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Carboxyl Free Radicals: Formyloxyl ($HCOO^•$) and Acetyloxyl ($CH_3COO^•$) Revisited

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Abstract: The structures of different electronic states of $HCOO^•$ were optimized at HF, MP2, MP4, and QCISD(T) levels with basis sets up to 6-311+G(D,P). Zero point energy (ZPE) corrections were calculated at the HF and MP2 levels and the total energies were evaluated at various high levels of ab initio calculations. The results indicate that the $^2B_2$ state of formyloxyl has the lowest electronic energy on the vibrationless Born–Oppenheimer surface. After inclusion of ZPE contributions, the total energies of the $^2B_2$ and $^2A_1$ states are within an energy gap of 3 kJ/mol. The "broken symmetry" state, $^2A'$ of C_s symmetry, is predicted to be a local minimum with a total energy comparable to those of $^2B_2$ and $^2A_1$. Geometry optimization and frequency calculations were also carried out for the acetyloxyl radical at MP2/6–31G(D) levels. The total energies of the electronic states of $CH_3COO^•$ were evaluated at MP2+ZPE and G2(MP2) levels. Electronic states identifiable as B_2-, A_1-, and A'-like were found. The $^2A'(A')$ electronic state is predicted to be less than 10 kJ/mol above, and the $^2A'(A_1)$ state more than 20 kJ/mol above, the $^2A''(B_2)$ ground state.

1. Introduction

The formyloxyl and acetyloxyl free radicals, $HCOO^•$ and $CH_3COO^•$, are prototypical carboxyl radicals. These are characterized by the fact that they have several low-lying electronic states which may be significantly populated at ambient temperatures and which may originate from different chemical processes. Such radicals are undeniably intermediates in the Kolbe and Hunsdiecker reactions,[1] although in each case, the intermediate acyloxyl free radical undergoes rapid loss of CO_2, prior to yielding products of radical processes. Experimentally, only those acyloxyl systems which decarboxylate relatively slowly to yield *un*stable free radical products, e.g., $ROCO_2$,[2,3] $ArCO_2^•$[4–7], alkynyl$CO_2^•$[3,8] or vinyl-$CO_2^•$,[3,8] have been detected spectroscopically. Formyloxyl[9] is in this category, but acetyloxyl is not.[9–11] Simple orbital interaction considerations yield the molecular orbital ordering shown in Figure 1. The carboxyl group orbitals are classified in the local C_{2v} point group, and the spatial symmetry of each doublet state is entirely defined by the symmetry of the singly occupied orbital. The order of the MOs shown in Figure 1 is that expected for a strongly bent OCO moiety. At this geometry, the ground electronic state is expected to be the σ radical, $^2B_2$. As the OCO angle opens up, the b_2 and a_1 orbital energies will converge rapidly, the a_2 and b_1 orbitals less so, and a different ordering of electronic states may ensue. The chemistry of the σ and π radicals is expected to be very different. Hydrogen atom abstraction, for example, should be more efficient with a σ radical. Even between the σ radicals, for example, evolution of CO_2 would be substantially easier from the $^2A_1$ as opposed to the $^2B_2$ electronic state. An additional complication is the possibility that the acyloxyl radical may undergo a reduction of its symmetry from local C_{2v} to C_s due to a vibronic Jahn–Teller instability. The reduction of symmetry permits mixing of the $^2B_2$ and $^2A_1$ states (Figure 1) yielding a state of symmetry $^2A'$ with the spin substantially localized to one of the oxygen atoms.

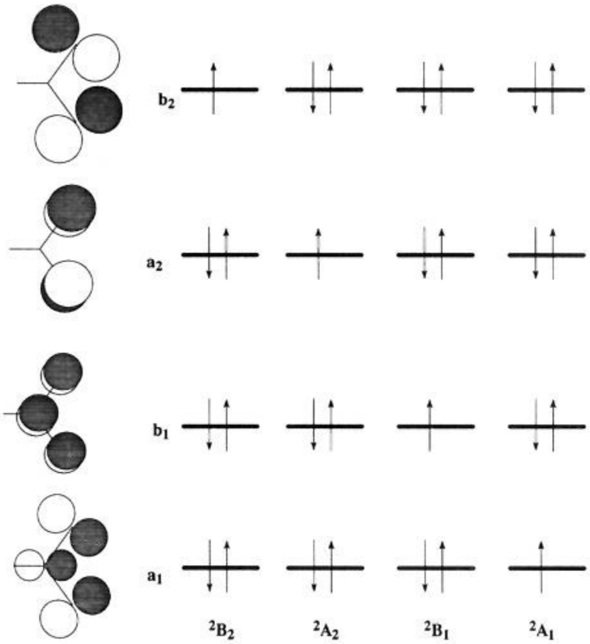
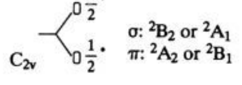
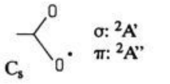


Figure 1. Orbital level diagram for the carboxyl group.





Some ESR data are available that bear on the structures and electronic states of acyloxyl radicals. It is generally agreed[3–8,10] that the ground state is a σ radical. The majority of the early

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ESR solid state low temperature data, including data for benzoyloxyl, had been interpreted[6] to indicate an unsymmetrical spin distribution, i.e., the $^2A'$ state, but this interpretation was questioned by McBride and Merrill, who convincingly demonstrated that the benzoyloxyl radical has a symmetrical spin distribution, namely a $^2B_2$ ground state.[7] McBridge and Merrill further reported that photodecarboxylation, presumably from the $^2A_1$ state, could be accomplished with light as red as 100 kJ/einstein.

