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CERTAIN PROBLEMS IN THE STRUCTURE OF TIN-CONTAINING COMPLEXES OF 3,6-DI-TERT-BUTYL-o-BENZOQUINONE AND METALLOTROPIC TRANSITIONS IN THESE SYSTEMS

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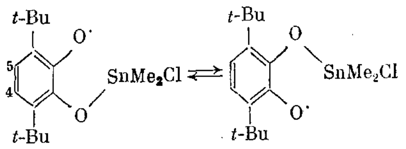
The interaction of organometallic compounds with ortho-quinones leads to the formation of paramagnetic complexes [1]. This interaction can be regarded in general form as a reaction of ligand substitution at the central atom of the organometallic compound, in the process of which there is a one-electron reduction of the ortho-quinone to form a metal-containing radical [2]

$$Q + MR_n \to \dot{Q}MR_{n-1} + R^{\cdot}$$

We had used this type of interaction previously to prepare trimethylstannyl and dimethylchlorostannyl derivatives of 3,6-di-tert-butyl-o-benzoquinone [3]. Analogous radicals have been obtained by the interaction of ortho-quinones of various structures with trisubstituted silanes, stannanes, and germanes [4-7]. An investigation of the ESR spectra of the Sn-containing radicals that we obtained [3] showed that the radical with the $SnMe_2Cl$ grouping is characterized by typical metallotropy, manifested in the temperature dependence of the spectral picture. At high temperatures, we observe equivalent HFI from the ring protons ($a_{H^4} = a_{H^5}$);



a triplet is registered, and when the temperature is reduced, this changes to a doublet of doublets ($a_{H^4} > a_{H^5}$). In the intermediate temperature region we find a characteristic alternation of HFI line widths, which can be used along with well-developed theory [8] to determine the kinetic parameters of intramolecular exchange.

In the ESR spectra of the radical containing the $SnMe_3$ grouping, regardless of the temperature, we observe a triplet spectrum, indicating a symmetrical distribution of spin density in the pyrocatechol ligand

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TABLE 1. HFI Constants of Radicals Containing Organotin Fragments (pentane solvent)

Compound	R^1	R^2	R^3	a_{H^4}	a_{H^5}	$\Delta a = a_{H^4} - a_{H^5}$	$a_{H^4} + a_{H^5}$	^{117}Sn	^{119}Sn
(I)*	Me	Me	Me	3,65	3,65	0	7,3	12,8	13,3
(II)	Ph	Me	Me	3,65	3,65	0	7,3	12,6	13,1
(III)	Ph	Ph	Me	4,65	2,45	2,2 †	7,3	12,3	12,8
(IV)	Ph	Ph	Ph	5,2	2,1	3,1 †	7,3	11,7	12,2
(V)*	Cl	Me	Me	5,0	2,5	2,5	7,5	20,2	21,5
(VI)	Cl	Ph	Me	4,8	2,7	2,1	7,5	17,7	18,6
(VII)	Cl	Ph	Ph	4,7	2,8	1,9	7,5	16,0	16,5
(VIII)	Cl	$C_6H_4CH_3$	$C_6H_4CH_3$	4,7	2,8	1,9	7,5	16,0	16,5
(IX)	Cl	C_6H_4Cl	C_6H_4Cl	4,7	2,8	1,9	7,5	16,0	16,5
(X)	Cl	$Cl_3C_6H_2$	$Cl_3C_6H_2$	4,7	3,1	1,6	7,8	14,0	14,5
(XI) ‡	Cl	Cl	Cl	3,9	3,9	0	7,8	7,2	7,2

* Data of [3].

† Obtained at low temperatures, when the rate of "stannotropy" is less than the characteristic time of the ESR.

‡ The constant of HFI with one Cl atom, observed in the ESR spectra of this radical, is 0.63 Oe.

