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σ Ground State of the Benzoyloxy Radical

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Received January 3, 1977

Abstract: The ground state of benzoyloxy radical is examined by two methods: (1) the comparison of the direction cosines of the experimental g tensor reported² with the x-ray crystallographic data of the host molecule in single crystals, and (2) calculation of the g tensors in various possible ground states of acetoxy radical as a model. The two considerations agree and support the assignment of the ${}^2A'$ σ ground state of the benzoyloxy radical, rather than the 2A_2 π state.

Several acyloxy radicals³⁻⁸ have been observed in single crystals by electron spin resonance (ESR) and their g tensors were reported. All of these radicals were found to have σ ground states on the basis of their g tensors. Hyperfine tensors were reported for some of these radicals³⁻⁶ and the same conclusions were obtained from this information. All acyl radicals⁹⁻¹⁶ obtained in single crystals and in polycrystalline matrices are also reported to be σ radicals based on their g tensors and hyperfine tensors.

The most common assumption for utilizing eigenvectors (direction cosines) for spectral assignment in single crystals is that the local symmetry of radicals is fundamentally the same as the radical precursor in the matrix. This assumption has been justified in the case of acyl type radicals by observing a large ${}^{13}\text{C}$ hyperfine splitting constant.^{13,16}

Kikuchi et al.¹⁷ applied the semiempirical NDDO MO method¹⁸ to formyloxy and acetoxy radicals and predicted σ ground states.

Recently, Karch et al.² reported the g tensor of the benzoyloxy radical obtained during the course of the investigation of radical pairs in crystalline acetylbenzoyl peroxide. They tentatively assigned the ground state as a 2A_2 π state of C_{2v} symmetry on the basis of INDO and ab initio STO-3G calculations and ${}^{13}\text{C}$ CIDNP. In view of the characterization of σ ground states for all previously characterized acyl and acyloxy radicals, the π ground state assignment for benzoyloxy radical in single crystal is quite unusual. Since an experimental g tensor was reported² it is possible to characterize the ground state of this radical from experimental data alone.

The reliability of a NDDO prediction of the correct ground state for radicals is not absolute owing to the uncertainties of semiempirical MO calculations of total energies. However, it can reliably predict a variety of molecular properties if the symmetry and ground state are given. The g tensors of several σ -type radicals have been successfully estimated¹⁹ in this way.

We present here (1) a reexamination of the ground state of benzoyloxy radical in single crystal from an analysis of the reported g tensor alone and (2) a calculation of the g tensor of acetoxy radical as a model by the semiempirical NDDO MO method.

Results and Discussion

A. g Tensor Analysis. Table I shows the reported² principal values and direction cosines of the g tensor for the benzoyloxy radical produced by the photolysis of crystalline acetylbenzoyl peroxide and the bond directions of the host molecule calculated from the orthogonal axes (a^* , b , c).²⁰ The directions are portrayed against the background of a partial skeleton of acetylbenzoyl peroxide in Figure 1.

Since g_2 is $(\Delta g)_{\min}$ for this radical, the unpaired electron orbital should lie very close to this direction. The g_2 axis of this radical lies 86.5° away from the direction of a π type orbital while the g_3 axis is perpendicular to the carboxyl plane within 7° (see Table I). The sum of the angles of the g_2 and g_3 axes with the O_3C_3 bond is 95.5°, which is 5.5° larger than it should be. This angle deviation is quite consistent with a deviation of g_3 of 7° from the normal to the carboxyl plane. It may originate from distortion from its undamaged position and/or nonplanarity of the radical carbon by the above amount. Thus the unpaired electron orbital cannot be a π orbital unless the carboxyl plane has turned sideways dramatically ($\sim 80^\circ$) with respect to its undamaged position.

Two extreme cases can be considered for the unpaired electron orbital for this radical: (1) the unpaired electron is located *mostly* along the cleaved bond on O_3 with C_s symmetry; (2) the unpaired electron is equally distributed between O_3 and O_4 with C_{2v} symmetry. The first case is a ${}^2A'$ state and the second case will be either the 2A_1 or 2B_2 states² (Figure 2). Taking case 1 first, an idealized P_σ orbital on the O_3 atom of the radical will make angles of 90 and 20.9° with the $\text{C}_3\text{-O}_3$ and $\text{O}_2\text{-O}_3$ bond directions, respectively, of the host molecule

