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Is the oxygen “side-on”, or “end-on” and fluctional, in peroxy radicals with magnetically equivalent oxygen atoms?

K.U. Ingold and Gino A. DiLabio

Abstract: The g values that have been measured for the group-14 peroxy radicals are sufficiently similar to suggest that they all have very similar structures. However, the ^{17}O hyperfine splittings seem to indicate that tin peroxy radicals have structures that differ from their lighter group-14 analogs. We hypothesize that the oxygen atoms in tin peroxy radicals are magnetically equivalent because they undergo a rapid 1,2-shift. Density-functional and wave-function theory calculations support this view.

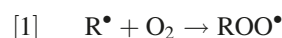
Key words: electron paramagnetic resonance spectroscopy, density-functional theory, group-14 peroxy radicals.

Résumé : Les valeurs g qui ont été mesurées pour les groupes hydroxyles du groupe 14 sont suffisamment semblables pour suggérer qu'ils ont tous des structures très semblables. Toutefois, les dédoublements hyperfins du ^{17}O semblent indiquer que les peroxydes de l'étain possèdent des structures qui diffèrent de celles de leurs analogues plus légers du groupe 14. On croit que les atomes d'oxygène des peroxydes de l'étain sont magnétiquement équivalents parce qu'ils subissent un rapide déplacement 1,2. La théorie de la fonctionnelle de la densité et celle de la fonction d'onde supportent toutes les deux cette hypothèse.

Mots-clés : spectroscopie de résonance paramagnétique électronique, théorie de la fonctionnelle de la densité, radicaux peroxydes du groupe 14.

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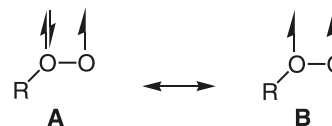
The oxidative degradation of organic materials, such as lubricating oils, plastics, edible fats, and even lipids in living organisms, are free-radical, two-step, chain processes (see reactions. [1] and [2]).



The economic costs of such degradation have led to exhaustive research on the kinetics, thermodynamics, and reaction mechanisms of these autoxidation processes and on methods for their retardation (inhibition). There has also been extensive research on the structures of the chain-propagating alkylperoxy radicals, ROO^\bullet , primarily by electron paramagnetic resonance (EPR) spectroscopy. Most organic radicals have g values near that of the free electron (2.0023) as a consequence of the almost complete quenching of orbital angular momentum. In contrast, alkylperoxy radicals have much higher g values (range: 2.014–2.017)¹ because their orbital angular momentum is incompletely quenched.²

The use of ^{17}O -labelled dioxygen to trap carbon-centered radicals has revealed that alkylperoxy radicals have two magnetically

inequivalent oxygen atoms.^{1,3–6} This is readily understood by consideration of the two canonical structures, **A** and **B**.



In $\text{Me}_3\text{COO}^\bullet$, inductive electron donation by the *tert*-butyl group and conjugative electron delocalization stabilize **B**, with ^{17}O labelling indicating that **A** and **B** make contributions of approximately 60% and 40%, respectively.^{3,4} The relative importance of **A** increases as the inductive electron-donating ability of R declines and, with the electron-withdrawing trichloromethyl group, the unpaired spin density on the outer oxygen atom reaches 70%.^{6,7–9}

Other triorgano group-14 peroxy radicals have been prepared and examined by EPR spectroscopy.¹ Relevant EPR data are given in Table 1. Table 1 contains the isotropic g values measured in cyclopropane solution¹⁰ and the two ^{17}O hyperfine splittings (hfs) for triorgano-silylperoxy radicals,¹¹ -germylperoxy radicals,¹² and -stannylperoxy radicals.^{11,13} These hfs have not been measured for plumbylperoxy radicals. The g values of these peroxy

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Table 1. EPR parameters for some triorgano group-14 peroxy radicals.

Peroxy radical	<i>g</i> value	<i>a</i> _{17O} (inner) (G)	<i>a</i> _{17O} (outer) (G)	<i>a</i> _{17O} ref.
Me ₃ COO•	2.0154 ^a	17.6 ^b	23.45	4
Ph ₃ COO•	2.014 ^c	14.3 _{av} ^{c,d}	24.3 _{av} ^{c,d}	5
Cl ₃ COO•	2.0153 ^e	10.4 _{av} ^{e,f}	28.2 _{av} ^{e,f}	6
(Me ₃ C) ₃ SiOO•	2.0294 ^g	14.6	25.4	11
Me ₃ GeOO•	2.024 ^h	~15 ⁱ	~25 ⁱ	12
(<i>n</i> -Bu) ₃ SnOO•	2.024 ^j	25	25	13
Me ₃ PbOO•	2.034	NA ^k	NA ^k	NA ^k

Note: Isotropic parameters measured in cyclopropane solution are from ref. 10 unless otherwise noted.