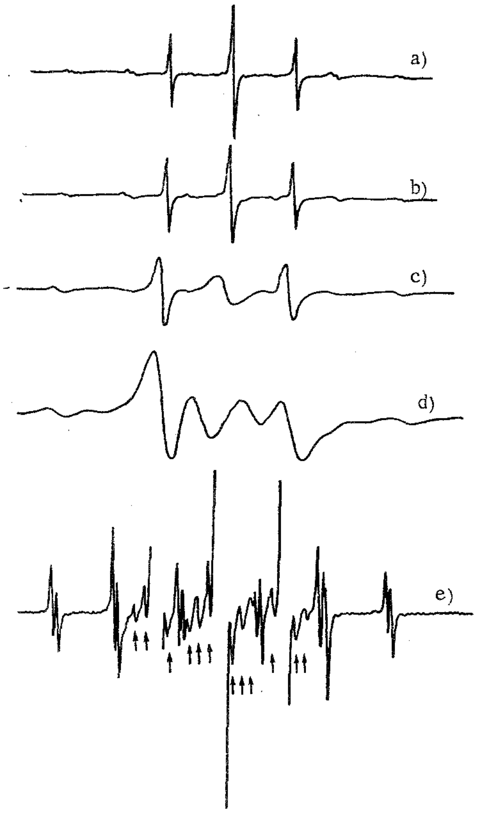
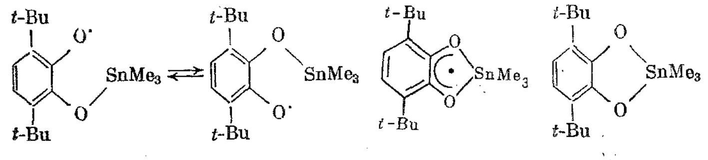


Fig. 1. ESR spectra of radical (IV) at different temperatures (°C): a) −50; b) −80; c) −110; d) −130; e) −40. The arrows indicate the ^{13}C lines. Pentane solvent.

(equivalent HFIs with the ring protons, $a_{H^4} = a_{H^5}$). This corresponds to either a fast (on the ESR time scale) intramolecular migration of the trimethyltin (A) ⇌ (A') or to the formation of a chelate structure with a pentacoordinated Sn atom (B).



(A) (A') (B) (C)

We rejected the third possible structure (C), corresponding to an Sn-centered radical, since the HFI with the protons of the pyrocatechol ligand is close to that with the corresponding anion-radical [9], and the HFI with

TABLE 2. Effect of Solvent on HFI with ^{117}Sn and ^{119}Sn Nuclei, and Kinetic Parameters of Migration of Triphenylstannyl in the Radical (IV)

Solvent	^{117}Sn	^{119}Sn	$a_{H^4}+a_{H^5}$	$\nu(20°)$	ν_0	$E_a \pm 0.5$, kcal/mole
Toluene	11,7	12,2	7,3	$3\cdot10^{9}$	$6\cdot10^{11}$	3,2
Pentane	11,7	12,2	7,3	$2\cdot10^{10}$	$1{,}2\cdot10^{13}$	3,8
THF	11,2	11,8	7,3	$1{,}7\cdot10^{10}$	$2\cdot10^{13}$	4,2
DMFA	9,65	10,1	7,3	$9\cdot10^{9}$	$9\cdot10^{13}$	5,3
DMSO	10,2	10,7	7,1	–	–	–

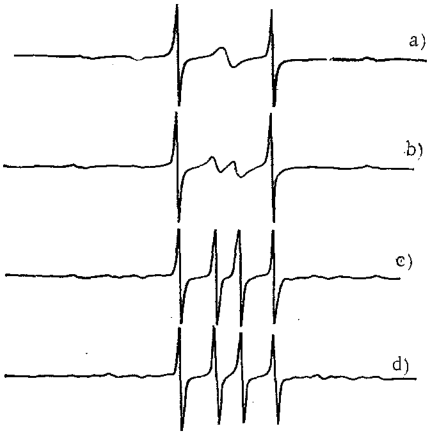
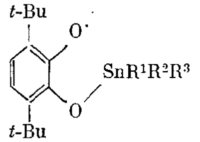


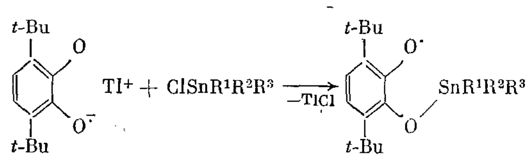
Fig. 2. ESR spectra of radical (VII) at various temperatures (°C): a) 155; b) 80; c) 0; d) −40. Toluene solvent.

the ^{117}Sn and ^{119}Sn nuclei is quite small.

