

Studies of organotin(IV)-orthoquinone systems¹

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Abstract

The primary process in the reaction of hexaphenylditin with various substituted orthoquinones (Q) is shown to involve attack by the quinone at a phenyl ligand. The intermediate thus formed decomposes to yield $\text{Ph}_3\text{Sn}(\text{SQ}^-)$, where $\text{S}(\text{Q}^-)$ is the corresponding semiquinonate. Rearrangement of these species in solution gives rise to biradicals, while intramolecular electron transfer may lead to the formation and precipitation of $\text{Ph}_2\text{Sn}(\text{CAT})$, where CAT^{2-} is the corresponding substituted catecholate. The identification of these processes depends in part on electron paramagnetic resonance spectroscopy. The reaction of Ph_3SnCl or Ph_2SnCl_2 with $\text{Na}(\text{TBSQ}^-)$ ($\text{TBSQ}^- = 3,5\text{-di-}i\text{-tert-butyl-ortho-benzo-semiquinonate}$) results in the formation of $\text{Ph}_2\text{Sn}(\text{TBSQ}^-)$, which can undergo redistribution and intramolecular electron transfer, so that the solution chemistry of these latter systems is similar to that of the products of the $\text{Sn}_2\text{Ph}_6 + \text{Q}$ reaction. © 1998 Elsevier Science S.A.

Keywords: Orthoquinones; Hexaphenylditin; Intramolecular electron transfer reactions; Ligand redistribution

1. Introduction

In a number of recent investigations, we have demonstrated that the oxidation of Main Group elements, or compounds of those elements in low oxidation states, by orthoquinones involves a sequence of one electron transfer processes [1]. Preparative, spectroscopic and crystallographic results all support this conclusion [2], which is at odds with earlier assumptions about the nature of the redox reactions of such molecules. It has also been shown that nucleophilic attack by a substituted *o*-quinone can be an important primary step in these processes.³ With some elements, the oxidation of organic derivatives has also been studied, and in the particular case of diphenyl ditelluride, the presence of semiquinone species in the reaction mixture confirmed the importance of one-electron transfer [3]. When the oxidant was tetrahalogeno-*o*-benzo-

quinone ($\text{X}_4\text{C}_6\text{O}_2\text{-}o$; X = Cl, Br), the final product was the unusual organotellurium(IV) catecholate $[(\text{X}_4\text{C}_6\text{O}_2)\text{TeC}_6\text{H}_5]_2\text{O}$ [4].

The present work began as an extension of these investigations to the formally tin(III) compound hexaphenylditin. The subsequent inclusion of tetraphenylditin, and of the species formed in the metathetical reactions of semiquinonate salts and organotin(IV) halides, reflects a common solution chemistry in these systems, involving both ligand redistribution processes and intramolecular electron transfer reactions.

2. Experimental section

2.1. General

Hexaphenylditin, tetraphenylditin, organotin halides and substituted orthoquinones were used as supplied (Aldrich). Solvents were dried and carefully degassed before use. All experimental work was carried out in an atmosphere of dry nitrogen, using conventional vacuum line techniques.

Infrared spectrum of samples in KBr discs were recorded on a Nicolet 3-DX instrument. Electron paramagnetic resonance (EPR) spectra were run on a Bruker ESP-300E spectrometer, using techniques described

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¹ Dedicated to Professor Ken Wade on the occasion of his 65th Birthday in recognition of his outstanding contributions to Main Group Chemistry.

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³ D.L. Boucher, M.A. Brown, B.R. McGarvey, D.O. Tuck, unpublished results.

previously [1]. Mass spectroscopy involved heated samples in a Shimadzu 14-B spectrometer operating in the E.I. mode, with Sun Sparc software. Elemental analysis was by Canadian Microanalytical Services. ^{119}Sn NMR spectra were recorded on a Bruker AC 200 instrument operating at 74 MHz; chemical shifts are relative to $\text{Sn}(\text{CH}_3)_4 = 0$.

In this paper, as elsewhere, we use the symbolism $\text{Q} \leftrightarrow \text{SQ}^{\cdot-} \leftrightarrow \text{CAT}^{2-}$ to identify the *o*-quinone \leftrightarrow semiquinonate \leftrightarrow catechol sequence of ligands, with appropriate prefixes.

2.2. Hexaphenylditin + 3,5-di-*tert*-butyl-1,2-benzoquinone (TBQ)

A solution of Sn_2Ph_6 (0.31 g, 0.45 mmol) in *n*-hexane (20 ml) was heated with a suspension of TBQ (0.1 g, 0.45 mmol) in the same solvent (20 ml). The reaction mixture immediately became brown–black and a colourless solid precipitated. This was collected, washed and dried, and identified as tetraphenyltin (melting pt. 223–229°C; cf. lit. value 228–230°C. ^{119}Sn NMR (CHCl_3) $\delta = -137$ ppm; cf. lit. value [5] -137 ± 2 ppm ($\text{C}_2\text{H}_3\text{Cl}_3$)). Identical phenomena were observed when TBQ was dissolved in dichloromethane (10 ml), and when the TBQ: Sn_2Ph_6 ratio was increased to 2:1 or 4:1. On cooling, the reaction mixture deposited additional quantities of Ph_4Sn ; further cooling and evaporation of solvent gave a dark grey solid, identified as $\text{Ph}_3\text{Sn}(\text{TBSQ}^{\cdot-})$. Anal. Calcd. for $\text{C}_{32}\text{H}_{35}\text{O}_2\text{Sn}$: C 67.4, H 6.19. Found: C 67.6, H 5.93.

