A computational study of the fluctional behaviour of group 14 substituted *ortho*-semiquinone radicals

K.U. Ingold and Gino A. DiLabio

Abstract: The dynamics of the 1,4-migration of some *O*-substituted 3,5-di-*tert*-butyl-*ortho*-semiquinone radicals have been calculated by density-functional theory (DFT). There is very good agreement in the rate constant and Arrhenius parameters between these calculations and experimental values for migration of H, D, and the Me_3Si group. For the Me_3Sn group, the calculations indicate an incredibly fast migration ($k^{293K} = 2.0 \times 10^{12}$ s^{-1}), a result that is consistent with experimental data ($k^{293K} > 10^9$ s^{-1}). Other *O*-substituents examined by DFT and compared with experimental data were H_3C and Me_2ClSn.

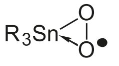
Key words: semiquinone radicals, group migration, group-coupled electron transfer, kinetics, density functional theory.

Résumé : Faisant appel à la théorie de la fonctionnelle de la densité (TFD), on a calculé la dynamique de la migration-1,4 de quelques radicaux 3,5-di-*tert*-butyl-*ortho*-semiquinones *O*-substituées. Il existe un très bon accord entre les constantes de vitesse et les paramètres d'Arrhenius calculées et les valeurs expérimentales pour la migration de H, D et du groupe Me_3Si. Pour le groupe Me_3Sn, les calculs prédisent une vitesse de migration incroyablement rapide ($k^{293K} = 2{,}0 \times 10^{12}$ s^{-1}), une valeur qui est en accord avec les données expérimentales ($k^{293K} > 10^9$ s^{-1}). Les autres *O*-substituants examinés par la TFD et comparés avec des données expérimentales sont le H_3C et Me_2ClSn.

Mots-clés : radicaux semiquinones, migration de groupe, transfert d'électron couplé à un groupe, cinétique, théorie de la fonctionnelle de la densité.

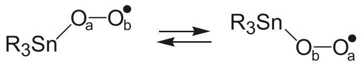
[Traduit par la Rédaction]

An anomaly in the electron paramagnetic resonance (EPR) spectra of tri-organo group 14 peroxyl radicals, $R_3XOO^\bullet$, recently drew our attention.[1] Briefly, the *g*-values for this family of radicals are rather similar (increasing from 2.015 for X = C, through 2.024 for X = Sn, to 2.034 for X = Pb), which implies that they all have rather similar structures. However, their ^{17}O hyperfine splittings (hfs) appeared inconsistent with similar structures. For X = C, Si, and Ge, the two oxygen atoms are magnetically inequivalent, with the outer ^{17}O hfs being larger than the inner ^{17}O hfs (outer/inner ^{17}O hfs ratios 1.33 (C), 1.74 (Si), 1.67 (Ge)), which implies an $R_3X{-}O{-}O^\bullet$ structure for these peroxyls. However, for X = Sn the two oxygen atoms had been reported[2] to be magnetically equivalent.[3] This led to the suggestion that trialkyltin peroxyl radicals have "a penta-coordinate, 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, structure ***A***.[2] Since this appeared unlikely in view of the similarities in the *g*-values of the group 14 peroxyls, we hypothesized that $R_3SnOO^\bullet$ radicals had a similar structure, with the magnetically equivalent oxygen atoms arising from a fast (on the EPR time scale, i.e., > ~10^7 s^{-1}) 1,2-shift of the R_3Sn group, reaction 1. Density-functional theory (DFT) calculations supported this hypothesis, giving inequivalent oxygen atoms (outer/inner ^{17}O hfs ratio = 1.47 (Sn)), with $k_1 = 5 \times 10^8$ s^{-1} at the experimental temperature of ~200 K.[1]



A

[1]



Since the computed rate constant for reaction 1 could not be checked against experimental data, we searched for analogous reactions for which such data were available and settled on the 1,4-shift of some trisubstituted group 14 moieties between the two oxygen atoms in 3,6-di-*tert*-butyl-*ortho*-semiquinone radicals, reaction 2.[4]

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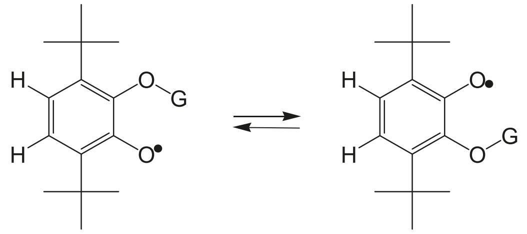
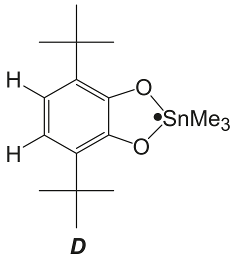