With the aim of determining the reasons for such a difference in the behavior of radicals containing $SnMe_2Cl$ and $SnMe_3$ groups, we investigated a series of radicals of the general type



where R^1, R^2, and R^3 are groups with various electronegativities. We can assume that the results from ESR measurements will enable us to delve more deeply into the general relationships in radical metallotropy. For the first four of the radicals investigated, the groups R^1, R^2, and R^3 were Ph and Me in all possible combinations. These radicals were obtained by exchange reactions of the corresponding monochloride with Tl 3,6-ditertbutyl-o-semiquinolates in pentane,



$R^1 = R^2 = R^3 = Me$ (I); $R^1 = Ph$, $R^2 = R^3 = Me$ (II); $R^1 = R^2 = Ph$, $R^3 = Me$ (III);
$R^1 = R^2 = R^3 = Ph$ (IV).

In the ESR spectrum of the radical (IV) (Fig. 1) at temperatures above −40°C, we observe a triplet due to equivalent HFIs with the ring protons; we also observe HFIs with the ^{117}Sn, ^{119}Sn, and ^{13}C nuclei, an analysis of which will be given in the subsequent discussion (Table 1). When the temperature is lowered, the central component of the triplet is broadened (Figs. 1b and 1c), and at −130°C the spectrum consists of a doublet of doublets, corresponding to localization of the organometallic group on one of the O atoms; this indicates that, on the ESR time scale, intramolecular migration processes have stopped, and a structure of the type of (A) is realized for the radical (IV). Analogous relationships were obtained for the radical (III). In the case of the radical (II), we were not successful in completely freezing the "stannotropy," even at −144°C; in the range from −110° to −144°C, we observe only a broadening of the central component of the triplet. The ESR spectrum of the radical (I), as already mentioned, is independent of temperature.

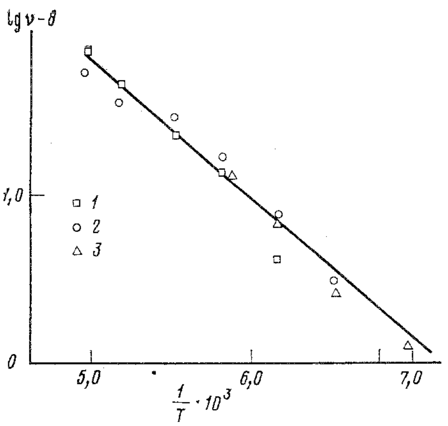


Fig. 3

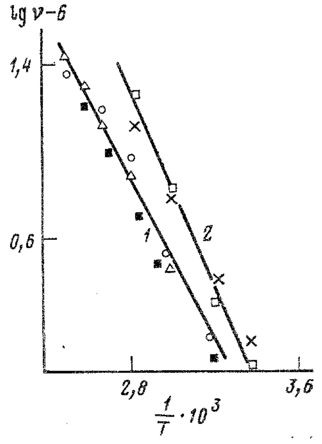


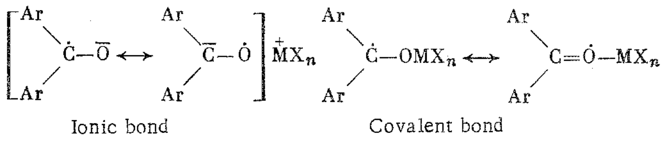
Fig. 4

Fig. 3. Arrhenius dependences of frequency of migration of tin-containing groups in radicals (II)-(IV): 1) (IV); 2) (III); 3) (II). For (II), the temperature change of the nominal frequency is indicated, for illustration of the similar energy barriers to migration.