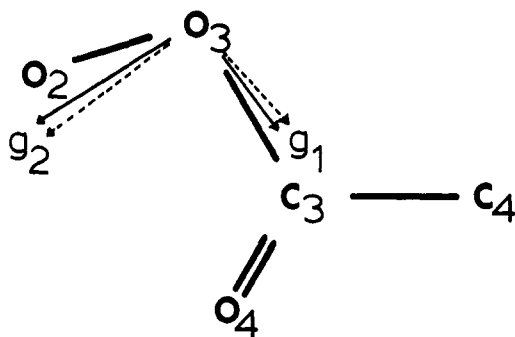


Figure 1. The principal axes of the g tensors for benzoyloxy radical are portrayed against the background of the undamaged partial skeleton of acetylbenzoyl peroxide (solid line, experimental; broken line, calculated). The experimental g_3 direction is perpendicular (within $\sim 7^\circ$) to the plane of carboxyl group.

Table I. Principal Values and Direction Cosines of g Tensor for Benzoyloxy Radical and Bond Directions of the Host Molecule

	Principal values	Direction cosines for a^*bc			Comparison with x-ray data	
		a	b	c		
g_1	2.0228	-0.1948	0.4609	-0.8658	95.9	(5)
					112.3	(4)
					6.0	(2)
					69.9	(1)
					93.4	(5)
g_2	2.0041	-0.9046	0.2568	0.3402	89.5	(2)
					23.5	(4)
					20.1	(1)
					32.3	(3)
					6.8	(5)
g_3	2.0082	0.3791	0.8495	0.3670	83.2	(4)
					84.0	(2)
					88.9	(1)
					84.0	(3)
\parallel C ₃ -C ₄ (1)	-0.7752	0.09789	0.6242			
\parallel C ₃ -O ₃ (2)	-0.1618	0.5490	-0.8200			
\parallel C ₃ -O ₄ (3)	-0.8266	0.5480	-0.1283			
\parallel O ₃ -O ₂ (4)	-0.7109	0.1610	0.6846			
\perp O ₃ C ₃ O ₄ (5)	0.4501	0.7805	0.4338			

if their geometries are same. This direction should then correspond to $(\Delta g)_{\min}$ and indeed g_2 is very close to this direction (within 1°). In case 2, $(\Delta g)_{\min}$ should be along the C₃-C₄ bond, and g_2 of this radical is about 20° from the direction assuming no reorientation upon radical formation. The unpaired electron orbital may be represented by

$$\psi_0 = d_3 p_\sigma(O_3) - d_4 p_\sigma(O_4)$$

where $p_\sigma(O_i)$ is the oxygen in-plane 2p orbital. The g_1 axis will lie somewhere in the shaded region²¹ shown depending on the d_3^2/d_4^2 ratio. Comparing the directions of the g_1 axis with the

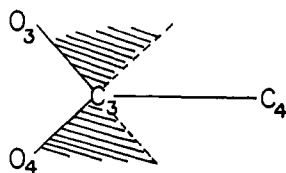


Figure 2. Qualitative pictures of the unpaired electron orbitals for the corresponding symmetries and states.

coupling are those from the filled orbitals to the half-filled orbital.² The ground state of this radical may be written as

$$\dots (a_1')^2(a_1'')^2(a_2')^2; {}^2A'$$

where the primed orbitals are symmetric, and doubly primed orbitals are antisymmetric with respect to reflection in the O₃C₃O₄ plane. When the magnetic field is applied along the g_1 direction and thus approximately in the O₃C₃O₄ plane and parallel to the C₃-O₃ bond, the ground state ${}^2A'$ will be coupled with excited states of ${}^2A''$ symmetry such as

$$\dots (a_1')^2(a_1'')(a_2'')^2; {}^2A''$$

The filled a_1'' molecular orbital with this character is the π orbital of C₃O₃O₄. The energy of this π orbital is expected to be higher than that of the filled σ orbitals. Because of the small energy separation and large spin-orbit coupling constant of oxygen, g_1 should show the largest shift from the free spin values of the components of the g tensor. This is the case for this radical ($\Delta g_1 = 0.0205$). When the magnetic field is parallel to g_3 (approximately perpendicular to the O₃C₃O₄ plane), the ${}^2A'$ ground state should be coupled with an ${}^2A'$ excited state. The excited state may be described as

$$\dots (a_1')(a_1'')^2(a_2')^2; {}^2A'$$

The Δg_3 value (0.0059) is considerably smaller than the Δg_1 value. Two effects may cause this difference: a large energy difference and a small net coupling. The filled a_1' orbital participating in this mixing may be a σ orbital with the electron density spread along O₃-C₃-C₄.