After the removal of Ph_4Sn , the EPR of the filtrate (Fig. 1a) established the presence of a free radical species ($S = 1/2$), identified subsequently as $\text{Ph}_3\text{Sn}(\text{TBSQ}^{\cdot-})$ (see Section 3). The *g*-value and hyperfine coupling constants for this and related species are presented in Table 1; the coupling constants were derived by simulating the experimental spectra, using the program Simfonia. In addition, low temperature spectra identified the presence of three biradical species (Fig. 1b). With increasing TBQ: Sn_2Ph_6 ratios, the biradical spectrum increased in intensity relative to the $S = 1/2$ signal, but was otherwise unchanged. The *D*-values derived from this spectrum are also given in Table 1.

In a subsequent experiment, the filtrate was irradiated with UV (480-W lamp, 1 h). The concentration of the presumed Sn–Sn biradicals (see Section 2.3) appeared

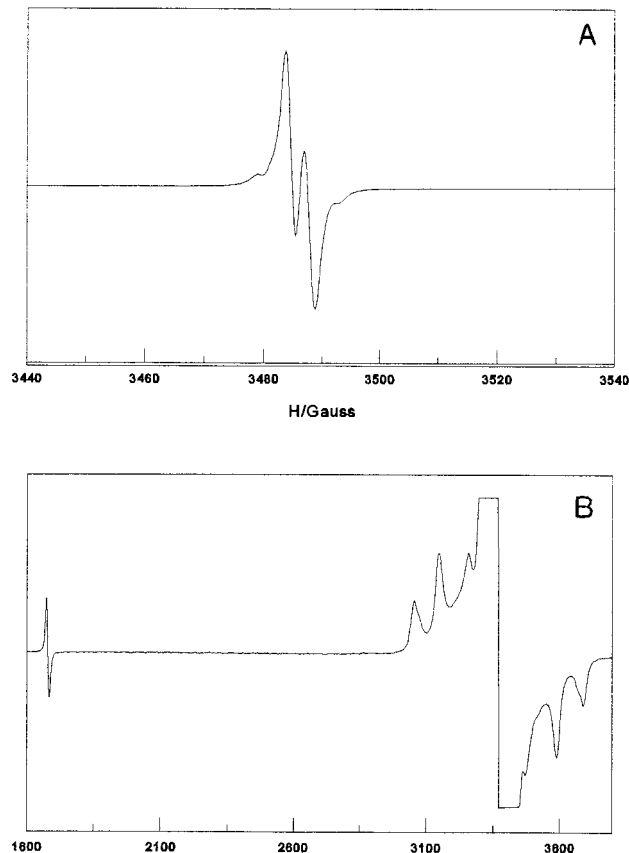


Fig. 1. EPR spectra of solution, in *n*-hexane, for the reaction of Sn_2Ph_6 with 3,5-di-*tert*-butyl-benzoquinone. (A) Dilute solution at room temperature; (B) Frozen solution spectrum (77 K) showing half field transition and evidence of three biradical species ($D = 251, 236, \text{ and } 172 \times 10^{-4} \text{ cm}^{-1}$).

to increase relative to the $\text{Ph}_2\text{Sn}(\text{TBSQ}^{\cdot-})_2$ species. The *g*-value for the $S = 1/2$ signal changed only slightly after irradiation, with $g = 1.992$ at 23°C, and 2.0061 at 77 K.

2.3. Hexaphenylditin + 9,10-phenanthrenequinone (PQ)

When a solution of PQ (1.00 g, 4.80 mmol) and Sn_2Ph_6 (2.8 g, 4.0 mmol) in dichloromethane (20 ml) was refluxed for 1 h, the product was a brown solution from which a brown solid precipitated on the addition of *n*-hexane, followed by cooling. This solid was identi-

Table 1
EPR parameters (g , a_{Sn} , a_{H}) for $\text{Ph}_3\text{Sn}(\text{SQ})$ species, and D for related biradical species

Q	g	a_{Sn} (G)	a_{H} (G) ^a	D ($\text{cm}^{-1} \times 10^{-4}$)
TBQ ^b	2.000389	10.2	3.03, 0.46, 0.36	251, 236, 172
PQ	2.0037	11.51	1.93, 0.46	104, 63
NQ ^a	2.00375	8.50	5.3, 1.4(2), 1.1	not detected
Br_4Q	2.0348	11.2		147
$\text{Ph}_3\text{SnCl} + \text{Na}(\text{TBSQ})$	2.00393	10.4	2.95, 0.33(9), 0.5	299, 278, 204
$\text{Ph}_2\text{SnCl}_2 + \text{Na}(\text{TBSQ})$	2.00389	10.2	3.03, 0.46, 0.36(9)	

fied as $\text{Ph}_3\text{Sn}(\text{PSQ}^\cdot)$. Anal. Calcd. for $\text{C}_{32}\text{H}_{23}\text{O}_2\text{Sn}$: C 68.9, H 4.15. Found: C 68.9, H 4.34. Yield 1.20 g. Predominant peaks in the mass spectrum at $m/e = 558$, M^+ , 351 $\text{Sn}(\text{C}_6\text{H}_5)_3^+$, 274 $\text{Sn}(\text{C}_6\text{H}_5)_2^+$, 197 SnC_6H_5^+ and 120 Sn^+ , are in keeping with this formulation.

