{2}B_{ikkk}f_{kk} + B_{ikik}f_{ik}$$
$$F_{ki} = \frac{1}{2}A_{ki}F_c + \frac{1}{2}B_{mikm}g_{mm} + \frac{1}{2}B_{kiii}f_{ii}$$
$$+ \frac{1}{2}B_{kikk}f_{kk} + B_{kiki}f_{ki},$$

where r and s run over two orbitals, i and k, and where p runs over orbitals which are doubly occupied in the Ψ_g configuration. The J_p, K_p, and H_{core} operators have their usual meanings, and the f_{rs} and g_{rs} operators are defined by:

$$f_{rs}(1)\phi_t(1) = \left(\int \frac{1}{r_{12}}\phi_r(2)\phi_s(2)d\tau_2\right)\phi_t(1)$$
$$g_{rs}(1)\phi_t(1) = \left(\int \frac{1}{r_{12}}\phi_r(2)\phi_t(2)d\tau_2\right)\phi_s(1).$$

If the variation method is applied so as to minimize the E_{elec} with respect to the LCAO coefficients, $\mathbf{c}$, of:

$$\phi_r = \boldsymbol{\chi}\mathbf{c}_r,$$

equations equivalent to Eq. 3 are obtained:

$$\left.\begin{aligned} \boldsymbol{F}_\lambda\mathbf{c}_\lambda &= \mathbf{c}_\lambda\boldsymbol{\varepsilon}_\lambda \\ \boldsymbol{F}_i\mathbf{c}_i &= \mathbf{c}_i\boldsymbol{\varepsilon}_i \\ \boldsymbol{F}_m\mathbf{c}_m &= \mathbf{c}_m\boldsymbol{\varepsilon}_m \\ \boldsymbol{F}_k\mathbf{c}_k &= \mathbf{c}_k\boldsymbol{\varepsilon}_k, \end{aligned}\right\} \tag{4}$$

where the matrices, $\boldsymbol{F}_\lambda$, $\boldsymbol{F}_i$, $\boldsymbol{F}_m$, and $\boldsymbol{F}_k$, are evaluated with the corresponding operator and the set of AO's. The configuration expansion coefficients and the orbital expansion coefficients are determined by an iterative procedure described elsewhere.[20] The spin density at the rth AO is obtained by means of:[21]

$$\rho_r = \left(1 - \frac{4}{3}C_2^2\right)c_{rm}^2 + \left(\frac{2}{3}C_2^2 + \frac{2}{\sqrt{3}}C_1C_2\right)c_{ri}^2$$
$$+ \left(\frac{2}{3}C_2^2 - \frac{2}{\sqrt{3}}C_1C_2\right)c_{rk}^2 + \frac{4}{\sqrt{6}}(C_2C_3 - C_0C_2)c_{ri}c_{rk}.$$

The open-shell restricted SCF solutions, which are being compared with the MC-SCF results, are obtained by the repeated diagonalization of the correct general SCF operator for the doublet state given by Hirao and Nakatsuji.[22] This gives correct converged solutions even when the usual Roothaan open-shell treatment diverges.

The semi-empirical MINDO/3 approximation[13] is used to evaluate the matrix elements. The calculation of the simplest nitrogen-center radical, NH_2, by this approximation gives satisfactory results for both the molecular structures of the Π_N and Σ_N states and the energy separation between these two states.[24]

Results and Discussion

Formyloxyl Radical. Formyloxyl has the possibility of existing in the symmetric C_{2v} structure and is a good example for use in examining the difference between the results obtained by the SCF and MC-SCF methods. In the Ψ_g configuration for the Π state of formyloxyl, the lowest π MO(π), the second π MO(π^0), and the highest π MO(π^*) are doubly-occupied, singly-occupied, and unoccupied MO's respectively. In the MC-SCF formalism, the π, π^0, and π^* MO's are assigned to the i, m, and k MO's of Eq. 1 respectively. In the calculation of the $\Sigma(B_2)$ state, the π^0, $\sigma(b_2)$, and π^* MO's are assigned to the i, m,

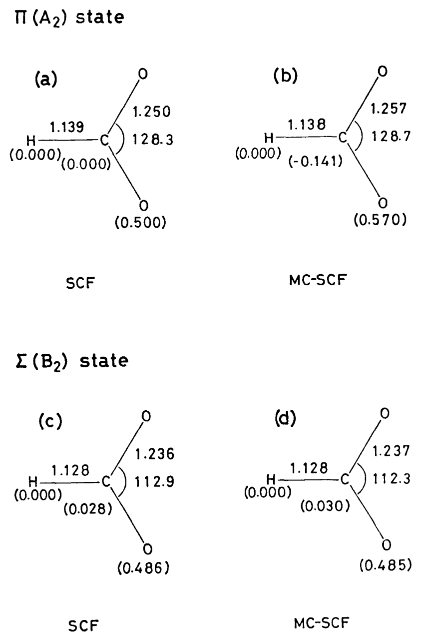


Fig. 1. The structures and spin distributions of the Π and Σ states of the C_{2v} formyloxyl radical.
Atomic spin densities are in parentheses. Bond lengths are in Å, and bond angles in degrees.