Fluorescence from photodissociative excitation of formic acid and methyl formate has been attributed to formyloxyl,[9] but the electronic states involved were not identified. The details of the electronic states and geometries are fundamental to an understanding of the chemistry of this species and its higher homologs. In spite of numerous theoretical investigations,[12–16] serious doubts remain even as to the ground electronic state and the local geometry of the carboxyl fragment. This is surprising in the light of the apparent simplicity of the molecule. However, the molecule is far from simple computationally, because the UHF wave function is unstable with respect to spatial symmetry.[16,17] Geometry optimization of either the σ or π radical yields a structure of C_s symmetry with one short and one long CO bond, with the result that the spin density is strongly localized to the singly bonded oxygen. Although in the case of the formyloxyl, and to some extent the acetyloxyl, species symmetry constraints may be imposed to preserve the local symmetry of the orbitals, in general, a multireference SCF or CI calculation is apparently required to yield a wave function stable toward symmetry breaking.[14,16]

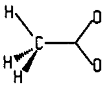
Peyerimhoff and co-workers[12] carried out multireference double excitation CI calculations on both formyloxyl and acetyloxyl, using a moderate sized basis set. They constrained the geometry of formyloxyl to have C_{2v} symmetry and varied the remaining structural parameters within this constraint. The lowest electronic state of HCOO• was found to be $^2B_2$, a σ radical with an OCO angle of 113°. The other two electronic states which were investigated, $^2A_1$ and $^2A_2$, were found to lie 30.1 and 57.3 kJ/mol above the $^2B_2$ state, with OCO angles of 139° and 122°, respectively. Since the asymmetric stretching vibration of the OCO group reduces the symmetry and permits vibronic (Jahn–Teller) mixing of the $^2B_2$ and $^2A_1$ states, Peyerimhoff and co-workers also carried out calculations on structures with the CO bonds asymmetrically distorted by a small amount from the symmetrical minimum energy geometries of the $^2B_2$ and $^2A_1$ states. The former, but not the latter, suffered a small lowering of the energy, suggesting that the $^2B_2$ structure may not be a minimum.

Davidson and co-workers[13] carried out an extensive examination of the potential energy surfaces of the lower-lying electronic states formyloxyl at the MCSCF/3-21G level of theory, partially repeated with a somewhat larger basis set. Energies of stationary points were obtained at higher accuracy by large CI calculations. At the highest level of theory, DZP-SDQ-CI, the lowest electronic state of formyloxyl was found to be $^2B_2$. However, it could not be concluded definitively that this did not correspond to a transition structure connecting two equivalent C_s structures, designated $^2A'$, with unequal CO bonds. The relative energies of the four electronic states of C_{2v} symmetry, $^2B_2$, $^2A_1$, $^2A_2$, and $^2B_1$, were 0.0, 15.8, 23.6, and 375.4 kJ/mol, respectively. The order of the relative stabilities agreed with that of Peyerimhoff et al.[12] but the energy separations differed markedly. The $^2A'$ and $^2A''$ states of C_s symmetry, which are also stationary points on the MCSCF potential energy surface, are 10.5 and 34.1 kJ/mol less stable than $^2B_2$, respectively. It should be noted that the "symmetry breaking" structure $^2A'$ is the second lowest electronic state of HCOO• at the highest theoretical level in the study by Davidson and co-workers.[13]

McLean et al.[14] have specifically addressed the problem of symmetry breaking in molecular calculations in an attempt to obtain a prescription for reliable prediction of equilibrium geometries, using formyloxyl as a test case. With a large MCSCF configuration space and subsequent multireference CI, McLean and co-workers reported an "unequivocal demonstration that the equilibrium structures of both σ and π radicals have C_{2v} symmetry". The separation between the lowest state $^2B_2$, and lowest π state, $^2A_2$, was calculated to be 38.3 kJ/mol. The energy and geometry of the $^2A_1$ state were not determined.

Calculations on the formyloxyl radical and the negative ion $HCOO^-$ were reported at the G2 level by the present authors[15] as part of a detailed investigation of the electron affinities of a large number of three-heavy-atom species. The properties of the lowest energy structure of formyloxyl as obtained by *unconstrained* optimization at the UMP2/6-31G(D) level was reported in that study. The state was *erroneously* reported as being the $^2B_2$ state.[15] In fact, it is the $^2A_1$ state, a result contrary to all previous high level computations.

The difficulties associated with symmetry breaking are exacerbated in the case of acetyloxyl, since the highest symmetry available to the species is C_s, corresponding to structures in which one CH bond lies in the plane of the OCO group (**1**), or in the plane bisecting the OCO group (**2**). In structure **1**, which corresponds to a minimum for acetic acid and acetate anion, the two σ radical states which are equivalent to $^2B_2$ and $^2A_1$ of formyloxyl are not separated by symmetry. In the case of structure **2**, adopted by Peyerimhoff et al. in their study, the states have symmetry designations of $^2A''(^2B_2)$ and $^2A'(^2A_1)$, respectively. Through partial optimization at the CI level, Peyerimhoff et al.[12] found that the lowest state of acetyloxyl **2** is a $^2A''(^2B_2)$. The next two states, $^2A'(^2A_1)$ and another $^2A''(^2A_2)$, are nearly degenerate and lie 45.6 kJ/mol above. The $^2A'(^2A_1)$ state had a long CC bond, 1.6 Å, and a very flat stretching potential, suggesting easy dissociation to CO_2 and methyl radical.



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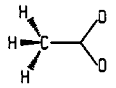

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In molecules which lack elements of symmetry, the evidence from the previously discussed theoretical studies suggests that heroic measures would be required to ensure the absence of theoretical artifacts which could invalidate any conclusions reached. There is, in fact, no *a priori* reason that the "symmetry-broken" situation is not correct, and no definitive experimental evidence as yet to resolve the issue. In the present study, we reinvestigate the lower electronic states of formyloxyl and acetyloxyl at several high levels of ab initio calculations in order to (a) provide more accurate information on the structures and relative stabilities of the lowest electronic states and (b) determine whether procedures can be developed that will permit accurate descriptions of the states of carboxyl radicals in the more general case, where symmetry cannot be used to advantage.

The computational details are described in section 2. The results have been presented and discussed with those of literature in section 3. Finally our conclusions are stated in section 4.