The filtrate was EPR-active, with strong mono- and biradical signals. Slow evaporation of this solution gave small quantities of crystals identified crystallographically and analytically [6] as $\text{Ph}_2\text{Sn}(\text{PSQ}^\cdot)_2$; the D -values for this compound have been reported elsewhere as 63 and $104 \times 10^{-4} \text{ cm}^{-1}$. In addition to this biradical, the solution also yielded the compound $\text{Ph}_2\text{Sn}(\text{PCAT})$. Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{O}_2\text{Sn}$: C 64.9, H 3.77. Found: C 65.3, H 4.13. Mass spectral peaks were detected at $m/e = 493$, M^+ . When the mole ratio $\text{PQ}:\text{Sn}_2\text{Ph}_6$ in the initial reaction mixture was 2:1, this diolate was the only product identified.

2.4. Hexaphenylditin and 1,2-naphthoquinone (NQ)

Stirred solutions of NQ (0.32 g, 2.02 mmol) and Sn_2Ph_6 (0.70 g, 1 mmol) in dichloromethane (total volume 40 ml) were mixed, with the immediate precipitation of a black solid which was insoluble in all common organic solvents other than dimethylsulphoxide. This solid was collected, dried and characterized as $\text{Ph}_3\text{Sn}(\text{NSQ}^\cdot)$. Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{O}_2\text{Sn}$: C 66.2, H 4.17. Found: C 66.1, H 4.35. Prominent mass spectral ions were at 508 M^+ , 351 $\text{Sn}(\text{C}_6\text{H}_5)_3^+$, 274 $\text{Sn}(\text{C}_6\text{H}_5)_2^+$, 197 SnC_6H_5^+ , 120 Sn^+ . This solid was EPR active. The green filtrate from this reaction showed a well-resolved room temperature EPR spectrum, corresponding to $\text{Ph}_3\text{Sn}(\text{NSQ}^\cdot)$, with only a weak biradical component (Fig. 2). No sensible D -values could be derived from this system.

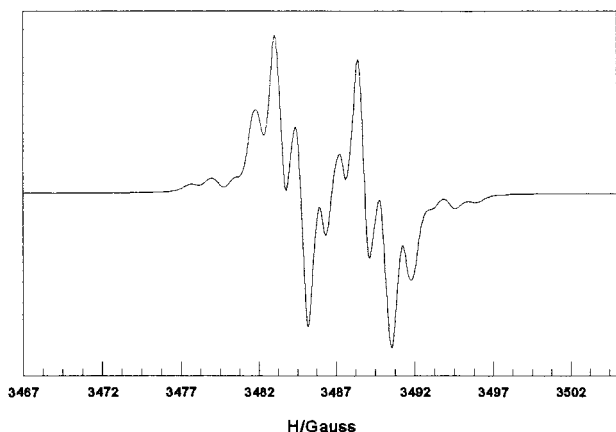


Fig. 2. EPR spectrum of a solution of $\text{Ph}_3\text{Sn}(\text{NSQ})$ in dichloromethane at room temperature ($\text{NSQ} = 1,2$ -naphthoquinone anion). Simulation gives $g = 2.00375$, $a_{\text{Sn}} = 8.50 \text{ G}$, $a_{\text{H}} = 5.3 \text{ G}(1)$, $1.4 \text{ G}(2)$, $1.1 \text{ G}(1)$.

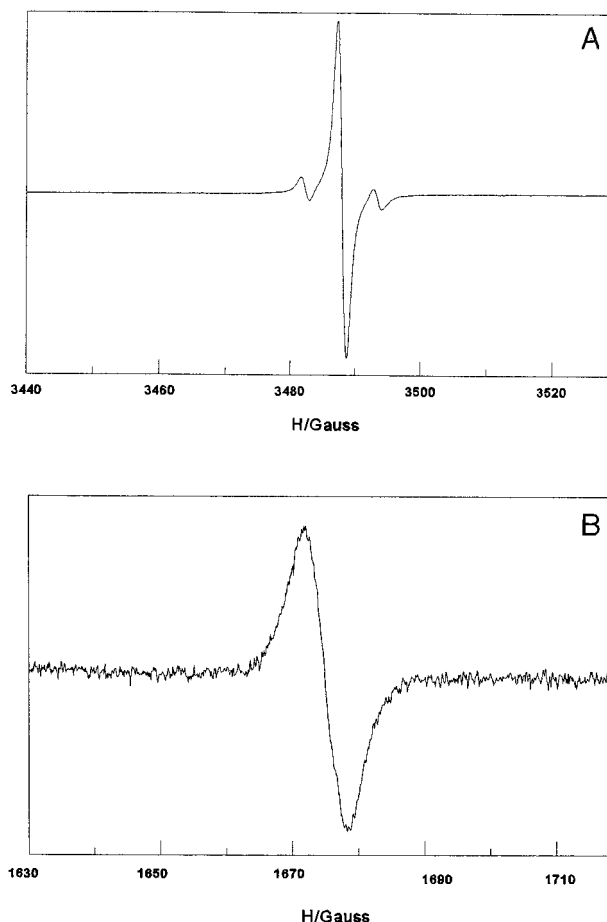


Fig. 3. EPR spectra of a dichloromethane solution from the reaction of Sn_2Ph_6 and tetrabromo-*o*-benzoquinone. (A) Dilute solution at room temperature. Simulation gives $g = 2.00348$, $a_{\text{Sn}} = 11.2 \text{ G}$; (B) Frozen solution spectrum (77 K) showing half field transition for a biradical species ($D = 147 \times 10^{-4} \text{ cm}^{-1}$).