Fig. 4. Arrhenius dependences of migration frequency in radicals (VII)-(X): 1) (VII), (VIII); 2) (IX), (X).

In examining the parameters of the ESR spectra of the radicals (I)-(IV) (see Table 1), attention is drawn to the decrease in HFI with the ^{117}Sn and ^{119}Sn nuclei and the increasing difference between the ring proton HFI constants $\Delta a = (a_{\mathrm{H}^4} - a_{\mathrm{H}^5})$ with increasing number of phenyl groups. At the same time, the sum $(a_{\mathrm{H}^4} + a_{\mathrm{H}^5})$ remains constant.

It is known [6] that when the change is made from an ionic bond of an anion-radical with a metal cation (anion-radicals of ketyls, semiquinones) to a covalent bond (metal-containing radicals), the HFI constants in the aromatic fragments increase

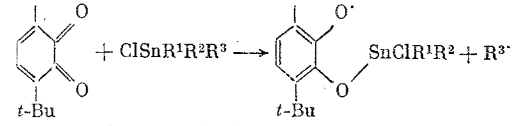


(With the covalent bond, the contribution of the structure with an unpaired electron on the oxygen is negligibly small.)

The sum of the HFI constants $(a_{\mathrm{H}^5} + a_{\mathrm{H}^4})$ in the radicals (I)-(IV) (Table 1) is considerably greater than in the anion-radical of 3,6-di-tert-butyl-o-benzosemiquinone, which is 6.7 Oe [9]. This suggests that in these radicals, the Sn—O bond is covalent-polar. This view is supported by the constancy of the sum $(a_{\mathrm{H}^4} + a_{\mathrm{H}^5})$ for (IV) in solvents differing in solvating power (Table 2). Only in the DMSO do we find a distinct decrease in this sum, indicating an increase in the ionic character of the Sn—O bond in this solvent [10].

With increasing polarity of the solvent, we also observe a certain decrease in the constants of HFI with ^{117}Sn and ^{119}Sn. It is known that with a purely ionic M—O bond (ionic bonds formed by anion-radicals with metal cations), an increase in the polarity of the solvent may reduce a_{M} to zero (formation of a solvent-separated ion pair) [11]. The observed decrease in $a_{^{117}\mathrm{Sn}}$ and $a_{^{119}\mathrm{Sn}}$ when the change is made to DMFA apparently indicates an increase in the degree of ionicity of the Sn—O bond.

A different picture is observed when one of the alkyl or phenyl substituents is replaced by a Cl atom. We obtained such radicals through the reaction of a ligand substituent of the ortho-quinone with an appropriate monohalogen derivative; in a nonpolar or low-polarity medium, the phenyl or alkyl group is replaced.



$R^1 = R^2 = Me$ (V); $R^1 = Ph$, $R^2 = Me$ (VI); $R^1 = R^2 = Ph$ (VII); $R^1 = R^2 = C_6H_4CH_3$ (VIII); $R^1 = R^2 = C_6H_4Cl$ (IX); $R^1 = R^2 = C_6H_2Cl_3$ (X); $R^1 = R^2 = Cl$ (XI).

TABLE 3. Kinetic Parameters of Migration of Tin-Containing Fragments in Corresponding Adducts of 3,6-Di-tert-butyl-o-benzoquinone (toluene solvent)