2. Computation Details

All ab initio calculations presented here were performed with the Gaussian 92 molecular orbital packages.[18] Literature results indicate that the relative stabilities, or even which one is the absolute minimum,

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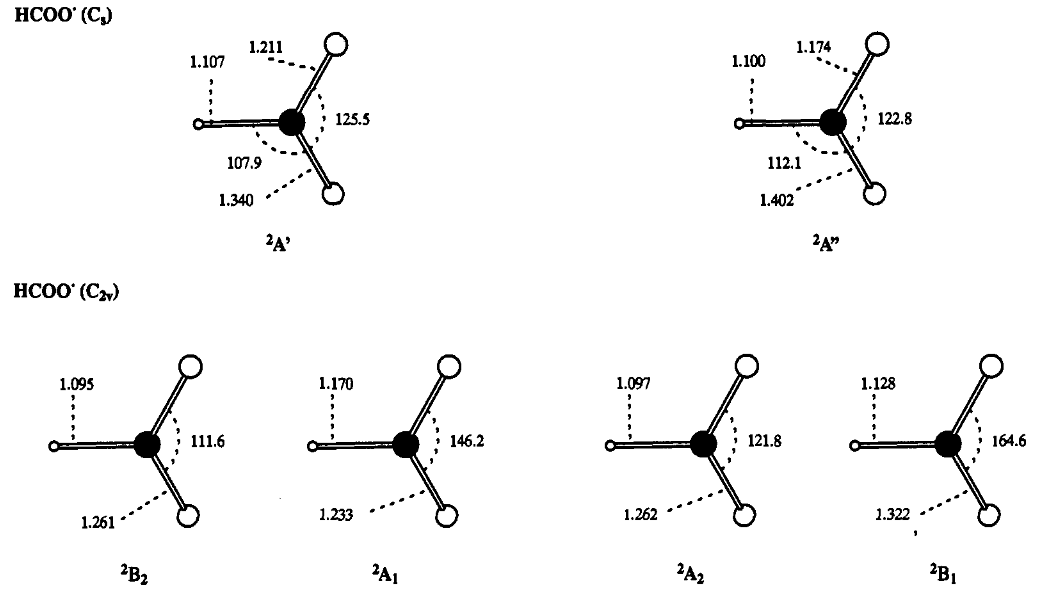

Figure 2. MP2/6-31G(D) optimized structures for HCOO• in different electronic states. Solid balls represent carbon atoms. Large open balls are oxygen and small open balls are hydrogen. Bond lengths are in angstraoms and angles are in degrees.

of the electronic states of HCOO• vary with the level of calculations. For a thorough study, we optimized the formyloxyl radical geometries for the six possible electronic states at unrestricted HF, MP2, MP4, and QCISD-(T) levels with basis sets up to 6-311+G(D,P). For each of the calculations on σ radicals reported here, the value of $\langle S^2 \rangle$ is less than 0.79. Higher values of $\langle S^2 \rangle$ were found for the π radicals which are not the major focus of the present work. The correlation energies were evaluated at each of the geometries at MP4, CI, G2(MP2), and G2 levels. For the acetyloxyl radical, the geometry optimizations were carried out at the MP2/6-31G(D) level and the correlation corrections were estimated at the G2-(MP2) level.

The G2(MP2) procedure[19] includes a geometry optimization with the standard Hartree–Fock method and the 6-31G(D) split-valence basis set (HF/6-31G(D)), a vibrational frequency calculation at the HF optimized geometry, MP2/6-31G(D) geometry optimization, and two single-point post-HF calculations, i.e. QCISD(T)/6-311G(D,P) and MP2/6-311+G-(3DF,2P), on the MP2 optimized geometry in order to obtain an accurate estimate of the correlation energy. Harmonic frequency analysis is required by the G2(MP2) procedure for an estimate of the zero point vibrational energy (ZPE). This quantity is not particularly sensitive to the accuracy of the frequencies themselves and so the HF/6-31G(D) level with an appropriate empirical correction is usually adequate for the purpose. Of course, frequencies determined at this level will not be reliable if the wave function is unstable to symmetry breaking, as may happen in the present case. If used in considering the zero-point energy, the vibrational frequencies calculated at the HF/6-31G(D) level were scaled by a factor of 0.89.[20] Compared with the G2 theory,[21] the G2(MP2) method provides a similar level of accuracy, but significant saving in computational time and disk storage. Thus it can be applied to systems of moderate size.[19]

The present study found that the ZPE contributions play an important role in determining the relative stabilities among the close lying electronic states. In some cases, the frequencies and ZPEs were also evaluated at the MP2/6-31G(D) level, and scaled by a factor of 0.95 in the calculation of ZPE contributions to the total energies. We recognize that the existence of very low lying states may render the use of perturbation procedures suspect. However, as discussed below, it proved not to be possible to obtain ZPE values at the QCISD(T) level.

Use of the G2 prescription for determining the correlation energy contribution is of particular significance since the accuracy of this method has been amply demonstrated. Relative energies correct to within 20 kJ/mol may be expected, provided the reference geometry and the zero-point energy corrections are adequately determined.

3. Computational Results and Discussion

The structures of formyloxyl and acetyloxyl radicals, optimized at the MP2/6-31G(D) level, are plotted in Figures 2 and 3, respectively. The symmetry types and the characteristic geometrical parameters are also listed in the figures. The optimized geometric parameters of formyloxyl at various levels of ab initio calculations are submitted as supplementary data in Table S-I, and the energies evaluated at such geometries are reported in Table S-II. The relative stabilities of these species are listed in Table 1 and the vibrational frequencies for the three lowest electronic states of the formyloxyl radical evaluated at HF/6-31G(D), MP2/6-31G(D), or MP4/6-31G(D) levels are given in Table 2. The experimental vibrational frequencies of CO_2 and $HCOO^-$ are also collected there for comparison. The most accurate estimates of relative energies of the formyloxyl electronic states are collected in Table 3. Table S-III reports the optimized geometries for the stationary points found on the electronic potential surfaces of the acetyloxyl radical, and the energies of these molecules are given in Table S-IV. The relative energies of these structures are collected in Table 4 and the vibrational frequencies of the acetyloxyl radical calculated at the MP2/6-31G(D) level were given in Table 5.