2.5. Hexaphenylditin and tetrahalogeno-*o*-quinone (BrQ, ClQ)

A solution of Sn_2Ph_6 (1.40 g, 2 mmol) and BrQ (1.70 g, 4 mmol) in dichloromethane (20 ml) was refluxed for 5 h. The resultant deep brown solution was EPR active; biradical signals were also detected (Fig. 3a,b). Addition of *n*-hexane followed by cooling gave a red precipitate of $\text{Ph}_3\text{Sn}(\text{BrSQ}^\cdot)$. Anal. Calcd. for $\text{C}_{24}\text{H}_{15}\text{O}_2\text{Br}_4\text{Sn}$: C 37.3, H 1.95. Found: C 37.3, H 1.91. Mass spectral peaks at 774 M^+ , 620 $\{\text{M}-2(\text{C}_6\text{H}_5)\}^+$, 351, $\text{Sn}(\text{C}_6\text{H}_5)_3^+$, 274 $\text{Sn}(\text{C}_6\text{H}_5)_2^+$, 197 SnC_6H_5^+ , 120 Sn^+ , were in keeping with this formulation.

A similar procedure was used for the chloro analogue. When the quinone (1.23 g, 5 mmol) was refluxed in toluene or dichloromethane (50 ml) with hexaphenylditin (1.75 g, 2.5 mmol), the deep red solution which had a very strong EPR signal. The frozen solution showed an intense central transition with zero

field splitting, and an intense half field transition. The zero-field splitting indicated the presence of more than one biradical. Tetraphenyltin precipitated after some time, and was removed by filtration. The filtrate was evaporated to give a viscous red syrup which failed to crystallize or solidify under a variety of conditions; analysis (Found: C, 55.17; H, 5.21), suggested that this was a mixture of compounds, which could not be separated.

2.6. Tetraphenyltin and 3,5-di-*tert*-butyl-*o*-benzoquinone

A solution of TBQ (0.22 g, 1 mmol) in dichloromethane (10 ml) was added to a stirred solution of Ph_4Sn (0.21 g, 0.5 mmol) in the same solvent (10 ml). The mixture immediately became deep brown. The EPR spectrum of this mixture at room temperature was that of a single free radical species, essentially identical to the $S = 1/2$ region of the spectrum obtained from $\text{Sn}_2\text{Ph}_6 + \text{TBQ}$ (Table 1).

2.7. Diphenylmercury and 3,5-di-*tert*-butyl-*o*-quinone.

A solution containing equimolar quantities (ca. 2 mmol) of these substance in chloroform was refluxed for 1 d, but no evidence of a reaction was obtained, in that there was no perceptible change of colour, and no EPR activity was detected

2.8. Reaction of triphenyltin chloride with Na(TBSQ)

In this work, and that with diphenyltin dichloride, deep blue solutions of $\text{Na}(\text{TBSQ}^-)$ in *n*-hexane were prepared by the reaction of 3,5-di-*tert*-butyl-catechol with sodium hydride (cf. Ref. [1]).

A solution of $\text{Na}(\text{TBSQ}^-)$ (4.5 mmol) in *n*-hexane (20 ml), and a dichloromethane (10 ml) solution of triphenyltin chloride (1.7 g, 4.41 mmol), were stirred together at room temperature. The resultant green mixture deposited NaCl (0.24 g, 4.10 mmol, 93%). When the filtrate was cooled after the removal of this precipitate, a colourless diamagnetic solid was thrown down. Mass spectrometry and IR spectroscopy suggested that this was a mixture of Ph_4Sn and $\text{Ph}_2\text{Sn}(\text{TBC})$. The former was dissolved in acetone, leaving a residue of $\text{Ph}_2\text{Sn}(\text{TBC})$. Anal. Calcd. for $\text{C}_{26}\text{H}_{30}\text{O}_2\text{Sn}$: C 63.3, H 6.13. Found: C 63.5, H 6.16. Mass spectrum, $m/e = 494$ (M^+). Repeated attempts to recrystallize this substance from various solvents yielded only tetraphenyltin, leaving a solution which was strongly EPR active. The spectra (Fig. 4a,b) showed the presence of both mono- and diradical species (Table 1).

In a later experiment, the $\text{Na}(\text{TBSQ}^-)$: Ph_3SnCl mole ratio was 2:1, and again Ph_4Sn and $\text{Ph}_2\text{Sn}(\text{TBC})$ were the solid products identified when the above procedure

was followed. The EPR spectrum of the filtrate obtained after removal of these solids was that of a monoradical, but no evidence was obtained for the presence of diradicals.

2.9. Reaction of diphenyltin dichloride with Na(TBSQ)

The experimental procedures followed those for the Ph_3SnCl - $\text{Na}(\text{TBSQ}^-)$ system. With a 1:1 mole ratio of Ph_2SnCl_2 and $\text{Na}(\text{TBSQ}^-)$, the initial brown solution had a strong EPR spectrum (Fig. 5), which showed presence of diradicals through a very weak feature at half-field. It was not possible to derive any values for the D -parameter from these results. For the monoradical component, $g = 2.0043$ (RT) and 2.0031 (77 K). The only solids obtained from the reaction mixture were Ph_4Sn and $\text{Ph}_2\text{Sn}(\text{TBC})$.