^aIn C₆D₆, ref. 10.

^bThe value of 16.4 G from ref. 3 has been corrected for sweep width error by a factor of 23.45/21.8 = 1.076, see footnote 2 in ref. 4.

^cAt 123 K in polycrystalline triphenylacetic acid.

^dBased on ¹⁷O hfs of 61 and 91 G and the suggestion⁵ that the other principal values of the ¹⁷O tensors are both approximately –8 G.

^eAt 93 K in a methanol glass.

^fBased on ¹⁷O hfs of 49.2 and 102.6 G at 93 K and the suggestion⁵ that the other principal values of the ¹⁷O tensors are both approximately –8 G.

^gValues for Me₃SiOO• and Ph₃SiOO• are 2.0277 and 2.0271, respectively.¹¹

^hPh₃GeOO• has the same *g*.¹²

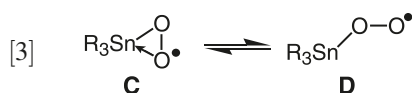
ⁱFrom the text of ref. 13.

^jGiven as 2.025 in ref. 11. This reference includes Me₃SnOO• (*g* = 2.024) and Ph₃SnOO• (*g* = 2.020).

^kNA: not available.

yls are somewhat greater than those of triorgano carbon centered radicals (as might be expected from the presence of heavier atoms attached to the O–O moiety). However, the *g* values of all the group-14 peroxy radicals are sufficiently similar to suggest that they all have very similar structures.

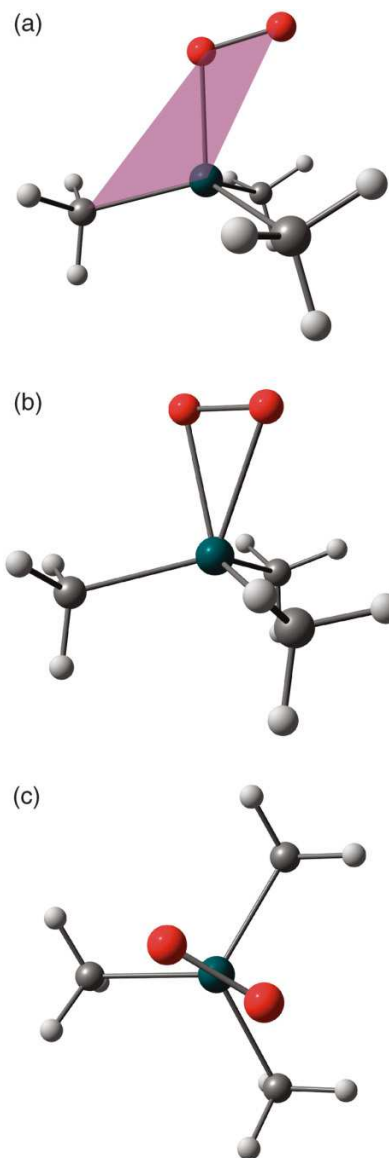
On the other hand, the ¹⁷O hyperfine splittings (hfs) appear to tell a different story. For *tert*-butylperoxy radical it has been established that the larger ¹⁷O hfs comes from the terminal (outer) O atom.⁴ The same is presumed to be true for all other alkylperoxy radicals and also for the silyl- and germylperoxy radicals.¹⁴ However, the tri-*n*-butylstannylperoxy radical was found to have two magnetically equivalent O atoms,^{11,13} and it was hypothesized to have “a pentacoordinate, trigonal bipyramidal structure in which the vacant Sn 5d orbitals are used to form a dative bond with the lone pair of electrons on the terminal oxygen of the peroxy function”^{10,12} (structure **C**). Later,¹³ it was found that stannylperoxy radicals reacted rather like alkylperoxy radicals,¹⁵ which led to the suggestion that structure **C** might be in equilibrium with the “usual structure for a peroxy radical” (**D**).¹³



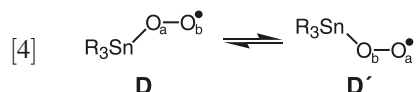
The possibility that **C** was simply the transition state structure for a rapid 1,2 shift of the trialkylstannyl group between the two oxygen atoms, appears not to have been considered.^{11,13}

In view of the foregoing, we hypothesized that the oxygen atoms in *n*-Bu₃SnOO• were magnetically equivalent because of a fast 1,2-shift of the *n*-Bu₃Sn group, **D** ↔ **D'**, rather than

Fig. 1. Perspective images representing (a) the minimum energy structure for Me₃XOO• and the (b) side and (c) top-down views of the transition state structure interconverting two equivalent structures of the type in (a). Atoms are represented as follows: H = white, C = gray, X = blue (X = C, Si, Ge, Sn, and Pb), and O = red. Atoms in the shaded area are coplanar.



because this radical had the symmetric structure, **C**. To check this hypothesis we turned to theory.