Formyloxyl radical: Depending on whether the oxygen atoms in HCOO• are identical or not, there exist two possible symmetric types for the geometry of the formyloxyl radical, C_{2v} and C_s. For the C_{2v} type, there are four possible symmetries for the electronic states, $^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$, corresponding to the symmetries of the occupied molecular orbitals (Figure 1). For the C_s type, two symmetry classifications of the electronic states are possible, $^2A'$ and $^2A''$, corresponding to σ and π radicals, respectively. Structures for all six states were found through geometry optimizations, with appropriate symmetry constraints and predefined orbital occupancies, at both HF/6-31G(D) and MP2/6-31G(D) levels. The similarity between the optimized geometric parameters at those two levels indicates that the correlation effects on geometries are minor. We will discuss briefly the structures based on the MP2 optimized geometries.

The characteristic parameter for the four electronic states of the C_{2v} structures of HCOO• is the OCO angle. This angle is

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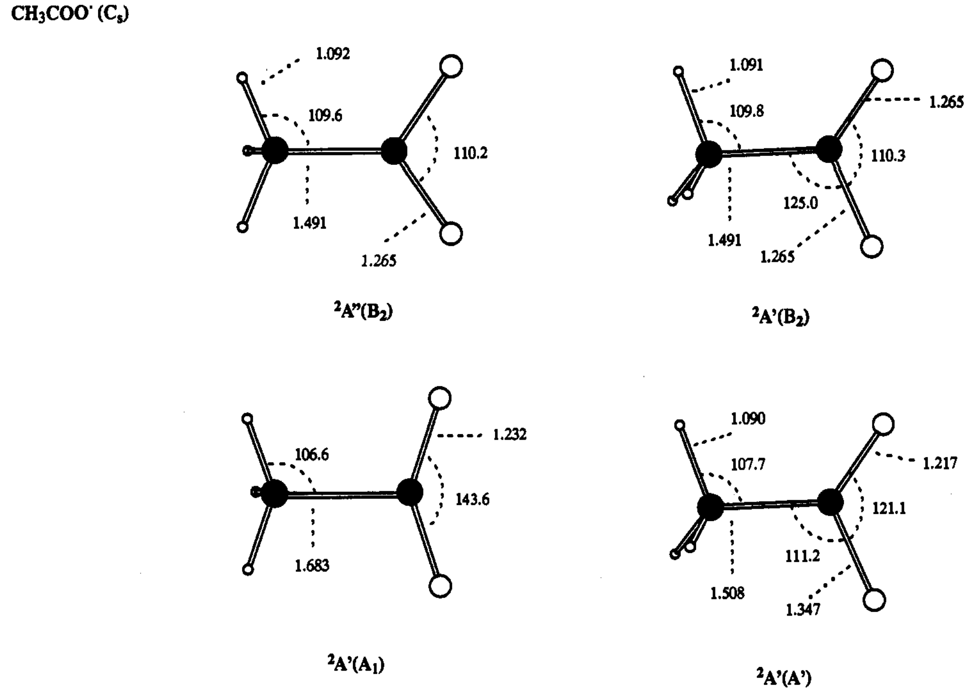

Figure 3. MP2/6-31G(D) optimized structures for $CH_3COO^{\bullet}$ in different electronic states. Solid balls represent carbon atoms. Large open balls are oxygen and small open balls are hydrogen. Bond lengths are in angstroms and angles are in degrees.

Table 1. Relative Electronic Energies (kJ/mol) (Without ZPE Corrections) of $HCOO^{\bullet}$

	C_s		C_{2v}			
	$^2A'$	$^2A''$	$^2A_1$	$^2B_2$	$^2A_2$	$^2B_1$
HF/6-31G(D)//HF/6-31G(D)	0.0	338.0	126.4	94.4	18.2	730.1
MP2/6-31G(D)//MP2/6-31G(D)	25.5	106.6	0.0	12.3	113.9	555.8
MP2/6-311G(D,P)//MP2/6-31G(D)	25.4		0.0	14.5		
MP2/6-311+G(3DF,2P)//MP2/6-31G(D)	33.2		0.0	17.4		
MP2/6-311G(D,P)//MP2/6-311G(D,P)	25.4		0.0	14.7	113.8	
MP4/6-31G(D)//MP4/6-31G(D)	13.4		0.5	0.0		
MP4/6-311+G(D,P)//MP2/6-311G(D,P)	16.3		0.2	0.0	56.6	
G2(MP2)^a	12.4		5.9	0.0		
G2^a			6.4	0.0		
QCSID(T)/6-311G(D,P)//MP2/6-31G(D)	7.4		8.8	0.0		
QCISD(T)/6-311+G(DP) //GCISD(T)6-311+G(D,P)	7.0		9.7	0.0	45.3	
ref 12			30.1	0.0	57.3	
ref 13			15.8	0.0	23.6	
ref 14				0.0	38.3	

[a] Excluding the ZPE contribution from the standard G2(MP2) and G2 procedure.

Table 2. Vibrational Frequencies (cm^{-1}) and ZPE (kJ/mol)

species	state	method^a	frequencies^b						ZPE
$HCOO^{\bullet}$	$^2A_1$	HF	573	920	1188	1363	1899	2248	49.0
		MP2	$669(a_1)^c$	$836(b_1)^d$	$1200(a_1)^e$	$1475(b_2)^f$	$2241(a_1)^g$	$2577(b_2)^h$	53.8
	$^2B_2$	HF	697	1254	1420	1662	2075	3286	62.2
		MP2	$667(a_1)^c$	$1169(b_1)^d$	$1309(b_2)^f$	$1531(a_1)^i$	$2317(b_2)^h$	$3182(a_1)^g$	60.9
			$646^{c,j}$		$1477^{f,j}$	$1314^{i,j}$	$961^{h,j}$	$3197^{g,j}$	54^k
	$^2A'$	HF	637	1151	1198	1517	2018	3244	58.4
		MP2	$506(a')^c$	$1020(a'')^d$	$1073(a')^l$	$1391(a')^f$	$1793(a')^m$	$3044(a')^g$	52.8
		MP4	473	995	1055	1365	1733	2989	51.5
CO_2^{n}		expt	667^c	1343^i	2349^h				30.0
$HCOO^-$^{o}		expt	762^c	1069^i	1351^h	1383^d	1585^f	2803^g	53.5