With a mole ratio of 1:2, the EPR spectrum appeared to be that of a mixture of two mono-radical species,

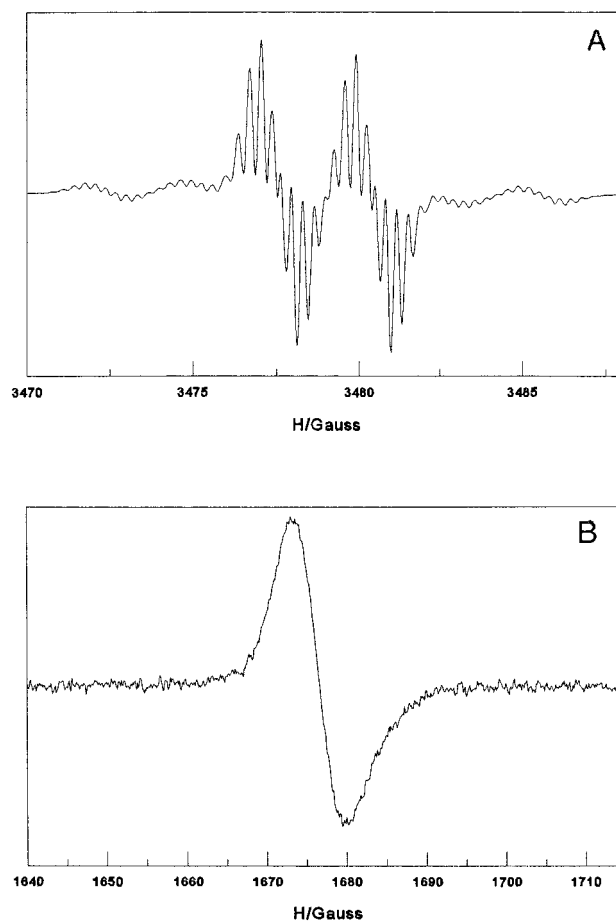


Fig. 4. EPR spectra of a *n*-hexane of products of the reaction of Ph_3SnCl with $\text{Na}(\text{TBSQ}^-)$ ($\text{TBSQ}^- = 3,5\text{-di-}i\text{-tert-butyl-}o\text{-benzosemiquinonate anion}$). (A) Dilute solution at room temperature. Simulation gives $g = 2.00393$, $a_{\text{Sn}} = 10.4$ G, $a_{\text{H}} = 2.87$ G(1), 0.33 G(9); (B) Frozen solution spectrum (77 K) showing half field transition for biradical species ($D = 299, 278, 204 \times 10^{-4} \text{ cm}^{-1}$).

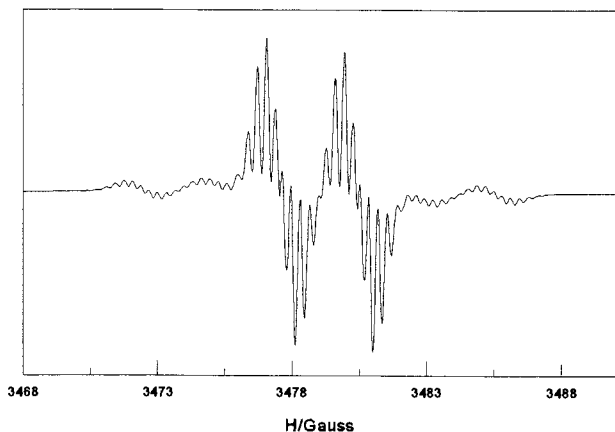


Fig. 5. EPR spectrum of *n*-hexane solution resulting from the reaction of Ph_2SnCl_2 and $\text{Na}(\text{TBSQ})$ at room temperature. Simulation gives $g = 2.00389$, $a_{\text{Sn}} = 10.2$ G, $a_{\text{H}} = 3.03$ G(1), 0.46 G(1), 0.36 G(9).

with no evidence for biradicals; $g \sim 2.0045$ (RT), 1.980 (77 K).

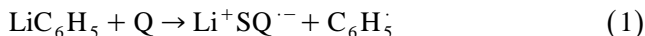
3. Results and discussion

3.1. Reaction of hexaphenylditin and *o*-quinones

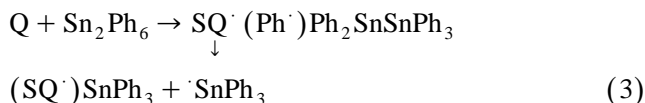
The behaviour of Sn–Sn bonded organotin compounds has been reviewed by Sawyer [7]. Especially relevant to the present work is the thermal stability of Sn_2Ph_6 , which was recovered in almost quantitative yield after 21 h in refluxing tetrahydrofuran (boiling pt. 66°C). The compound is unaffected by undiluted oxygen. Reaction with iodine yields Ph_3SnI quantitatively, and a cyclic intermediate has been proposed. Oxidation by organic peroxides (R_2O_2) produces Ph_3SnOR , and free radical species may be involved in such reactions.

We have recently shown that *o*-quinones coordinate to halides of Main Group elements, and that with SnCl_4 in particular a stable QSnCl_4 species can be crystallised.² In order to test the possibility that Sn_2Ph_6 might act as a Lewis acid towards such ligands, we investigated mixtures of Sn_2Ph_6 and a variety of mono- and bidentate nitrogen bases in chloroform, using ^{119}Sn NMR. The chemical shifts (ppm), with line widths (Hz) in parentheses, for solutions containing excess base, were for pyridine –142.5(35), γ -picoline –144.2(32), 2,2'-bipyridine –144.1(30) and *N,N,N,N'*-tetramethylethanediamine –142.8(38). The mean value is $-143.4 \pm 0.7(34)$, to be compared with –143.6(31) for a solution of Ph_6Sn_2 in the same solvent. We conclude that nucleophilic attack of the *o*-quinone at a tin centre of Ph_6Sn_2 is unlikely to be the primary process in the systems studied in this work. Tetraphenyltin also lacks acceptor properties [8], and a coordinative mechanism can also be ruled out for this substance.