Compound	R^1	R^2	R^3	$\nu(20°)$	ν_0	E_a ± 0.5, kcal/mole
(I)	Me	Me	Me	–	–	–
(II)	Ph	Me	Me	3.10^9	$6 \cdot 10^{11}$	3,2
(III)	Ph	Ph	Me			
(IV)	Ph	Ph	Ph			
(IVA)	$CH_3C_6H_4$	$CH_3C_6H_4$	$CH_3C_6H_4$			
(IVB)	ClC_6H_4	ClC_6H_4	ClC_6H_4			
(V) *	Cl	Me	Me	$8 \cdot 10^5$ $1{,}3 \cdot 10^6$ *	$5{,}5 \cdot 10^{12}$ $5{,}9 \cdot 10^{12}$ *	9,3 9,1 *
(VI)	Cl	Ph	Me	$2 \cdot 10^5$	$2{,}4 \cdot 10^{13}$	11,0
(VII)	Cl	Ph	Ph	$9 \cdot 10^4$	$1{,}6 \cdot 10^{11}$	8,5
(VIII)	Cl	$CH_3C_6H_4$	$CH_3C_6H_4$			
(IX)	Cl	ClC_6H_4	ClC_6H_4	$1{,}2 \cdot 10^5$	$2{,}7 \cdot 10^{12}$	10,0
(X)	Cl	$Cl_3C_6H_2$	$Cl_3C_6H_2$			
(XI)	Cl	Cl	Cl	–	–	–

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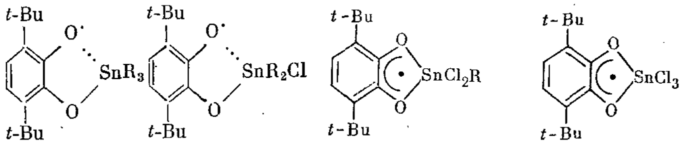
* Data of [3].

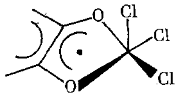
The ESR spectra of such radicals are considerably different from those of the radicals (I)-(IV), both in the magnitude of the HFI with the ^{117}Sn and ^{119}Sn nuclei and in the HFI with the ring protons (Fig. 2, Table 1). For the radicals (V)-(X), the sum of the constants of HFI with the ring protons is somewhat greater than for (I)-(IV), indicating a less ionic character of the Sn–O bond in the radicals (V)-(X), in comparison with (I)-(IV). For the radical (X), the sum $(a_{H_4} + a_{H^5})$ coincides with the value obtained from an analysis of the ESR spectra of the 3,6-di-tert-butyl-2-hydroxyphenoxyl radical [12]. At the same time, contrary to expectation, we find that with increasing acceptor properties of the substituents on the Sn atom, the difference Δa decreases (Table 1), and the constants of HFI with the ^{117}Sn and ^{119}Sn nuclei decrease in the same order.

It is known that the introduction of Cl atoms increases the Lewis acidity of the Sn atom [13], i.e., increases its coordination capability. The increase in coordination capability strengthens the intramolecular coordination between the univalent O atom and the Sn atom. Such coordination leads to a decrease in the differences between the mainly covalent bond and the coordination bond, which become equivalent as the number of Cl atoms is increased, leading to the formation of a chelate structure containing pentacoordinated tin with equalized Sn–O bonds [4]



This is quite probably the specific reason why Δa decreases in the series of radicals (V)-(X) when phenyl and chlorophenyl substituents are introduced to the Sn atom, increasing its coordination unsaturation.

In the ESR spectrum of the radical (XI), which contains the $SnCl_3$ grouping, regardless of the temperature, we find a symmetrical distribution of the unpaired electron in the pyrocatechol ligand $(a_{H^4} = a_{H^5})$ and HFI with one Cl atom; each component of the triplet of the ring protons contains a quartet 1:1:1:1 $(I_{Cl} = 3/2)$. The HFI with the ^{117}Sn and ^{119}Sn nuclei is considerably less than in (I)-(X) (Table 1). These spectral features of the radical (XI) are evidence in favor of the structure with a pentacoordinated Sn atom, which was first proposed on the basis of an analysis of the ESR spectra of an analogous adduct of acenaphthoquinone and other compounds [4]. The presence of HFI with one Cl atom and the small HFI of ^{117}Sn and ^{119}Sn are consistent with tetragonal pyramidal structure with one Cl atom at the vertex and the two other Cl atoms and the Sn atom lying close to the nodal plane