[a] 6-31G(D) basis set. [b] Assignment was made to the MP2 frequencies only. [c] OCO scissors motion or bend. [d] H out-of-plane wag. [e] CO symmetric stretch and CH stretch. [f] H in-plane wag. [g] CH stretch. [h] CO assymmetric stretch and wag. [i] CO symmetric stretch. [j] MCSCF/CI, ref 14, assigned by analogy with ref 16. [k] Estimated, assuming the MP2 value for the H out-of-plane wag. [l] C–O stretch. [m] C═O stretch. [n] Taken from ref 24. [o] For aqueous solution, from ref 25.

fairly narrow for the $^2B_2$ state (111.6°) and gradually opens up to the other states, 121.8° for $^2A_2$, 146.2° for $^2A_1$, and 164.4° for $^2B_1$. The changes in bond lengths are less significant from state to state. The two structures corresponding to the $^2A'$ and $^2A''$ states of C_s symmetry are very similar. With slightly more asymmetric oxygen atoms in the $^2A''$ structure, the unpaired

Table 3. Relative Total Energies (kJ/mol) of the Three Lower Electronic States of $HCOO^\bullet$

	+ 0.89 × ZPE(HF/6-31G(D))			+ 0.95 × ZPE(MP2/6-31G(D))		
	$C_s(^2A')$	$C_{2v}(^2A_1)$	$C_{2v}(^2B_2)$	$C_s(^2A')$	$C_{2v}(^2A_1)$	$C_{2v}(^2B_2)$
MP4/6-31G(D)//MP4/6-31G(D)	21.3	0.0	11.3	11.9	0.0	6.2
MP4/6-311+G(D,P)//MP2/6-311G(D,P)	24.5	0.0	11.6	15.1	0.0	6.5
G2(MP2)	14.9	0.0	5.9	5.5	0.0	0.8
G2		0.0	5.4		0.0	0.3
QCISD(T)/6-311G(D,P)//MP2/6-31G(D)	7.0	0.0	3.0	0.0	2.4	0.3
QCISD(T)/6-311+G(D,P) //QCISD(T)/6-311+G(D,P)	5.7	0.0	2.1	0.0	3.7	0.7

Table 4. Relative Energies (kJ/mol) of the Lowest Electronic States of $CH_3COO^\bullet$ [a]

	$^2A''(B_2)$	$^2A'(B_2)$	$^2A'(A_1)$	$^2A'(A')$
ΔE(MP2 + 0.95 × ZPE)	0.0	0.1	10.0	14.3
ΔE(G2(MP2))[b]	0.1	0.0	21.9	9.9

[a] See Figure 3 for structures. [b] 0.95 × ZPE(MP2/6-31G(D)) were used in place of 0.89 × ZPE(HF/6-31G(D)) in the standard G2(MP2) procedure.

spin is delocalized over all three heavy atoms. While in the $^2A'$ state, the spin is basically centered on the oxygen atom which forms a "single bond" with the carbon atom.

At the MP2/6-31G(D) level, the electronic energies of the π radical states, $^2A''$, $^2A_2$, and $^2B_1$, are much higher (>100 kJ/mol) than others, confirming previous conclusions that the correlation error is more significant for the σ radicals.[13,14] Consequently, the $^2A''$ and $^2B_1$ states, but not the $^2A_2$ state, were excluded from further higher levels of calculations. The $^2A_2$ state has been reported to be the second lowest electronic state of formyloxyl.[14] It has previously been noted that the tendency to break symmetry may be less with more complete basis sets.[17] In order to distinguish between basis set and correlation effects, geometry optimizations were carried out at MP2 levels with larger basis sets, and at MP4 and CI levels with the 6-31G(D) basis set, for $^2A_1$, $^2A_2$, and $^2B_2$ states. The similarities of the structures from level to level confirm that the geometry of the formyloxyl radical is not sensitive to the correlation level or the basis set used (larger than 6-31G(D)) in the calculations.

Two[13,14] of the three previous ab initio studies carried out using CI procedures found that the formyloxy radical has C_{2v} symmetry, with the $^2B_2$ electronic state being the absolute minimum, though fairly different relative stabilities of $^2A_1$ and $^2A_2$ states were predicted by all three groups.

Geometry optimization at the MP2/6-31G(D) level predicted minima to occur at six stationary points, as did HF optimizations, but with substantially different relative stabilities (Table 1). For the σ radicals, geometries were also optimized at the MP2/6-311G(D,P) level. All calculations at the MP2 level consistently predict the most stable state on the Born–Oppenheimer potential energy surface to be the $^2A_1$ state of the C_{2v} structure. The next state, $^2B_2$, lies 12 to 17 kJ/mol above depending on the basis set used in geometry optimization and energy evaluation. The $^2A'$ state of the C_s structure is 25–33 kJ/mol higher in energy than the $^2A_1$ state of the C_{2v} structure, as listed in Table 1. The $^2A_2$ state was predicted to be 113.8 kJ/mol higher than the $^2A_1$ state by direct optimization at the MP2/6-311(D,P) level.

The effect of electron correlation energy was further investigated for the few lowest electronic states of the formyloxyl radical. One set of MP4 single-point calculations, carried out at the MP4/6-311+G(D,P) level on the structures optimized at the MP2/6-311G(D,P) level (MP4/6-311+G(D,P)//MP2/6-311G(D,P)), predicted the $^2B_2$ state to be virtually degenerate with the $^2A_1$ state (only 0.2 kJ/mol above $^2B_2$) on the Born–Oppenheimer surfaces. The relative energies of the $^2A'$ and $^2A_2$ states were reduced, to 16.3 and 56.6 kJ/mol above the $^2B_2$ state, respectively. With optimized geometries for $^2B_2$ and $^2A_1$ states at the MP4/6-31G(D) level, the results are similar, i.e. the $^2A_1$ state is less stable by 0.5 kJ/mol than the $^2B_2$ state.