and *k* MO's respectively.[25] The optimized[26] molecular structures and spin distributions for the C_{2v} Π and Σ states are shown in Fig. 1. The SCF and MC-SCF methods predict a very similar molecular structure for the $\Pi(A_2)$ state and also for the $\Sigma(B_2)$ state. The spin distribution of the $\Sigma(B_2)$ state by SCF and MC-SCF also resemble each other. The negative spin density appears at the central carbon atom in the MC-SCF Π state. Although the molecular structure and spin distribution of the C_{2v} formyloxyl are not greatly afected by the inclusion of the excited configurations, the relative energy between the $\Sigma(B_2)$ and $\Pi(A_2)$ states is greatly reduced by the MC-SCF formalism (Table 1).

The SCF calculation gives a stable $\Pi(A'')$ structure for the distorted C_s formyloxyl.[27] This is shown in Fig. 2. This distorted C_s structure is 19.6 kJ mol⁻¹ more stable than the SCF C_{2v} $\Pi(A_2)$ state, and the unpaired electron is located mostly (90%) at one of the oxygen atoms in this structure. These results indicate that the SCF calculation predicts the distorted C_s structure instead of the symmetric C_{2v} one, as the most stable Π state. The C_{2v} structure of the allyl π radical has been determined from the experimental ESR coupling constants of allyl.[15] When the open-shell restricted SCF procedure is applied to the allyl radical, the distorted C_s structure is obtained, while the MC-SCF MINDO/3 procedure presented here gives the C_{2v} structure,[14] which is consistent with the experimental evidence for the allyl radical. Thus, the $C_s(\Pi)$ structure of the acyloxyl radical predicted by the present SCF calculation may not be correct for the Π state of acyloxyl.

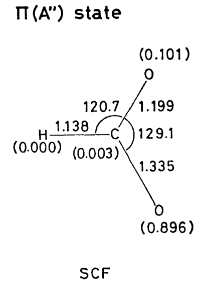


Fig. 2. The optimized structure and spin distribution (in parentheses) of the $\Pi(A'')$ state of the distorted C_s formyloxyl radical. The MC-SCF formalism does not give the stable structure for the distorted form.

Table 1. Relative energies (kJ mol⁻¹) of the Σ and Π states of the formyloxyl radical

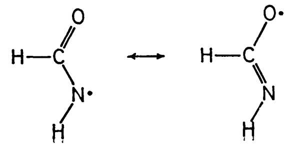
	SCF	MC-SCF
$\Sigma(B_2)$	0.0	0.0
$\Pi(A_2)$	59.8	9.2
$\Pi(A'')$	40.2	—

When the MC-SCF optimization of the nuclear framework, using the C_s structure in Fig. 2 as the initial structure, was carried out for the Π state, the symmetric Π structure shown in Fig. 1-(b) was obtained as the optimized one. It may be concluded that the stable C_s Π structure of formyloxyl predicted by the SCF calculation results from the doublet instability expected in the RHF solution for the C_{2v} structure of the three-electron π system, and that this instability is removed by the MC-SCF treatment. The wavefunction of the C_{2v} $\Pi(A_2)$ state, Fig. 1-(b), is:

$$0.974\Psi_g + 0.039\Psi_i^k(1) + 0.210\Psi_i^k(2) - 0.081\Psi_{ii}^{kk}$$

The contribution of the doubly-excited configuration, Ψ_{ii}^{kk}, to this state is small. It was found that the exclusion of the doubly-excited configuration from the present MC-SCF formalism also gives the $C_{2v}(A_2)$ structure, instead of the $C_s(A'')$ one, as the most stable Π state. Thus, the inclusion of the singly-excited configuration in the MC-SCF formalism appears to be sufficient to remove the doublet instability expected in the RHF solution of C_{2v} three-electron radicals. It should be noted that, if the symmetry of formyloxyl is restricted to C_{2v}, a reliable structure for the Π state is obtained by the restricted SCF calculation, since the SCF and MC-SCF structures of the Π states (Fig. 1) closely resemble each other. The reliable spin distribution can be obtained by the SCF calculation, followed by the CI calculation.