(XI)

As can be seen from Table 1, in which the radicals are listed in order of increasing total electronegativity of the substituents R, the sum $(a_{H^4} + a_{H^5})$ increases significantly in the series from (I) to (XI); as indicated

TABLE 4. HFI Constants and Spin Densities in 3,6-Di-tert-butyl-2-triphenylstannylphenoxyl Radical (IV)

Atom	Toluene			Dimethylformamide		
	ρ	$^{13}C_{theor}$	$^{13}C_{exp}$	ρ	$^{13}C_{theor}$	$^{13}C_{exp}$
O	0,157	–	–	0,149	–	–
$C^{1,2}$	0,168	0,9	1,3	0,172	1,2	1,3
$C^{3,6}$	0,021	3,8	3,6	0,021	3,8	4,0
$C^{4,5}$	0,154	3,0	2,7	0,150	2,8	2,5

TABLE 5. Effect of Solvent on Kinetic Parameters of "Stannotropy" in 3,6-Di-tert-butyl-2-chlorodiphenylstannylphenoxyl Radical (VII)

Solvent	a_{H^4}	a_{H^5}	$a_{H^4}+a_{H^5}$	^{117}Sn	^{119}Sn	$\nu(20°)$	ν_0	$E_a \pm 0,5$, kcal/mole
Toluene	4,7	2,8	7,5	16,0	16,5	$0,9 \cdot 10^5$	$0,2 \cdot 10^{12}$	8,5
Dioxane	4,7	1,6	6,3	16,6	17,0	$0,2 \cdot 10^6$	$0,2 \cdot 10^{12}$	8,0
Acetone	5,2	2,1	7,3	16,8	17,5	$1,1 \cdot 10^6$	$1,1 \cdot 10^{10}$	4,9
Acetonitrile	4,9	2,0	6,9	16,7	17,5	$4,4 \cdot 10^6$	$4,1 \cdot 10^{10}$	3,9

above, this is related to the decrease in the degree of ionicity of the Sn–O bond. Along with this, the difference between the constants of the ring protons Δa at first increases, from 0 to 3.1 Oe in the series of radicals from (I) to (IV), and then again decreases to 0 in the series from (V) to (XI).

The increase of Δa in the series of radicals (I)-(IV) is understandable if we assume a decrease in this series of the polarity of the Sn–O bond and a related decrease in the donor properties of the $OSnR_3$ group as the substituent in the ortho position of the phenoxyl ring. Let us remember that in the case of an ionic bond (the anion-radical of 3,6-di-tert-butyl-o-benzosemiquinone or the trialkylammonium cation), Δa = 0.7 Oe [14], but in the case of a covalent bond, this value amounts to 8-12 Oe, for example in 3,6-di-tert-butyl-2-hydroxyphenoxyl Δa = 8 Oe [12], and in 3,6-di-tert-butyl-2-acetyloxyphenoxyl Δa = 12 Oe [15].

Thus, with increasing acceptor properties of the tin-containing grouping, the spin density in position 5 decreases and Δa increases. This effect should also be observed in the series of radicals (V)-(XI), but it is masked by effects of coordination of the unpaired electron to the central atom as we go over to pentacoordinated Sn with a symmetrical distribution of spin density in the free-radical ligand.

These features of the structure of tin-containing radicals that we have examined are consistent with kinetic data obtained on intramolecular migration of the tin-containing fragments between the O atoms of the pyrocatechol ligand, in radicals (I)-(X).