B ***C***

In these radicals, the two *tert*-butyl substituents serve three practical functions: (1) they simplify the EPR spectra to splittings only by the two aromatic hydrogen atoms (and **G**), (2) they ensure that the group, **G**, points towards the O$^\bullet$ moiety (rather than away), and (3) they increase the persistence of the radicals, making the signals more intense and easier to measure than would be the case for the unsubstituted radicals. These two substituents probably cause some acceleration in the rates of reaction 2 relative to those of similar reactions in *ortho*-semiquinones that lack these bulky groups.

For **G** = Me$_3$Sn, reaction 2 has been reported to be so rapid that its rate constant could not be measured by EPR line-broadening effects even at 183 K, the lowest temperature employed[5] (a lower limit of 10^9 s^{-1} for this rate constant was later estimated at 293 K[6]). The possibility that the absence of line broadening effects with **G** = Me$_3$Sn was due to the formation of a symmetric bridged structure, ***D***, was considered improbable for two very good reasons[6]: (1) ***D*** would have considerable spin density on the tin and cause very significant hfs by the ^{117}Sn and ^{119}Sn isotopes, but these hfs were small (12.8 and 13.3 G, respectively)[6]; and (2) for **G** = Me$_3$Sn, the two ring protons give a 3.6 G triplet, indicating that they are magnetically equivalent. The 3.6 G hfs for this triplet was essentially identical to the hfs of the two ring protons in radicals with **G** = Me$_2$SnCl[5] and **G** = Me$_3$Si[6] at temperatures where these groups were migrating rapidly (on the EPR time scale) between the two oxygen atoms, namely 3.6 G[5] (3.7 G)[7] and ~3.9 G[6], respectively. For these last two **G**, the two aromatic hydrogen atoms become magnetically inequivalent at low temperatures, transforming into doublets of doublets: 5.2 and 2.6 G[5] (5.0 and 2.5 G)[7] for **G** = Me$_2$SnCl, and 8.4 and 0.62 G[6] for **G** = Me$_3$Si. For the tin-centered **G**, the earlier observations and conclusions have been confirmed by Davies and Hawari,[7] who greatly expanded the number of such tin-containing semiquinone radicals and who also examined the migration dynamics for **G** = Me$_2$PbCl.[8,9]



D

Values of k_2 and the Arrhenius parameters for reaction 2 have been estimated from EPR line-broadening effects and reported for **G** = Me$_2$SnCl[5,7] and Me$_3$Si[6] (see Table 1). The 1,4-shift for **G** = H$_3$C was too slow to measure.[6] It was concluded that the coordinative unsaturation of tin and silicon facilitates their coordination with a lone pair on the phenoxyl oxygen atom,[10,11] which lowers the barrier for group transfer.[6] It was suggested that Me$_2$SnCl migrates more slowly than Me$_3$Sn because the outer electrons of the chlorine interact with the tin d orbitals, reducing the coordinative unsaturation of the tin atom.[6] It is the dynamics of reaction 2 with **G** = Me$_2$SnCl and **G** = Me$_3$Si that we hoped to match by DFT computations to further support our hypothesis[1] that an R$_3$SnOO$^\bullet$ radical has 2 magnetically equivalent oxygen atoms[2] because of a rapid 1,2-shift of the R$_3$Sn group.

Since line-broadening effects have also been employed to determine the values of k_2 and the Arrhenius parameters for **G** = H[12] and **G** = D[12] (see Table 1), our calculations were extended to cover these two *ortho*-semiquinones.[18–21] Before we describe our computational results, it is important to recognize that there are "oddities" in the reported Arrhenius parameters listed in Table 1 that probably arise from the quite limited temperature range available in EPR line-broadening kinetic measurements. That is, chemical thermodynamics[22] teaches us to "expect" an Arrhenius pre-exponential factor (A) for reaction 2 with **G** = H and **G** = D of ~$10^{13–14}$ s^{-1}. The same value, or possibly a slightly lower value (~$10^{12.5–13.5}$ s^{-1}), should be expected for **G** = Me$_2$SnCl and **G** = Me$_3$Si, implying that the experimental values for the former group[5–7] may have been slightly overestimated. The experimental pre-exponential factors for **G** = H and **G** = D are more than one log unit lower than "expected". This suggests that quantum mechanical tunneling may be significant for both H and D transfers at the temperatures investigated, an idea that is supported by the slightly higher value of $\log A_2$ for **G** = D than for **G** = H (see Table 1).