B. g Tensor Calculation. The g tensors of acetoxy radical for several possible ground state (Figure 2) are calculated by Stone's perturbation equation²² with molecular orbitals and energy differences obtained by the restricted open-shell procedure²³ with the NDDO approximation. All the singly excited configurations are taken into account in the calculation of g tensors. The coordinate system used is as follows: Y, \parallel bisector of OCO (and \parallel C₃C₄) in plane; X, \perp Y in OCO plane; and Z, \perp OCO plane.

${}^2A_1(C_{2v})$.²⁴ The geometry employed for this state with the constraints of a planar framework with C_{2v} symmetry is C-O, 1.240 Å; C-C, 1.491 Å; and \angle OCO, 130° . The electron configuration for this species is

$$[2\pi(s)]^2[7\sigma(a)]^2[8\sigma(a)]^2[3\pi(a)]^2[9\sigma(s)]^1[4\pi(s)]^0[10\sigma(s)]^0$$

where s and a are symmetric and antisymmetric with respect to the plane bisecting the OCO plane. The resulting g shifts from the various coupling and principal values are collected in Table II: $g_{XX} = 2.0014$, $g_{YY} = 2.0023$, and $g_{ZZ} = 2.0211$.

${}^2B_2(C_{2v})$. The optimized geometry for this state with the constraints of a planar framework with C_{2v} symmetry is C-O, 1.247 Å; C-C, 1.491 Å; and \angle OCO, 110° . The electron con-

C₃-O₃ bond in Figure 1, d_3^2 should be much greater than d_4^2 for the benzoyloxy radical, discrediting the assumption of case 2.

The principal values of the g tensor in this radical are all shifted positively from the free electron g value (2.0023). This indicates that the *major* contributions of the mixing of the ground state and the excited states through the spin-orbit

Table II. Calculated g Tensor of Acetoxy Radical for a 2A_1 (σ, C_{2v}) Ground State

Excited confign	ΔE , eV	Δg_{XX}	Δg_{YY}	$\Delta g_{ZZ} \times 10^4$
$1\pi(s) \rightarrow 9\sigma(s)$	8.29	11	0	0
$2\pi(s) \rightarrow 9\sigma(s)$	4.78	10	0	0
$7\sigma(s) \rightarrow 9\sigma(s)$	4.04	0	0	31
$8\sigma(a) \rightarrow 9\sigma(s)$	0.76	0	0	159
$3\pi(a) \rightarrow 9\sigma(s)$	0.67	0	0	0
$9\sigma(s) \rightarrow 4\pi(s)$	4.86	-28	0	0
$9\sigma(s) \rightarrow 10\sigma(s)$	6.58	0	0	0
$9\sigma(s) \rightarrow 12\sigma(a)$	9.23	0	0	-2
$9\sigma(s) \rightarrow 13\sigma(s)$	9.31	-2	0	0
Others		0	0	0
Total		-9	0	188
Principal value		2.0014	2.0023	2.0211

figuration for this species is

$$[1\pi(s)]^2[5\sigma(s)]^2[6\sigma(s)]^2[2\pi(s)]^2[7\sigma(a)]^2[8\sigma(s)]^2[3\pi(a)]^2[9\sigma(a)]^1[4\pi(s)]^0[10\sigma(s)]^0$$

The calculated g shifts and principal values are shown in Table III: $g_{XX} = 2.0189$, $g_{YY} = 2.0039$, and $g_{ZZ} = 2.0193$.

${}^2A'(C_s)$. The geometry employed for this state with the constraints of a planar framework with C_s symmetry is C-O₃, 1.28 Å; C=O₄, 1.22 Å; C-C, 1.49 Å; $\angle OCO$, 130°; and CCO, 115°. The electron configuration obtained and used for the coupling is

$$(1\pi)^2(5\sigma)^2(6\sigma)^2(2\pi)^2(7\sigma)^2(8\sigma)^2(3\pi)^2(9\sigma)^1(5\pi)^0(10\sigma)^0$$

The principal g values are $g_1 = 2.0256$, $g_2 = 2.0024$, and $g_3 = 2.0119$. The direction cosines of these principal axes in the XYZ coordinate system are (0.9702, -0.2423, 0.0026), (0.2422, 0.9701, 0.0150), and (-0.0062, -0.0140, 0.9999), respectively. The calculated g value shifts and principal values are collected in Table IV.

C. Comparison and Conclusion. The ${}^2A_2(\pi, C_{2v})$ state gives $\Delta g_{ZZ} \approx 0$ within the geometrical restriction (planar) employed in this work. The ${}^2A_1(\sigma, C_{2v})$ calculation shows that Δg_{XX} is negative while experimentally this value has the largest positive shift. Therefore the two states, ${}^2A_2(\pi)$ and ${}^2A_1(\sigma)$, can be excluded from the possible ground state of this radical.