The increase in Δa with increasing number of phenyl substituents, in radicals (I)-(IV), has a decisive influence on the spectral manifestation of the "stannotropy." The fulfillment of the condition of rapid exchange ($\nu_{ex} \gg \gamma_e \Delta a$) for the radical (I) over the entire temperature range is related to the small magnitude of Δa. With increasing Δa, it becomes possible not only to observe alternating-broadened lines of the spectrum, for radical (II), but also to retard completely the exchange processes at low temperatures, for radicals (III) and (IV). From the Arrhenius dependence of the frequency of "stannotropy" for the radicals (III) and (IV) (Fig. 3), it can be seen that the frequency and the barrier of the process are practically independent of the number of phenyl groups. Let us note that the energy barrier of "stannotropy" for the radical (II), as estimated from the temperature changes of nominal frequency, does not differ from the barriers for the radicals (III) and (IV).

The solvating properties of the medium have very little effect on the kinetic parameters of "stannotropy." We may point out that with increasing solvation power of the solvent, there is a slight increase in the energy barrier of the process (see Table 2).

There is also very little effect from the introduction of substituents into the para position of the phenyl rings for the radicals (IV), (IVA), and (IVB) (Table 3). The differences are apparently within the limits of experimental error.

As can be seen from Table 3, the frequencies of migration of the $SnClRR^1$ fragments are several orders of magnitude lower, and the energy barriers higher, than in the radicals (I)-(IV) (Fig. 4). Such unexpectedly high barriers of "stannotropy" are at first glance difficult to reconcile with the increase in coordination capability of the central atom when the Cl atom is introduced. However, in the radicals (V)-(X), there is a strengthening of the Sn−O bond, since, as we have shown previously, its polarity is decreased, thus increasing the barrier to migration.

Thus, the metallotropy is governed by two opposing factors: the coordination capability of the central atom of the migrating fragment, and the strength of the metal−oxygen bond. In the radical (XI) and similar systems studied in [4], containing $SnCl_3$ and $SnCl_2R$ fragments, the coordination unsaturation of the Sn and the high strength of the Sn−O bond completely determine the symmetrical distribution of spin density of the free-radical ligand, the pentacoordinated mesomeric structure of these particles, and the absence of "stannotropy."

In the example of the radical (IV), we have been able to estimate the change in the constants of HFI with the ^{13}C nuclei and the redistribution of spin density in the free-radical ligand in relation to the properties of the medium (toluene and DMFA). With small concentrations of the radical (IV) and low UHF power of the ESR spectrometer, narrow lines are registered, so that HFI with ^{13}C nuclei can be determined. With a high amplification, three types of HFI with ^{13}C are observed (see Fig. 1e), corresponding the pairwise-equivalent ring C atoms; the relative intensity of the lines corresponds to the natural content of ^{13}C (1%) and pair-equivalence of ^{13}C. The assignment of these lines can be made by calculating the theoretical values of $a_{^{13}C}$ on the basis of an investigation of the density of spin distribution in the pyrocatechol ligand. In Table 4 we have listed values for the spin density (ρ) on the ring C atoms. In positions 4 and 5, ρ has been estimated from the HFI with the ring protons (Q = −23.7 Oe); in positions 3 and 6, it has been estimated from the HFI with these protons in the radical containing the $SnPh_3$ group and an unsubstituted pyrocatechol ligand [16]; in positions 1 and 2, it has been estimated on the basis of normalization of spin density $\sum_i \rho_i = 1$, deducting the spin densities in positions 3-6, and the ratios of distribution of the remaining spin density among the C^1, C^2, and O atoms in 3,6-di-tert-butyl-2-hydroxyphenoxyl [12].

Using this assumed distribution of spin density and the formula of Karplus and Frenkel relating the HFI with the ^{13}C nucleus and the magnitude of ρ in the aromatic fragment [8], we carried out theoretical calculations of the HFI with the ^{13}C nuclei in all positions of the aromatic ring of the radical (IV) (Table 4). The satisfactory agreement of the calculated and theoretical values provides us with grounds for accepting the assignment of HFI with ^{13}C that we have made. It can be seen that when the change is made to DMFA, the spin density in [4] is somewhat changed, most probably because of complex formation.