Using a density functional theory (DFT) approach,¹⁶ we computed the lowest energy structures for Me₃XOO• (X = C, Si, Ge, Sn, and Pb) radicals and subsequently verified the structures as minima by obtaining all positive vibration frequencies. We chose to use methyl-substituted group-14 peroxy radicals for simplicity, recognizing that more elaborate substituents (e.g., butyl groups) will not change our general conclusions. In all cases, the lowest energy structure was

Table 2. Zero-point corrected energies of $\text{Me}_3\text{XCOO}^\bullet$ “side-on” structures relative to “end-on” structures (ΔE),²⁴ calculated rate constants for $[\text{Me}_3\text{XOO}^\bullet]^\ddagger \rightleftharpoons [\text{Me}_3\text{XO}^\bullet\text{O}]^\ddagger$, and calculated EPR parameters for lowest energy, i.e., “end-on”, structures.

X	ΔE (kcal/mol)	k (s^{-1}) ^a	$a_{17\text{O}}$ (inner) (G)	$a_{17\text{O}}$ (outer) (G)	Calcd. (exptl.) ratio ^b
C	59.7	8×10^{-52}	16.9	23.2	1.37 (1.33)
Si	12.8	2×10^{-1}	13.1	23.2	1.77 (1.74)
Ge	15.0	1×10^{-3}	14.8	23.3	1.57 (1.67)
Sn	4.5	5×10^8	15.7	23.1	1.47 (1)
Pb	5.6	3×10^7	16.7	23.1	NA ^c

^aThermochemical corrections obtained at 200 K.

^bObtained as $a_{17\text{O}}(\text{outer})/a_{17\text{O}}(\text{inner})$.

^cNA: not available.

found to be “end-on”, as illustrated in Fig. 1a. Are “side-on” structures also minima? Calculations show that structures of this type represent transition states (TS) connecting equivalent end-on structures.²³ The energies of these TS structures, relative to their corresponding ground-state end-on radicals, are given in Table 2. Two views of a representative TS structure are shown in Figs. 1b and 1c.

The relative energies in Table 2 reveal a nonmonotonic decrease in the barrier to interconversion between equivalent end-on structures, through the side-on TS structure, with increasing atomic mass of the group-14 atom. Using the barrier heights associated with $\text{Me}_3\text{COO}^\bullet$,^{25–28} $\text{Me}_3\text{SiOO}^\bullet$, and $\text{Me}_3\text{GeOO}^\bullet$, together with conventional transition state theory gives rate constants at “EPR” temperatures, viz., 200 K, for interconversion between end-on structures that are too small for interconversion to be observed on the EPR time scale. However, the calculated rate constants associated with interconversion of $\text{Me}_3\text{SnOO}^\bullet$ and $\text{Me}_3\text{PbOO}^\bullet$ are very large, viz., $>10^7 \text{ s}^{-1}$, which lends support to the mechanism implied by reaction [4]. We note that our calculations indicate that the energy required to dissociate O_2 from the Me_3Sn moiety is ~ 33 kcal/mol, indicating that the interconversion is a concerted process. In contrast, the computed energy required to dissociate O_2 from $\text{Me}_3\text{COO}^\bullet$ is ~ 31.4 kcal/mol, indicating that the concerted process will never compete with dissociation.

To provide additional support for the interconversion via the reaction in reaction [4], we sought to calculate the $a_{17\text{O}}$ values of the group-14 trimethyl peroxy radicals. Our initial calculations were performed using “EPR-III” basis sets,²⁹ which are specifically designed to give reasonable hyperfine coupling constants. However, we found these basis sets to be inadequate for the systems investigated in the present work. Using $\text{Me}_3\text{COO}^\bullet$ as a single example, $a_{17\text{O}}$ values computed with EPR-III bases using a variety of computational methods were in very poor agreement with experiment, e.g., values (in G) obtained from the following methods for $a_{17\text{O}}$ (inner) and $a_{17\text{O}}$ (outer) were HF 23.6 and 48.3, BHandH³⁰LYP³¹ 19.3 and 28.5, B3¹⁷LYP³¹ 12.7 and 16.8, B3²LYP³¹ 8.6 and 10.9, B97¹³³ 13.3 and 20.0, HCTH407³⁴ 6.4 and 12.2, MP2 18.9 and 21.9, respectively; experiment 17.6 and 23.5, see Table 1. Similarly poor results were obtained for $\text{Me}_3\text{SiOO}^\bullet$. We therefore resorted to the use of diffusion augmented, correlation-consistent polarized core/valence triple-zeta polarization (aug-cc-CVpVTZ)³⁵ basis sets. Additional testing revealed