It is also important to keep in mind that theory is not yet capable of predicting Arrhenius parameters with high fidelity to experimental values. Although significant improvements in theoretical methods continue unabated, the exponential sensitivity of kinetic parameters to computed energies makes this a particularly challenging task for computational chemistry. For anything but the smallest systems, a better than order-of-magnitude accuracy from theory cannot (yet) be expected.

We begin with the intramolecular H and D transfer processes. (Analogous intramolecular transfers in diamagnetic systems have been studied by microwave and infrared spectroscopy.[23]) Our calculated values for log(A/s^{-1}) for ***B***→***C*** with **G** = H and **G** = D are about 12.6 and are therefore in reasonable accordance with our "thermochemical expectations", being roughly one log unit larger than the reported values. Computed rate constants, with tunneling corrections obtained using an Eckart approach,[24] are in excellent agreement with experimental values. The computed kinetic isotope effect (k_H/k_D) of 10 with tunneling (4.3 without tunneling) is in very good agreement with the experimental value of 10.7.

In addition to quantum mechanical tunneling, the mechanism for the hydrogen and deuterium exchange must also involve intramolecular proton-coupled electron transfer (PCET).[25] Figure 1*a* shows a side view of ***B*** (**G** = H) showing relevant orbitals. The minimum energy structure of ***B*** has an intramolecular hydrogen bond between the OH group

Table 1. Experimental and calculated[13–17] rate constants for reaction 2 at 293 K and Arrhenius parameters (E_a in kcal/mol).

	Experimental			Calculated		
G	k_2 (s^{-1})	log(A/s^{-1})	E_a	k_2 (s^{-1})	log(A/s^{-1})	E_a
H[a,b]	3.2×10^{9}	11.5	2.9	2.0×10^{9}[c]	12.7	2.0[d]
D[a,e]	0.3×10^{9}	11.8	4.5	0.2×10^{9}[f]	12.6	2.5[g]
H_3C[h,i]	$<10^{4}$			1.0×10^{-16}	13.1	39.6
Me_3Si[h,j]	2.5×10^{6}	13.2	9.3	5.9×10^{5}	12.4	9.0
Me_2SnCl[h,k]	2.5×10^{6}	14.4	10.7	6.9×10^{7}	12.8	5.3
Me_2SnCl[l]	2.2×10^{6}	14.1	10.4	6.9×10^{7}	12.8	5.3
Me_3Sn[h,m]	$>10^{9}$			2.0×10^{12}	12.8	0.7

[a] Experimental data in heptane, ref. 17.

[b] 273–393 K.

[c] Without tunneling: 2.3×10^{8} s^{-1}.

[d] Without tunneling: 5.8 kcal/mol.

[e] 293–393 K.

[f] Without tunneling: 5.3×10^{7} s^{-1}.

[g] Without tunneling: 6.6 kcal/mol.

[h] Experimental data in toluene, ref. 6.

[i] 263–473 K.

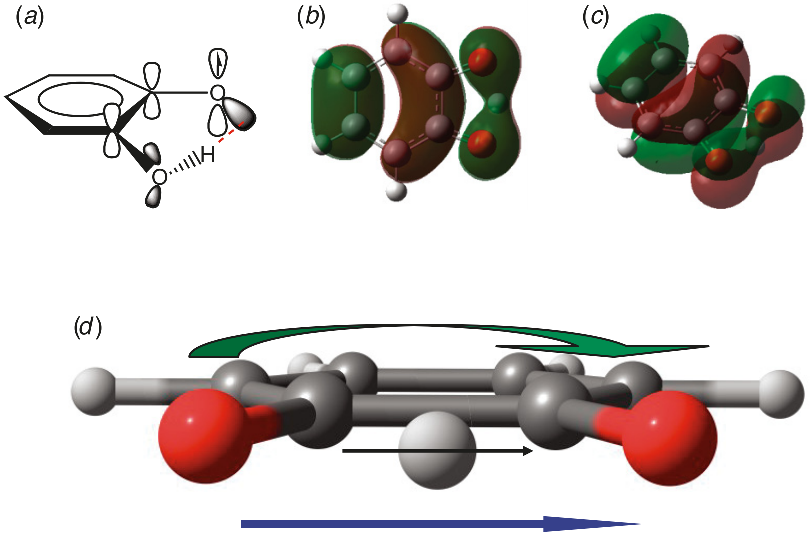
[j] 273–333 K.