The calculated g values from the 2B_2 state are reasonably close to the experimental values. However, there are two defects: (1) Δg_{XX} and Δg_{ZZ} are almost equal in the calculated value while experimentally $\Delta g_1 \gg \Delta g_3$. (2) Calculated principal directions do not agree with the experimentally obtained directions (calculated g_{XX} and g_{YY} axes are perpendicular and parallel to C₃-C₄ (Y) in plane, respectively). It agrees with the reasoning of 2B_2 exclusion in section A (vide supra).

The principal g values calculated from the ${}^2A'$ state agree remarkably well with experimental values. It shows $\Delta g_1 > \Delta g_3$ and at the same time the direction cosines calculated are very close to the experimental results. The direction of the calculated g_1 axis makes an angle of 14° with the X axis and approximately 5° with the experimental g_1 axis. Several highest occupied orbitals considered in section A (vide supra) for elucidating the experimental g tensor agree well with the electron configuration and geometry obtained from the ${}^2A'$ state calculation. The total spin densities from this calculation are 84, 3.4, 1.8, and 8.6% on O₃, O₄, C₃, and other groups, respectively.

The calculated $\Delta g_1/\Delta g_3 = 2.4$ is less than the experimental value 3.5. If the g tensor of the benzoyloxy radical is calculated instead of acetoxy radical, this ratio and $(\Delta g)_{\min}$ may be improved because of larger contribution from the lower π state $\rightarrow 9\sigma$ to Δg_1 and Δg_2 .

In this report we (1) examined the experimental g tensor of

Table III. Calculated g Tensor of Acetoxy Radical for a 2B_2 (σ, C_{2v}) Ground State

Excited confign	ΔE , eV	Δg_{XX}	Δg_{YY}	$\Delta g_{ZZ} \times 10^4$
$1\pi(s) \rightarrow 9\sigma(a)$	9.24	0	3	0
$6\sigma(s) \rightarrow 9\sigma(a)$	6.22	0	0	11
$2\pi(s) \rightarrow 9\sigma(a)$	5.49	0	23	0
$7\sigma(a) \rightarrow 9\sigma(a)$	4.29	0	0	0
$8\sigma(s) \rightarrow 9\sigma(a)$	0.99	0	0	165
$3\pi(a) \rightarrow 9\sigma(a)$	0.61	166	0	0
$9\sigma(a) \rightarrow 4\pi(s)$	5.51	0	-20	0
$9\sigma(a) \rightarrow 10\sigma(s)$	8.33	0	0	-9
$9\sigma(a) \rightarrow 11\sigma(s)$	11.04	0	0	-1
Others		0	0	4
Total		166	6	170
Principal values		2.0189	2.0029	2.0193

Table IV. Calculated g Tensor of Acetox Radical for a ${}^2A'$ (σ, C_s) Ground State

Excited confign	ΔE , eV	Δg_1	Δg_2	$\Delta g_3 \times 10^4$
$1\pi \rightarrow 9\sigma$	9.45	4	1	0
$2\pi \rightarrow 9\sigma$	6.04	3	0	0
$7\sigma \rightarrow 9\sigma$	4.86	0	0	15
$8\sigma \rightarrow 9\sigma$	1.97	0	0	87
$3\pi \rightarrow 9\sigma$	0.83	234	0	0
$9\sigma \rightarrow 4\pi$	7.99	-9	0	0
$9\sigma \rightarrow 10\sigma$	8.98	0	0	-6
$9\sigma \rightarrow 11\sigma$	11.41	0	0	-1
Others		1	0	1
Total		233	1	96
Principal values		2.0256	2.0024	2.0119

benzoyloxy radical in single crystal reported by Karch et al.² by comparing their directions with bond axes of the undamaged molecule in the crystal, and (2) calculated the g tensors in various possible ground states. The two considerations agree and support the assignment of the ${}^2A'\sigma$ ground state of the benzoyloxy radical. The underlying assumption in this discussion is that the radical geometry at low temperature is fundamentally the same as that of the undamaged species in single crystal. This is, we believe, a quite reasonable assumption on the basis of other ESR studies of large radicals in radiation damaged single crystals. Furthermore, the remarkable agreement of calculated (for C_s symmetry) and experimental g tensors justified this assumption by itself.

Acknowledgment. One of the authors (M.B.Y.) wishes to express his thanks to Dr. Machio Iwasaki for helpful suggestions and to Professor Robert Bohn for his critical reading of this manuscript.