that various methods with the aug-cc-CVpVTZ bases produced $a_{17\text{O}}$ values that are in better agreement with experiment, compared to those obtained with the EPR-III bases, but were still not satisfactorily accurate. Once again using the example of $\text{Me}_3\text{COO}^\bullet$, we obtained the following $a_{17\text{O}}$ (inner) and $a_{17\text{O}}$ (outer) values (all in G): BHandHLYP 18.4 and 27.0, MP2 17.9 and 21.0, respectively. It was clear that it was necessary to perform the calculations at a higher level of electronic correlation. We chose to use the coupled-cluster approach with single and double electronic excitation (CCSD) with all electrons (core and valence) correlated. The large size of the basis set and extent of correlation required that we use a local dense basis set (LDBS) approach,³⁶ in which we apply the aug-cc-CVpTZ basis set to the O atoms, and the remaining atoms were treated with smaller basis sets and (or) effective core potentials.^{21,22} Additional tests showed that $a_{17\text{O}}$ values obtained using the LDBS approach described above are within $\sim 0.5\%$ of those obtained using balanced basis sets (i.e., aug-cc-CVpTZ basis sets on all atoms).

Table 2 shows the $a_{17\text{O}}$ values obtained using the CCSD/LDBS approach described above. The values for $\text{Me}_3\text{COO}^\bullet$, $\text{Me}_3\text{SiOO}^\bullet$, and $\text{Me}_3\text{GeOO}^\bullet$ are within $\sim 8.4\%$ of the measured values presented in Table 1, an agreement that can be considered reasonable. For these three peroxy radicals, the calculated ratio of $a_{17\text{O}}$ (inner)/ $a_{17\text{O}}$ (outer) show excellent agreement with the experimentally determined ratios, and provide us with considerable confidence in the results of the calculations.

For $\text{Me}_3\text{SnOO}^\bullet$, theory predicts a large difference in inner (15.7 G) and outer (23.1 G) $a_{17\text{O}}$ values with a ratio of 1.49, whereas EPR measurements on ^{17}O -labelled (*n*-Bu)₃SnOO[•] indicate that both oxygen atoms are magnetically equivalent (25 G). Clearly, the equivalent measured $a_{17\text{O}}$ values result because of the low (calculated) barrier to interconversion between end-on structures. Calculations show similar results and would be observed for analogous lead peroxy radicals.

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- (15) Like alkylperoxy radicals, the stannylperoxy radicals decay with second-order kinetics. Values of $\log(A)$ and E_a for the reactions of $n\text{-Bu}_3\text{SnOO}^\bullet$ with 2,6-di-*tert*-butyl-4-methylphenol and Co(II) acetylacetonate are 7.5 and 7 $\text{(mol/L)}^{-1} \text{ s}^{-1}$ and 12 and 11.5 kcal/mol, respectively, while the corresponding values for $\text{Me}_3\text{COO}^\bullet$ are 4.6 and 0.8 $\text{(mol/L)}^{-1} \text{ s}^{-1}$ and 8.9 and 4.7 kcal/mol, respectively.¹¹
- (16) Structures were optimized at the B3¹⁷P86¹⁸ level of theory using 6-311+G(2d,2p) basis sets for C, H, O, Si, and Ge atoms. This approach has been shown to predict fairly accurate bond dissociation enthalpies in a broad range of compounds.¹⁹ Small-core, averaged relativistic effective potentials (AREPs) and accompanying (uncontracted) basis sets were used for the Sn²⁰ and Pb²¹ atoms. All calculations used the Gaussian 03 program package.²²
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- (23) All "side-on" structures were found to have a single imaginary vibration frequency. Displacement along this vibration mode generates structures that have "end-on" character.
- (24) The general trend in ΔE as a function of group-14 atomic mass was verified by performing QCISD(T) single-point energy calculations.
- (25) At the suggestion of a reviewer, we computed¹⁶ the zero-point corrected barrier associated with the interconversion of the phenylperoxy radical ($\text{C}_6\text{H}_5\text{OO}^\bullet$). As in the case of the 1,1-diphenylethoxy radical^{26,27} and triphenylmethoxy radical,²⁸ the phenylperoxy radical is predicted to have a stable spiro-type intermediate that is 20.4 kcal/mol higher in energy than the open form of the radical. The barrier to the formation of the intermediate is predicted to be 26.9 kcal/mol.
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