Contrary to the MP2 results, however, single-point calculations at the QCISD(T)/6-311G(D,P) level on the MP2/6-31G(D) optimized geometries of $^2B_2$, $^2A_1$, and $^2A'$ states predict that $^2B_2$ is the lowest electronic state, qualitatively in accord with earlier studies.[12-14] The energy gap between the $^2B_2$ and $^2A_1$ states is found to be 8.8 kJ/mol, much smaller than that of Peyerimhoff et al.[12] (30.1 kJ/mol) or Feller et al.[13] (15.8 kJ/mol). The electronic energy of the $^2A'$ state is found at this level to be actually lower by 1.4 kJ/mol than that of the $^2A_1$ state. Full geometry optimizations of $^2B_2$ and $^2A_1$ at the QCISD(T)/6-311+G(D,P) level gave very similar results—$^2A_1$ is 9.7 kJ/mol less stable than $^2B_2$.

We extended the investigation to the G2(MP2) and G2 levels, both of which were designed[19,21] to provide correlation correction comparable to or better than that of the QCISD(T)/6-311+G(3DF,2P) level. The full G2 correlation treatment, *without ZPE*, predicts the $^2A_1$ state to lie 6.4 kJ/mol above the more stable $^2B_2$ state, in substantial agreement with our own and other high-level treatments. The G2(MP2) level result, also without the ZPE contributions, is very similar—$^2B_2$ more stable than $^2A_1$ by 5.9 kJ/mol.

Of course, the correct energy includes the ZPE contribution. The vibrational frequencies and ZPE of the various electronic states of formyloxyl at various theoretical levels are listed in Table 2. It is apparent from inspection of Table 2 that the vibrational frequencies, and hence the ZPE values, are sensitive to the level of calculation (HF vs MP2). At each of these levels, the predicted frequency for the asymmetric CO stretch appears anomalously high for both the $^2A_1$ and $^2B_2$ states, 2577 and 2317 cm^{-1}, respectively. Although a similar value, 2349 cm^{-1}, is observed in CO_2, harmonic frequency analysis by McLean and co-workers,[14] using MCSCF/CI techniques (Table 2), predicts a considerably lower value, 961 cm^{-1}, for the asymmetric CO stretch of the $^2B_2$ state of formyloxyl. The probable origin of such anomalous results has been discussed by Schaefer and co-workers[16] in relationship to instabilities in the HF wave functions of species such as NO_2 and formyloxyl. Nevertheless, since similar high values of asymmetric CO stretch are calculated for each state, it is

Table 5. Vibrational Frequencies (cm^{-1}) of $CH_3COO^\bullet$ Calculated at MP2/6-31G(D) Levels

state	frequencies															ZPE
$^2A''(B_2)$	15	409	583	591	934	1037	1140	1444	1523	1531	1659	2387	3125	3219	3236	136.5
	62[a]	390[a]	535[a]	549[a]	913[a]	937[a]	1005[a]	1311[a]	1361[a]	1393[a]	1448[a]	1590[a]	2993[a]	3082[a]	3099[a]	124
$^2A'(B_2)$	45*i*	409	585	593	932	1038	1137	1443	1524	1530	1659	2387	3125	3219	3236	136.6
$^2A'(A_1)$	31*i*	393	475	607	639	974	1192	1276	1362	1523	1544	2623	3160	3296	3319	133.9
$^2A'(A')$	29	384	504	575	876	966	1095	1295	1441	1530	1535	1796	3127	3219	3247	129.3

[a] LCGTO-NLDA, ref 23.

reasonably certain that the prediction that the ZPE of the $^2A_1$ states is significantly less than the ZPE of the $^2B_2$ state is correct. The large difference in ZPE between these states is due to the very "soft" H–C stretch (2248 cm^{-1}) in the $^2A_1$ state which will lead to cleavage of the CH bond of HCOO•. The difference is sufficient to reverse the predicted order of these two states when added to the highest level Born–Oppenheimer energies (Table 3). By correcting the total energies by 0.89 × ZPE(HF), the relative stabilities of $^2B_2$ and $^2A_1$ will be reversed at both G2-(MP2) and G2 levels, with $^2A_1$ being the lowest state and $^2B_2$ lying about 6 kJ/mol above. On this basis, we used this state to determine the electron affinity of HCOO• at the G2 level in our previous publication.[15] After inclusion of the MP2/6-31G(D) ZPE corrections, all of our high-level calculations predict that the total energies of the $^2B_2$ and $^2A_1$ electronic states of formyloxyl are within 3 kJ/mol of each other. Attempts to carry out harmonic frequency analysis at the QCISD(T) level, with the 6-31G(D) basis set, were unsuccessful. In each case, small deviations from the C_{2v} equilibrium geometry, as required for the numerical evaluation of the force field at this level, led to points on the potential energy hypersurface at which the SCF procedure failed to converge after a reasonable number (100) of iterations.