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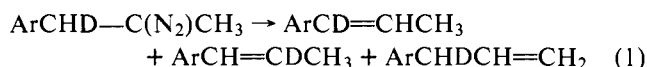
Pull-Push Mechanism for the 1,2-Hydrogen Rearrangement of Carbenes. Substituent and Deuterium Isotope Effects for Thermal Decomposition of 1-Phenyl-2-diazopropanes¹

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Abstract: Intramolecular and intermolecular deuterium isotope effects have been measured for the thermal carbene H rearrangements of three substituted 1-phenyl-2-diazopropanes-1-*d* in hexane at 25 °C. The isotope effects, k_H/k_D , vary from ca. 1.2 to 1.5, increasing with electron-withdrawing substituents, for the formation of both *cis*- and *trans*- β -methylstyrenes. Product ratios were determined for these compounds as well as the corresponding undeuterated ones, permitting calculation of intermolecular primary and secondary isotope effects. In addition, the competition among the *cis* and *trans* products and the product of H migration from the terminal methyl group permitted determination of Hammett ρ values of ca. -1 for the competition between benzylic and terminal migration. The results strongly indicate a "pull-push" mechanism, which can be pictured roughly as electrophilic attack on the C-H bond by the phantom p orbital of the carbene along with backside nucleophilic attack by the carbene unshared electron pair to push the H away and form the π bond. The data are believed to be consistent only with a nonzero barrier for the carbene hydrogen rearrangement.

We have determined product ratios and competitive isotope effects for the hydrogen shift rearrangement in the thermal decomposition of substituted 1-phenyl-2-diazopropanes-1-*d* (eq 1) and the corresponding undeuterated compounds,

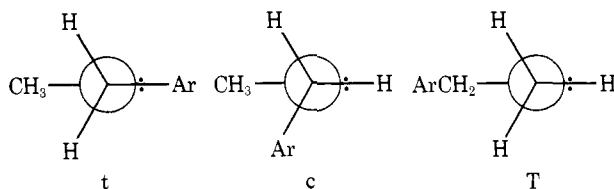


in hexane at 25 °C. Both *cis* and *trans* isomers of β -methylstyrene are produced. The reactions are believed to proceed through an intermediate singlet carbene.² Primary diazo compounds have been reported to undergo self-catalyzed, cationic decompositions in competition with the production of carbenes,³ but the secondary diazo compounds we have studied do not have an acidic hydrogen attached to the diazo carbon. Since our diazo compounds were generated under basic conditions and were allowed to decompose in the nonpolar solvent hexane, we believe that the reactions proceed exclusively by the carbene mechanism. Additional evidence includes the absence of appreciable deuterium loss during the reaction, ruling out significant proton intrusion from the glass surface, as discussed in the Experimental Section. It has also been found that 2-diazopropane is thermally unstable, with a half-life of 3 h at 0 °C in ether.⁴ Although we have studied product competition and not rates, our compounds decomposed at rates of the same order of magnitude as that for 2-diazopropane.

MO-following considerations suggest ready rearrangement through *gauche* hydrogen migration,⁵ and experiment indicates that an approximately perpendicular hydrogen (resembling *gauche*) rearranges more readily than an *antiplanar* one.⁶ MO calculations favor a *gauche* migration in the case of methylcarbene,^{7,8} but barriers to rearrangement of 0 and 21 kcal mol⁻¹, respectively, have been reported. The barrier for H

rearrangement of the triplet carbene was calculated as 88 kcal mol⁻¹.⁸

An experimental study of the mechanism of rearrangement seemed particularly desirable in view of the question about barrier height. The mechanism indicated to be favorable⁵⁻⁸ is quite interesting, since it involves a migration of H in a sort of spiral path and can be thought of as involving an electrophilic pull of hydride through the phantom p orbital of the carbene and concerted π -bond formation via backside attack of the carbene unshared electron pair to push the hydride off the carbon to which it was originally attached (*pull-push* mechanism), starting from approximate carbene conformations *t*, *c*, and *T* for formation of *trans*, *cis*, and terminal olefin.



Cyclic electron reorganizations cannot rigorously be described as hydride transfers—in fact, there is significant delocalization so that the unshared pair is not really distinguishable in the transition state⁵—but the electron density at the benzylic carbon and the polarization of the C-H bond being broken can be probed with substituent and isotope effects, giving the following information.

(1) Isotope effects, k_H/k_D , for hydrogen migration are near 1.4, similar to those reported in a few other carbene rearrangements,^{6,9-11} near the classical limit of 2^{1/2} and thus consistent with a very low or zero barrier.¹² (2) Hammett ρ values are approximately -1, some curvature being observed,