Formylaminyl Radical. The optimized structures and spin distribution for the Π and Σ states of formylaminyl are shown in Fig. 3. The difference in the molecular structures between the SCF and MC-SCF Π states is not very large, but it is important; the lengthening of the CO bond and the shortening of the CN bond are more obvious in the MC-SCF structure than in the SCF structure. This indicates



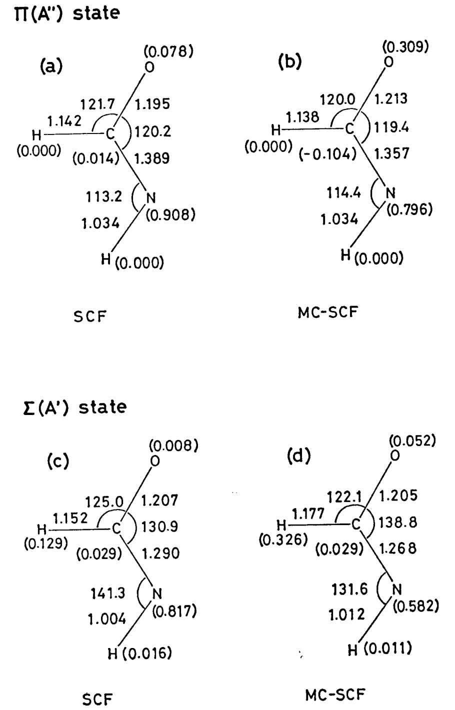


Fig. 3. The structures and spin distribution of the Π and $\sum$ states of the formylaminyl radicals. Atomic spin densities are in parentheses. Bond lengths are in Å, and bond angles in degrees.

that the single-determinant SCF calculation overestimates the contribution of one of the canonical structures to the Π electronic state of this radical. This trend also appears in the calculated spin distribution; the larger spin density on the oxygen atom is obtained in the MC-SCF structure. As is to be expected from the analysis of the formyloxyl radical, the difference between the SCF and MC-SCF structures for the Π state of the acylaminyl radical may result mainly from the unstable nature of the restricted SCF method for this radical. A large difference is observed in the SCF and MC-SCF spin distributions in the $\sum(A')$ state (Figs. 3c and 3d). This may come from the difference between the SCF and MC-SCF structures. The decrease in the HCN and CNH angles causes a larger interaction between the 1s AO of the H–C hydrogen atom and the hybrid odd-electron AO of the nitrogen atom, and the spin delocalization occurs from the nitrogen to the hydrogen atom. A similar trend has been observed in the spin distributions in the SCF $\sum(A')$ state, which are calculated as functions of the CNH angle.

The ESR spectra of several acylaminyl radicals have been obtained.[1,5] The nitrogen splittings are ≈15 G (1 G=10^{-4} T), and the N–CH_3 proton splittings are ≈29 G. These values are very similar to those of the dialkylamino radicals,[1,5] whose ground state is of the π-type, and also indicate that the odd-electron AO at the nitrogen atom is not the sp hybrid AO, but almost pure 2p AO. These ESR results support the Π_N ground state for the acylaminyl radical, although it is not possible absolutely to exclude a $\sum_N$ structure with the CNC angle of ≈180°. The MC-SCF results

Table 2. Relative energies (kJ mol^{-1}) of the $\sum$ and Π states of the formylaminyl radical

	SCF	MC-SCF
$\sum(A')$	0.0	7.1
$\Pi(A'')$	26.4	0.0

in Table 2 indicate that the ground state of formylaminyl is of the $\Pi(A'')$ type, which is consistent with the results of the ESR experiments. However, the energy difference between $\sum$ and Π is very small.

The *ab initio* STO-3 G and 4-31G calculations by Baird and Kathpal[6] show that the $\sum_N$ state is much (>40 kJ mol^{-1}) higher than the Π state, while the present results predict they will lie very close to one another. In their calculations of the formylaminyl radical, all the bond angles around the carbon atom were assumed to be 120°. As may be seen from Fig. 3, the bond angles around the carbon atom deviate greatly from 120°; the optimization of these angles is important in estimating the relative energy between the Π and $\sum$ states.

Significant differences have been observed between the SCF and MC-SCF molecular electronic structures for the formyloxyl and formylaminyl radicals. They come mainly from the doublet instability of the restricted SCF solutions for the 3π-electron radicals. The allyl 3π-electron system is described correctly by the present MC-SCF procedure;[14] the use of the multi-configuration wavefunction is recommended for the evaluation of the molecular and electronic structures for the lower-lying Π and $\sum$ states of acyloxyl and acylaminyl radicals.