Of even greater interest is the fact that with the MP2/6-31G-(D) ZPE corrections, the lowest symmetry broken σ state, $^2A'$, is predicted to be the lowest electronic state of formyloxyl. Even if the ZPE corrections for the C_{2v} states are overestimated due to the presence of the anomalously high asymmetric CO stretch frequencies (Table 2), the C_s structure is still predicted to occur within a few kJ/mol of the lower energy C_{2v} states. We expended considerable efforts to satisfy ourselves that the $^2A'$ state is a valid stationary point (minimum) on the Born-Oppenheimer potential surface, since this would have considerable ramifications on the study of the structures of less symmetrical carboxyl radicals, including incidentally, acetyloxyl. Optimizations at the MP2 level with different basis sets invariably yield a local minimum for the $^2A'$ state, about 26 kJ/mol *above* the $^2A_1$ state, the absolute minimum at this level, and 15 kJ/mol higher than $^2B_2$. Geometry optimizations at the MP4/6-31G(D) level also predict that the $^2A'$ structure of C_s symmetry is a stationary point, with electronic energy about 13 kJ/mol above the $^2B_2$ and $^2A_1$ states (which are almost degenerate at the MP4/6-31G(D)//MP4/6-31G(D) level). A vibrational frequency calculation at the MP4 level (see Table 2) confirms that $^2A'$ corresponds to a well-defined local minimum. Geometry optimization at QCISD(T)/6-311+G(D) did not converge to the preset criteria of Gaussian 92 after 50 steps and was terminated when the maximum gradient among all 5 geometric parameters equaled 1.87×10^{-3} hartree/bohr, about five times the predefined criterion for convergence. The vibrationless electronic energy of the $^2A'$ state is 7 kJ/mol higher than that of the $^2B_2$ state and 3 kJ/mol lower than that of the $^2A_1$ state. Including the ZPE corrections still suggests that the A′ state is energetically comparable with the $^2B_2$ or $^2A_1$ state.

Although rarely used these days, the absolute energy in a variational calculation can be used as a measure of the quality of the wave functions or as a measure of the distance remaining from the exact non-relativistic Born–Oppenheimer energy. Although not fully variational,[22] the geometry-optimized QCISD-(T)/6-311+G(D,P) energies of the $^2A'$, $^2A_1$, $^2B_2$, and $^2A_2$ states are lower (by approximately 160 kJ/mol) than the lowest energy previously reported for any of the electronic states. That the broken symmetry $^2A'$ state persists as a local minimum at the highest levels of calculation strongly suggests that it may indeed be real, that is, a valid stationary point on the "experimental" potential energy surface of formyloxyl, and presumably other acyloxyl free radicals. At the very least, thermodynamic considerations based on $^2A'$-like structures will not be seriously in error.

The present study, which incorporates post-HF calculations at MP, G2, and CI levels, suggests a pattern of results which may be interpreted in terms of a deficiency in the MP results, and consequently in the G2 results, since they incorporate some MP components. The pattern is best seen in Table 3 (for example, the right hand side set of data) where the three σ states of formyloxyl are compared at the highest levels. The (presumably) most accurate method, QCISD(T), yields the result that the three states are essentially degenerate. By contrast, the MP4 calculation places the $^2A'$ state 12–15 kJ/mol above the $^2A_1$ state, and the $^2B_2$ state near midway. The G2 procedures, which incorporate both MP and CI components, yield intermediate results, somewhat closer to the CI values. The premise of the perturbation theory method is that the single determinantal wave function describing the lowest state is well separated from doubly or more highly excited configurations, a requirement which is not well satisfied in the carboxyl system. Consequently, the correlation correction for the symmetric states, $^2A_1$ and $^2B_2$ (-like), is overestimated (for the $^2A_1$ more than for the $^2B_2$).

Acetyloxyl radical: In parallel to the study of the formyloxyl radical, we investigated the lower electronic states of acetyloxyl, CH₃COO•. Due to the methyl substitution, the highest point group for CH₃COO• is C_s. At the MP2/6-31G(D) level optimizations, four structures, corresponding to local minima on the Born–Oppenheimer potential energy hypersurface, were found. All have C_s symmetry and are distinguished as $^2A''(B_2)$, $^2A'(B_2)$, $^2A'(A_1)$, and $^2A'(A')$ (Figure 3).

The $^2A''(B_2)$ structure has two equivalent oxygen atoms and one hydrogen atom in a plane perpendicular to the plane defined by the OCO group. Frequency calculation suggest that this structure is a local minimum (see Table 5), although the lowest frequency, corresponding to methyl torsion, is very low (15 cm^{-1}). The OCO angle is 110.2°, a value consistent with that found in the $^2B_2$ state of formyloxyl (112°), hence the qualifier, (B₂), indicating the symmetry in the local C_{2v} point group. The optimized OCO angle is consistent with that reported by Peyerimhoff et al. (112°).[12] The CC bond length was found to be 1.491 Å, also in good agreement with the value of 1.5 Å of ref 12. The three C–H distances are almost identical and the deviations from the tetrahedral angle are less than 0.1°. Modern density functional methods (LCGTO-NLDA) have been applied by Sicilia et al. to compute the heat of formation of acetyloxyl, evidently in its $^2A''(B_2)$ state.[23] The LCGTO-NLDA and MP2/6-31G(D) geometries are in close agreement, differing at most by 0.02 Å in the length of the CC bond. All calculated angles are within 1°. A 30° rotation of the methyl group leads to another stationary structure with C_s symmetry, labeled $^2A'(B_2)$, with essentially unchanged local OCO geometry (Figure 3), and unchanged energy. After inclusion of ZPE (MP2/6-31G(D)//MP2/6-31G(D) + 0.95ZPE level and G2(M2)), the energies of $^2A''(B_2)$ and $^2A'(B_2)$ states are basically degenerate (within 0.1 kJ/mol).

The predicted frequencies (Table 5) of the $^2A'(B_2)$ conformer are essentially identical to those of the $^2A''(B_2)$ conformer except for the methyl torsional mode which is calculated to have an imaginary frequency. Even discounting the values of the lowest frequency modes (which should in any case be treated as unhindered rotor modes), we are uncertain of the reliability of the predicted values, especially for the CO stretching modes. The UHF wave functions of both B₂-like conformers are predicted to be unstable toward symmetry breaking, as was the case for the $^2B_2$ state of formyloxyl. The most anomalous feature is the high value of the asymmetric CO stretch, 2387 cm^{-1} (2317 cm^{-1} in formyloxyl, Table 2). A similarly high value, 2349 cm^{-1}, is

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observed in CO_2, but the value in formate anion is much smaller, 1351 cm^{-1}. The LCGTO-NLDA frequencies of Silica et al.,[23] which were determined numerically, agree well with the MP2 values for acetyloxyl except for the asymmetric CO stretch mode. The assignments of the predicted frequencies were not reported by Sicilia et al.,[23] but the mode closest in frequency to the MP2 asymmetric CO stretch mode, after the CH stretches have been accounted for, is 1590 cm^{-1} (Table 5). If the value of the asymmetric CO stretch frequency is overestimated significantly, then the predicted value of the ZPE correction will also be too high. Both the MCSCF/CI ZPE estimate for formyloxyl (Table 2) and the LCGTO-NLDA estimate of ZPE for acetyloxyl (Table 5) suggest that the ZPE for the B_2(-like) states may be too high by about 6 kJ/mol. In other words, the B_2(-like) states may be about 6 kJ/mol more stable than predicted by the usual method of adding the ZPE corrections.