We have recently shown [9] that *o*-quinones will oxidise the phenyl group of LiPh by the processes



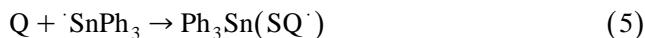
and the attack of *o*-quinone at a phenyl group of Ph_6Sn_2 is therefore the most probable initiating process. Whether this is a cooperative process involving two neighbouring phenyl groups is not clear, although the absence of reaction with HgPh_2 ($\text{C}-\text{Hg}-\text{C} = 180^\circ$) suggests such a mechanism. Leaving this aside, the proposed reaction sequence is:



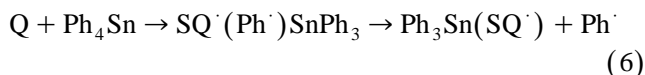
followed by



or



The comparable sequence for Ph_4Sn is:



This last process is exactly analogous to that proposed by Davies and Hawari [10] for the reaction of organotin compounds with 3,6-di-*tert*-butyl-1,2-benzoquinone.

The common feature of Eqs. (3) and (6) is the formation of $\text{Ph}_3\text{Sn}(\text{TBSQ}^{\cdot-})$ and in the case of the reaction of TBQ with both Sn_2Ph_6 and Ph_4Sn , the EPR parameters of the monoradical formed are identical. The identification of this radical as $\text{Ph}_3\text{Sn}(\text{TBSQ}^{\cdot-})$ depends in part on the similarity in the hyperfine constants for this molecule and the analogous product identified by Davies and Hawari [8], who reported $a_{\text{Sn}} = 12.0$ G, $a_{\text{H}} = 3.7$ G. We assign the a_{H} values given in Table 1 to H4 (3.03 G), H6 (0.46 G) and *t*- C_4H_9 (0.36 G), partly by comparison with results from earlier work on $\text{TBQ} + \text{SnX}_2$, [11] and $\text{TBQ} + \text{InX}$ [12] ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), partly by analogy with the work of Davies and Hawari [10], and partly on the basis of the simulation procedure.

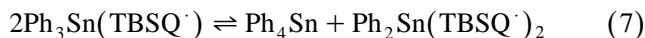
It follows that the remaining values in Table 1 refer to the analogous $\text{Ph}_3\text{Sn}(\text{SQ}^{\cdot-})$ species derived from the reactions described in Section 2. There seems to be no method of rationalising the specific results in terms of the detailed structure of the semiquinone in question. The more important point is that all these reactions involve the same initiating processes.

3.2. Related reactions

The striking features of the $\text{Sn}_2\text{Ph}_6/\text{TBQ}$ system are the precipitation of Ph_4Sn and formation of biradical

species (Table 1), and the precipitation of Ph_4Sn . The experimental evidence for these latter include a resonance for the frozen solution at magnetic field half that of the corresponding monoradical (e.g., Figs. 3 and 4), and weak features adjacent to the central resonance. (e.g., Fig. 1). In favourable circumstances, these may lead to measurement of the zero-field parameters D and E , which in turn may allow estimates of the effective distance between the radical sites in a molecule. In the case of phenanthrenequinone, we also identified the mononuclear biradical $\text{Ph}_2\text{Sn}(\text{PSQ}^\cdot)_2$, and the catecholate $\text{Ph}_2\text{Sn}(\text{CAT})$, but with naphtha- and tetrabromo-*o*-quinones, the only product recovered was the monoradical $\text{Ph}_3\text{Sn}(\text{SQ}^\cdot)$. The significance of these differences presumably lies in (i) the different oxidising strength of the *o*-quinone or semiquinones involved, and (ii) the solubility of the various species in question.

For TBQ, we suggest that the explanation of the formation of these products requires both intramolecular electron transfer, and solution redistribution processes. The latter are related to the known tendency of organotin(IV) halides, and other species, to undergo ligand redistribution in solution, as evidenced by a number of ^{119}Sn NMR studies [13]. We therefore suggest that the formation of $\text{Ph}_3\text{Sn}(\text{TBSQ}^\cdot)$ (Eq. (6)) is followed by:

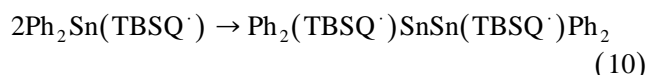
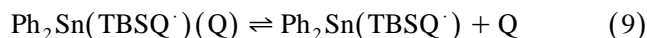
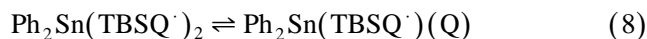