Appendix

A_{pq} and B_{pqrs} in Eq. 2 are expressed by the following configuration expansion coefficients; all the other values are zero.

$$A_{ii} = -C_1^2 - C_2^2 - 2C_3^2$$

$$A_{kk} = C_1^2 + C_2^2 + 2C_3^2$$

$$A_{ik} = A_{ki} = \sqrt{2}\,(C_0C_1 + C_1C_3)$$

$$B_{iiii} = B_{kkkk} = C_3^2$$

$$B_{iikk} = -C_1^2 - C_2^2 - 4C_3^2$$

$$B_{miim} = B_{immi} = \frac{1}{2}(C_2^2 - \sqrt{3}\,C_1C_2)$$

$$B_{mkkm} = B_{kmmk} = \frac{1}{2}(C_2^2 + \sqrt{3}\,C_1C_2)$$

$$B_{mikm} = B_{immk} = \frac{\sqrt{6}}{2}(C_0C_2 - C_2C_3)$$

$$B_{ikii} = B_{kiii} = -\sqrt{2}\,C_1C_3$$

$$B_{ikkk} = B_{kikk} = \sqrt{2}\,C_1C_3$$

$$B_{ikik} = B_{kiki} = C_0C_3$$

$$B_{ikki} = 2(C_1^2 + C_3^2).$$

References

1) For a review for the aminyl radical, see W. C. Danen and F. A. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, **14**, 783 (1975).

2) For a review for the acylaminyl radical, see P. Mackiewicz and R. Furstoss, *Tetrahedron*, **34**, 3241 (1978).

3) J. M. McBride and R. A. Merrill, *J. Am. Chem. Soc.*, **102**, 1723 (1980), and the references cited therein.

4) O. Kikuchi, *J. Synth. Org. Chem.*, **37**, 678 (1979).

5) T. Koenig, J. A. Hoobler, C. E. Klopfenstein, G. Hedden, F. Sunderman, and B. R. Russell, *J. Am. Chem. Soc.*, **96**, 4573 (1974).

6) N. C. Baird and B. Kathpal, *J. Am. Chem. Soc.*, **98**, 7532 (1976).

7) T. Koenig, R. A. Wielesek, and J. G. Huntington, *Tetrahedron Lett.*, **1974**, 2283.

8) O. Kikuchi, *Tetrahedron Lett.*, **1977**, 2421.

9) O. Kikuchi, K. Utsumi, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **50**, 1339 (1977).

10) J. Paldus and J. Cizek, *J. Chem. Phys.*, **52**, 2919 (1970).

11) J. McKelvey and W. J. Hehre, *Mol. Phys.*, **25**, 983 (1973); J. M. McKelvey and G. Berthier, *Chem. Phys. Lett.*, **41**, 476 (1976).

12) J. Paldus and A. Veillard, *Chem. Phys. Lett.*, **50**, 6 (1977).

13) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

14) O. Kikuchi, *Chem. Phys. Lett.*, **72**, 487 (1980).

15) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

16) K. Yamaguchi and H. Fukutome, *Prog. Theor. Phys.*, **54**, 1599 (1975).

17) G. Das and A. C. Wahl, *J. Chem. Phys.*, **56**, 1769 (1972).

18) G. A. Segal, *J. Chem. Phys.*, **53**, 360 (1970).

19) H. Basch, *J. Chem. Phys.*, 55, 1700 (1971).

20) O. Kikuchi and K. Aoki, *Bull. Chem. Soc. Jpn.*, **47**, 2915 (1974).

21) O. Kikuchi, Thesis, Tokyo Kyoiku University (1969).

22) K. Hirao and H. Nakatsuji, *J. Chem. Phys.*, **59**, 1457 (1973).

23) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

24) The HNH angle of the NH_2 radical estimated by MINDO/3 is 102° for the Π state and 136° for the $\sum$ state, and the energy difference between these states is estimated to be 24 kcal/mol. The corresponding experimental values⁶⁾ are 103°, 144°, and 31 kcal/mol respectively.

25) In the $\sum$ state of formyloxyl and formylaminyl, four electrons occupy the π orbitals, and the doublet instability may not occur. When the OCO or OCN angle becomes small, the energy difference between the π^0 and π^* levels decreases and the doubly-excited configuration from π^0 to π^* becomes important to the $\sum$ state. Moreover, the preliminary CI calculations showed that the singly-excited $\pi \rightarrow \pi^*$ configuration is important for the acylaminyl radical. For the above reasons, the π^0 and π^* MO's are assigned to the *i* and *k* orbitals in Eq. 1 for the $\sum$ state of the acyloxyl and acylaminyl radicals.

26) The variable metric method proposed by Fletcher was employed; R. Fletcher, *Computer J.*, **13**, 317 (1970).

27) The SCF MINDO/3 energies of $\sum(A_1)$ and the distorted $\sum(A')$ states are lower than those of the $\sum(B_2)$ and $\Pi(A_2)$ states. In these states, the CH distance is >1.2 Å and the OCO angle is >150°. These are, thus, transient states dissociative to $H+CO_2$.