With one hydrogen atom perpendicular to the OCO plane, a stationary structure, $^2A'(A_1)$, was obtained. The OCO angle was found to be 143.6° (147° in the $^2A_1$ state of formyloxyl). The long CC bond (1.683 Å) indicates that the acetyloxyl radical in this state is ready to dissociate to $CH_3^{\bullet}$ and CO_2. The methyl group is also flattened, with HCH angles of 112.6° and 113°. A small imaginary frequency (31*i* cm^{-1}) is also calculated for the methyl torsional mode, suggesting free rotation about the CC bond, as in the case of the $^2A''(B_2)$ state. In contrast to the situation for the $^2A''(B_2)$ state, however, after rotation by 30° about the CC bond (which removes the limitation that the two oxygen atoms must be identical), geometry optimization at MP2/6-31G(D) leads to a symmetry-breaking A′-like (formyloxyl) structure, $^2A'(A')$. This structure is actually energetically *less* stable than $^2A'(A_1)$. Thus we have the bizarre result that optimization without constraints leads to a structure with higher energy, a consequence of the fact that the wave function of the $^2A'(A_1)$ at this level has internal instability. It is entirely possible that rotation about the CC bond in acetyloxyl is accompanied by decomposition to $CH_3^{\bullet}$ and CO_2 with little or no activation.

At the MP2/6-31G(D)//MP2/6-31G(D) + 0.95ZPE level, the $^2A'(A_1)$ state is calculated to be 10.0 kJ/mol less stable than the $^2A''(B_2)$ state. At the G2(MP2) level, this difference is larger still, 22 kJ/mol. As discussed above in connection with formyloxyl and Table 3, the G2(MP2) procedure may exhibit a slight bias toward the A_1-like electronic configuration. Accordingly, the relative energy of 22 kJ/mol should be regarded as a minimum. This result is in sharp contrast to the equivalent situation in formyloxyl, where the two symmetrical σ states were found to be nearly degenerate at the G2(MP2) level, with $^2B_2$ slightly favored in the QCISD(T) calculation. Evidently, substitution by the alkyl group raises the energy of the A_1-like state relative to the B_2-like state by about 20 kJ/mol. The destabilization due to alkyl (and other groups) may be due to increased steric repulsion originating from the necessity to accommodate a smaller ∠CCO angle.

The A′-like structure of the acetyloxyl radical was predicted to be a local minimum on the MP2/6-31G(D) surface. The OCO angle of the $^2A'(A')$ state is 121.1°, slightly smaller than that in the $^2A'$ state of $HCOO^{\bullet}$, and the two CO bond lengths of both formyloxyl and acetyloxyl are similar (differing only in the third decimal places). Energetically, this state is higher, by 14.3 kJ/mol, than the lowest state, $^2A''(B_2)$, at the MP2/6-31G(D)//MP2/6-31G(D) + 0.95ZPE level. At G2(MP2) levels, the relative stabilities between the $^2A'(A_1)$ and the $^2A'(A')$ states are reversed, with the latter being 12 kJ/mol more stable, and 10 kJ/mol above the $^2A''(B_2)$ state. The computational bias mentioned above implies that the energy difference between the $^2A''(B_2)$ state and the "broken symmetry" $^2A'(A')$ state should be less than 10 kJ/mol, although this expectation may be countered by an overestimate of the ZPE correction for the B_2-like state.

4. Summary

For the formyloxyl radical, the present highest level ab initio calculations predicted that the $^2B_2$ and $^2A_1$ states are essentially degenerate, being separated by less than 3 kJ/mol. The vibrational energy contributions, which are difficult to determine reliably for this system, are very important in dealing with closely lying electronic states of radicals. All indications from a thorough study on the "symmetry breaking" state, $^2A'$ of C_s symmetry of formyloxyl radical, lead to the conclusion that this state corresponds to a local minimum with a total energy comparable to that of the $^2B_2$ or $^2A_1$ states.

The lowest electronic state of the acetyloxyl radical is B_2-like, with unhindered methyl rotation, equal CO bond lengths, and delocalized spin distribution. The presence of the methyl group leads to substantial destabilization of the symmetric A_1-like state, by at least 20 kJ/mol, relative to the case of formyloxyl. This state is probably unstable with respect to CC bond rupture. The "broken symmetry" structure, $^2A(A')$, was also found to be a true minimum and the second lowest electronic state, lying less than 10 kJ/mol above the B_2-like ground state.

The relative energies cited above for acetyloxyl are at the G2-(MP2) level. The results for the $^2B_2$ and $^2A_1$ states of formyloxyl indicate that the G2(MP2) procedure is equivalent to G2 in predicting the relative energies. Comparison to QCISD(T) calculations suggests that the perturbation theoretical Møller–Plesset treatments may overestimate the correlation error for the acyloxyl system, and that this bias also applies to the G2 treatments to a lesser extent.

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Supplementary Material Available: Optimized geometries for $HCOO^{\bullet}$ (Table S-I); MP2/6-31G(D) optimized geometries for the lowest electronic states of $CH_3COO^{\bullet}$ (Table S-II); electronic energies of $HCOO^{\bullet}$ at different levels of calculations (Table S-III); total energies of the lowest electronic states of $CH_3COO^{\bullet}$ (Table S-IV) (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.