Since Ph_4Sn is almost insoluble in either *n*-hexane or dichloromethane, Eq. (7) will be displaced to the right hand side by the precipitation of Ph_2Sn , resulting in the formation of the biradical $\text{Ph}_2\text{Sn}(\text{TBSQ}^\cdot)_2$ in solution. The EPR properties of biradicals of the type $\text{M}(\text{TBSQ}^\cdot)_2\text{L}$ ($\text{M} = \text{Mg}, \text{Zn}, \text{Cd}$; $\text{L} = 2,2'$ -bipyridine, N,N,N',N' -tetramethylethanediamine) have been discussed earlier [14]. The zero-field parameters obtained experimentally were compared with those calculated for various configurations, and the stereochemistries of the complexes thereby identified. For such six-coordinate complexes with bidentate ligands, the only possible isomer is the *cis*-form, and reasonable agreement was found between calculated and experimental values, which were in the range $150\text{--}250 \times 10^{-4} \text{ cm}^{-1}$ [1] for those elements. For the compound $\text{Si}(\text{DBSQ}^\cdot)_2(\text{DBC})$ ($\text{DBSQ}^\cdot = 4,6\text{-di-}i\text{-tert-butyl-1,2-benzosemiquinone}$ anion; $\text{DBC}^{2-} = \text{corresponding catecholate}$), the D -value (exptl.) [15] is $301 \times 10^{-4} \text{ cm}^{-1}$. Given this range of values, it is difficult to assign any one of the values in Table 1 to $\text{Ph}_2\text{Sn}(\text{TBSQ}^\cdot)_2$ with any confidence; on the other hand, the order of magnitude is clearly appropriate for such a molecule, and Eq. (7) is supported to that extent.

Further confirmation comes from the recent crystallographic characterisation of the diradical species $\text{Ph}_2\text{Sn}(\text{PSQ}^\cdot)_2$, noted briefly above. The structure of this six-coordinate tin(IV) complex confirms the presence of two semiquinonate ligands, with typical $r(\text{Sn}-\text{O})$

and $r(\text{C}-\text{O})$ distances [6]. The zero-field parameters of this molecule are similar to those discussed in the last paragraph. It is reasonable to ask whether Eq. (7) can be extended to other redistribution products such as $\text{PhSn}(\text{TBSQ}^\cdot)_3$ and $\text{Sn}(\text{TBSQ}^\cdot)_4$. We find no evidence for such tri- or tetradical species, which might require seven- and eight-coordination at tin, and therefore confine the discussion to Eq. (7).

Table 1 shows that the frozen reaction solution contains three biradical species, which cannot be adequately accounted for by Eq. (7). Following arguments used elsewhere [1,11] involving intramolecular electron transfer, we propose the processes:



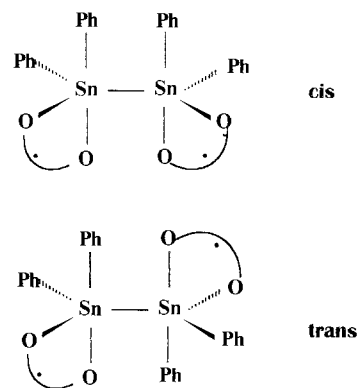
This sequence results in tin-tin bonded species, and again the earlier work shows that two stereoisomers of such analogous molecules are possible (Scheme 1).

In the case of the analogous $\text{Cl}_2(\text{TBSQ}^\cdot)\text{SnSn}(\text{TBSQ}^\cdot)\text{Cl}_2$ species identified in studies of the SnCl_2/Q system, the zero-field parameters of 228 and $65 \times 10^{-4} \text{ cm}^{-1}$ were assigned on the basis of calculations to the *cis*- and *trans*-isomers respectively [10].

In one case ($\text{Sn}_2\text{Ph}_6 + \text{PQ}$) the product $\text{Ph}_2\text{Sn}(\text{PCAT})$ was identified, and although this was the only reaction involving Sn_2Ph_6 to yield such a product, similar diphenyltin catecholates were found in the reaction between Ph_3SnCl and NaSQ^\cdot (see Section 3.3). In the present system, we suggest that the isomerisation



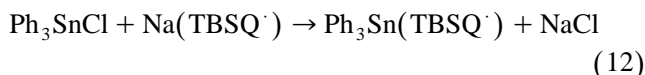
is followed by loss of *o*-quinone and precipitation of $\text{Ph}_2\text{Sn}(\text{PCAT})$, and this clearly depends on the prior formation of the bis-semiquinone complex, only detected in the particular case of phenanthrenequinone. Isomerizations to Eq. (11) have been identified earlier [1].



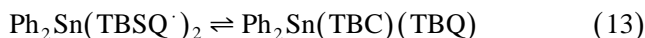
Scheme 1.

3.3. The reaction between Ph_3SnCl and $\text{Na}(\text{TBSQ}^\cdot)$

The original intent of this part of the study was to prepare $\text{Ph}_3\text{Sn}(\text{SQ}^\cdot)$ compounds by metathesis, but the experimental results for $\text{Ph}_3\text{SnCl} + \text{Na}(\text{TBSQ}^\cdot)$ showed that the solution chemistry is more complicated than expected. The near-quantitative elimination of NaCl shows that the first reaction is indeed.

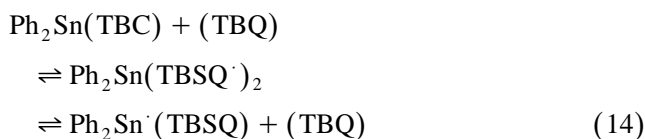


It is important to note that a freshly prepared solution of Ph_3SnCl in dichloromethane (the reaction medium) showed only a single ^{119}Sn NMR signal at -46.5 ppm (cf. -48 ± 11 ppm reported in the literature [5]), so that the presence of other possible redistribution products in the starting solution can be ignored. This initial reaction is followed by the precipitation of a mixture of Ph_4Sn and $\text{Ph}_2\text{Sn}(\text{CAT})$. We suggest that Eq. (12) is followed by the redistribution process (Eq. (7)) and an isomerisation corresponding to Eq. (11), namely

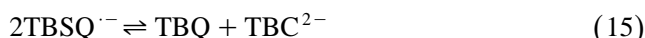


with subsequent loss of TBQ and precipitation of $\text{Ph}_2\text{Sn}(\text{TBC})$.