[k] 163–223 K.

[l] Experimental data in xylene, ref. 7. 208–404 K. This reference also includes the following kinetic data: **G**; $k_2/10^{6}$ s^{-1}; log(A/s^{-1}); E_a (kcal/mol): Bu_2SnCl, 0.47, 13.6, 10.6; Ph_2SnCl, 0.49, 14.4, 11.7; $(MeCO_2)_3Sn$, 25, 14.1, 8.9; Me_2PbCl, 4.6, 11.7, 6.7.

[m] 183–403 K.

Fig. 1. (*a*) Simplified illustration of the orbitals of the minimum energy structure of ***B*** (di-*tert*-butyl groups omitted). The lone-pair orbitals are shaded gray and singly occupied orbitals are white. The intramolecular hydrogen bond is indicated by the red dashed line, which also indicates the path transited by the proton during the exchange reaction. (*b*) Top-down and (*c*) tilted views of the hydrogen exchange transition state (TS) of an unsubstituted semiquinone with its singly occupied molecular orbital (SOMO). The SOMO is π-type and delocalized across the O···H···O centres as well as through the ring. The colours of the orbital represent its relative phases. (*d*) Side view of a ball-and-stick model of the hydrogen exchange TS of semiquinone. The black arrow indicates the direction of transfer of a proton, the path for which lies in the plane of the ring. The blue arrow shows one possible route of the transferring electron, along a path that is parallel to the path of the proton but out of the plane of the ring. The green, curved arrow shows a second route for the electron, along a path through the ring orbitals and also out of the plane of the ring.



and the lone pair of electrons on the (formal) $O^{\bullet}$ centre. This hydrogen bond lies in the plane of the ring. Hydrogen exchange cannot occur easily via a hydrogen atom transfer (i.e., a proton with its electron) because the lone pair on the "receiving" oxygen atom cannot accept an extra electron. Instead, exchange occurs through a transition state involving a proton transfer from the OH group to the $O^{\bullet}$ across the hydrogen bond. Concurrent with proton transfer, an electron

Fig. 2. Transition state structures for reaction 2 with (*a*) **G** = CH_3, R(H_3C–O) = 2.09 Å, (*b*) **G** = Me_3Si, R(Me_3Si–O) = 1.98 Å, and (*c*) **G** = Me_2SnCl, R(Me_2ClSn–O) = 2.24 Å.

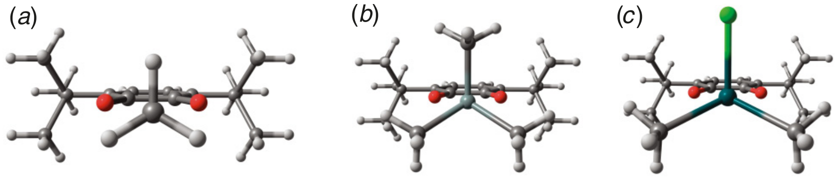
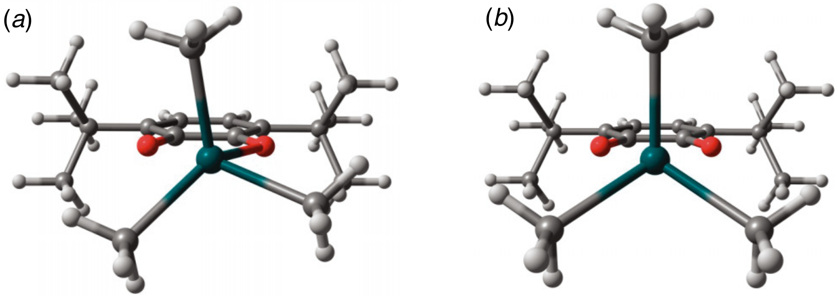


Fig. 3. (*a*) The minimum energy and (*b*) transition state (R(Me_3Sn–O) = 2.27 Å) structures for ***B*** with **G** = Me_3Sn.



is transferred via the π-type bond involving the O···H···O atoms, which is perpendicular to the ring. This is clearly seen in the singly occupied molecular orbital (SOMO) of the hydrogen exchange transition state (TS) illustrated in Figs. 1*b* and 1*c*. The conjugative delocalization of the O orbitals into the ring provides a second "route" for the electron to take in the PCET process and this is also demonstrated by the SOMO shown in Figs. 1*b* and 1*c*. The path taken by the proton and possible paths used for transferring the accompanying electron are illustrated in Fig. 1*d*. Theory has previously implicated multiple paths for transferring the electron in PCET processes that involve the following bimolecular identity reactions: oxime + iminoxyl,[26] toluene + benzyl, and phenol + phenoxyl.[27]

In principle, processes similar to PCET as described for **G** = H and D in reaction 2 should also occur for other **G**, provided that the central atom in **G** is able to undergo facile valence shell expansion. If this is the case, we may generalize the PCET mechanism to "GCET", or group-coupled electron transfer. It is clear that for **G** = CH_3, GCET is not able to occur. This is simply because pentavalent carbon is energetically highly disfavoured (i.e., there is no energetically low-lying empty orbital on CH_3). The calculations indicate that the O–CH_3 bond would need to lengthen by 0.65 Å to reach the TS structure. Therefore, the barrier to group transfer is very high and results in a very low rate constant. A picture of the TS associated with reaction 2 for **G** = CH_3 is shown in Fig. 2*a*.

Additional calculations indicate that the barrier associated with hydrogen atom transfer from **G** = CH_3 to the (formal) O• is much more likely than group transfer. The activation barrier for this endothermic process is predicted by theory to be about 25.5 kcal/mol.

The calculated kinetic parameters with **G** = Me_3Si are in very gratifying agreement with experimental values. To reach the TS (see Fig. 2*b*), the O–$SiMe_3$ bond must lengthen by approximately 0.25 Å. This results in a much lower barrier height and larger rate constant for transfer with **G** = Me_3Si than for transfer with **G** = CH_3. A detailed examination of the reaction coordinate reveals that the TS can be reached by rotation of the $SiMe_3$ group about the Si–O bond. The resultant steric repulsion between the methyl groups on **G** and the neighbouring *tert*-butyl substituent is then sufficiently high that the Me_3Si–O bond is lengthened to the TS value.

For **G** = Me_2SnCl, the predictions made by theory are in somewhat poorer agreement with experimental data. However, the calculated log(A/s^{-1}) is in line with thermochemical expectations, vide supra. Calculations predict a rather small activation energy of 5.3 kcal/mol, which contributes to the large rate constant. The minimum energy structure of ***B*** with **G** = Me_2SnCl has the chlorine atom pointed toward the adjacent *tert*-butyl group. To reach the TS (Fig. 2*c*), the Me_2(Cl)Sn group must rotate by about 90° while the Me_2(Cl)Sn–O bond must lengthen by about 0.09 Å.

The case of **G** = Me_3Sn is particularly interesting. The calculations indicate that ***B*** (**G** = Me_3Sn) has an asymmetric energy minimum wherein there is no Me–Sn bond exactly perpendicular to the plane of the aromatic ring (Fig. 3*a*). This minimum energy structure produces all positive vibration frequencies, verifying that it is indeed a minimum on the potential energy surface. Similarly, the TS structure, shown in Fig. 3*b*, was verified as such with the calculations giving one imaginary frequency associated with group transfer (reaction 2). The magnitude of the imaginary frequency is only 37.8 cm^{-1}, indicating that reaching the TS requires very little energy. In fact, the Me_3Sn–O bond length in the minimum energy structure only needs to be lengthened by about 0.03 Å to reach its TS length. Vibrational analyses and potential energy surface scans show that the TS can be reached from the minimum energy structure by a slight rotation of the Me_3Sn group about the Sn–O bond, as is evident upon examination of Fig. 3. Inclusion of thermal corrections (293 K) to the electronic energies results in a predicted E_a of 0.70 kcal/mol. This calculated E_a value is too small to be reliable but it does imply that transfer of the **G** = Me_3Sn group is extremely facile, in accordance with the experimental observations.[28,29] Moreover, theory indicates that the minimum energy structure should be represented by ***B*** and not by ***D***, which is also in accordance with the conclusions reached by Prokof'ev et al.[6] on the basis of EPR spectral evidence, vide supra.

The present calculations are in sufficiently good agreement with experimental data that it is fairly safe to conclude that we have been employing appropriate methodology to study these kinds of dynamic processes and they therefore provide additional support for our earlier conclusion[1] that the R_3Sn group in $R_3SnOO^\bullet$ radicals undergoes such a fast 1,2-shift that the two oxygen atoms are magnetically equivalent on the EPR time scale.

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