In addition to the solid products just noted, the filtrate contains biradicals, with D -values similar to those found for the $\text{Ph}_6\text{Sn}_2/\text{TBQ}$ reaction. These are presumed to arise by Eqs. (8)–(10). It will be clear that we have postulated two possible competing processes for the intramolecular electron transfer processes in $\text{Ph}_2\text{Sn}(\text{TBSQ})_2$.



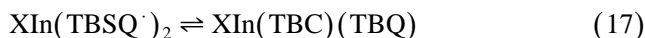
The left-hand product is the result of intraligand electron transfer



whilst the right-hand product arises from the oxidation of $\text{TBSQ}^{\cdot-}$ by tin(IV)



As noted above, the analogue of Eq. (15) has been observed in indium chemistry [1]



The relative importance of the competing processes in Eq. (14) should depend, inter alia, on solvent and temperature, to the extent that these parameters affect the solubility of $\text{Ph}_2\text{Sn}(\text{TBC})$, and it is therefore reasonable that different products are observed in solid and solution phases.

3.4. The reaction between Ph_2SnCl_2 and $\text{Na}(\text{TBSQ})$

As with Ph_3SnCl , the ^{119}Sn NMR spectrum of a freshly prepared solution of Ph_2SnCl_2 in dichloromethane- d_2 showed a single resonance at -29.8 ppm (cf. -32 ± 0.8 ppm reported [5] for a solution in CH_2Cl_2). The initial reaction with a 1:1 mole ratio of reactants gave a solution containing one monoradical, and Ph_4Sn and $\text{Ph}_2\text{Sn}(\text{TBC})$ as solids; a mole ratio of 2:1 ($\text{NaTBSQ}^\cdot:\text{Ph}_2\text{SnCl}_2$) gave a mixture of two monoradicals. A detailed analysis of the EPR spectra was not possible.

The isolation of Ph_4Sn and $\text{Ph}_2\text{Sn}(\text{TBC})$ suggests that $\text{Ph}_3\text{Sn}(\text{TBSQ}^\cdot)$ is one of the radicals formed in these reactions. A large number of possible reactions can be constructed for this system, involving redistribution of $\text{Ph}_x\text{SnCl}_y(\text{TBSQ}^\cdot)_z$ molecules in solution ($x + y + z = 4$), and the evidence presently available does not allow any single set of reactions to be identified.

3.5. General conclusions

The initial reaction of a series of substituted ortho-quinones with Sn_2Ph_6 yields the monoradical species $\text{Ph}_3\text{Sn}(\text{SQ}^\cdot)$. The nature of reaction products which may be derived subsequently from these radicals appears to depend on the properties of the *o*-quinone, and of the reaction conditions. Redistribution processes in solution are an important feature of these systems, as they are in other areas of tin(IV) chemistry. Reactions involving Ph_4Sn , and metathetical reactions between $\text{Na}(\text{TBSQ}^\cdot)$ and Ph_3SnCl or Ph_2SnCl_2 , give related products, and a common solution chemistry and intramolecular electron transfer processes underlies all these systems.

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References

- [1] M.A. Brown, B.R. McGarvey, A. Ozarowski, D.G. Tuck, *Inorg. Chem.* 35 (1996) 1560, and refs. therein.
- [2] D.G. Tuck, *Coord. Chem. Rev.* 112 (1992) 215.
- [3] T.A. Annan, A. Ozarowski, Z. Tian, D.G. Tuck, *J. Chem. Soc., Dalton Trans.* (1992) 2931.
- [4] Z. Tian, D.G. Tuck, *J. Organomet. Chem.* 462 (1993) 125.
- [5] R.K. Harris, J.D. Kennedy, W. McFarlane, in: R.K. Harris, B.E. Mann (Eds.), *AMR and the Periodic Table*, Academic Press, New York, 1978, p. 342 et seq.

- [6] A.S. Batsanov, J.A.K. Howard, M.A. Brown, B.R. McGarvey, D.O. Tuck, *Chem. Commun.*, (1997) 699.
- [7] A.K. Sawyer, *Organotin Compounds*, Vol. 3, Marcel Dekker, New York, 1972, p. 823.
- [8] M.A. Brown, B.R. McGarvey, A. Ozarowski, D.G. Tuck, *J. Am. Chem. Soc.* 118 (1996) 9691.
- [9] A.G. Davies, P.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon, Oxford, 1982, Chap. 11, p. 535.
- [10] A.G. Davies, J.A.A. Hawari, *J. Organomet. Chem.* 231 (1983) 53.
- [11] T.A. Annan, B.R. McGarvey, A. Ozarowski, D.G. Tuck, R.K. Chadha, *J. Chem. Soc., Dalton Trans.* (1989) 439.
- [12] T.A. Annan, R.K. Chadha, P. Dean, D.H. McConville, B.R. McGarvey, A. Ozarowski, D.O. Tuck, *Inorg. Chem.* 29 (1990) 3936.
- [13] A.G. Davies, P.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon, Oxford, 1982, Chap. 11, p. 548.
- [14] A. Ozarowski, B.R. McGarvey, C. Peppe, D.G. Tuck, *J. Am. Chem. Soc.* 113 (1991) 3288.
- [15] A.I. Prokofev, T.I. Prokofev, N.N. Bubnor, S.P. Solodovnikov, I.S. Bebestotskaya, V.V. Ershov, M.I. Kabachnik, *Dokl. Chem. (Engl. Trans.)* 234 (1977) 276.