Apparently this also leads to the observed change in the kinetic parameters of "stannotropy." In the radical (IV), the Sn−O bond is comparatively polar; in toluene, the coordination of the univalent O atom to Sn is sufficient for rupture of the Sn−O bond, i.e., for the act of migration. In DMFA, the coordination unsaturation of the Sn is somewhat lower because of its additional coordination with the DMFA, and the spin density on the O atom is less than in toluene (Table 4). This is responsible for the higher energy barrier in DMFA than in toluene, 5.3 vs 3.2 kcal/mole (Table 2).

Different relationships are found in the case of the radical (VII) (Table 5). Here the Sn−O bond is less polar than in (IV), and its rupture in toluene by attack by a univalent O atom requires a greater activation energy (8.5 kcal/mole). For the migration process, the decisive role is played by the formation of a donor-acceptor bond closing the ring of the transition state. Such reactions are accelerated in polar media, and this is reflected in the decrease of the activation energy of "stannotropy" in the radical (VII) to 3.9 kcal/mole in acetonitrile.

EXPERIMENTAL

The ESR spectra were recorded in a Varian E-12A spectrometer.

The phenyldimethyltin chloride $PhMe_2SnCl$ and diphenylmethyltin chloride $Ph_2MeSnCl$ were obtained by dealkylation of Ph_2Me_2Sn and Ph_2MeSn under the influence of iodine, followed by treatment of the iodide with NaOH and dilute HCl [17-19]. The triaryltin chlorides were obtained by the Kocheshkov reaction by the action of $SnCl_4$ on the corresponding tetraarylstannanes [19, 20]. The tetrakis-(3,4,5-trichlorophenyl)stannane was synthesized by the interaction of 3,4,5-trichlorophenylmagnesium bromide with $SnCl_4$.

Tetrakis-(3,4,5-trichlorophenyl)stannane. To a solution of 3,4,5-$Cl_3C_6H_2MgBr$ (from 31 mmoles of 3,4,5-$Cl_3C_6H_3$ and 32 mmoles of Mg in 50 ml of absolute ether), under Ar, there was added with vigorous stirring and cooling (water bath) a solution of 2.09 g (8 mmoles) of $SnCl_4$ in 50 ml of absolute benzene. The reaction mixture was refluxed for 6 h and then decomposed with dilute (1/1) HCl; the precipitate was filtered off and washed with ether. After recrystallization from DMFA, obtained 5.5 g (81%) of a white crystalline substance with m.p. 266-270°C. Found: C 34.31, H 0.99, Sn 14.31%. $C_{24}H_8Cl_{12}Sn$. Calculated: C 34.27, H 1.00, Sn 14.11%.

Tris(3,4,5-trichlorophenyl)stannyl Chloride. A mixture of 4.2 g (5 mmoles) of $(3,4,5\text{-}C_{13}C_6H_2)_4Sn$ and 0.52 g (2 mmoles) of $SnCl_4$ was heated for 7 h at 270°C; the cool reaction mixture, brown in color, was treated with ether and then filtered, and the solvent was driven off. After three recrystallizations from octane with activated carbon, obtained 0.7 g (12%) of white needle crystals with m.p. 200-201°C. Found: C 31.25, H 1.33, Sn 17.46%. $C_{18}H_8Cl_{10}Sn$. Calculated: C 31.06, H 0.87, Sn 17.06%.

The radicals (I)-(IV) were obtained by mixing solutions of thallium o-semiquinolate with the monohalide organotin compounds, under vacuum at ~ 20°C. The same procedure was used in carrying out the reaction of the ligand substituent of the organotin compounds with the o-quinone. The radicals (V) and (VII)-(X) were obtained from the corresponding monochloro derivatives of Sn containing identical organic ligands, one of which splits out upon interaction with the o-quinone, indicating the great strength of the Sn–Cl bond.

Subsequently, we investigated the relative ease of splitting out phenyl and methyl ligands in the reaction of 3,6-di-tert-butyl-o-quinone (TBQ) with $ClSn(C_6H_5)Me$ and $ClSnMe_2C_6H_5$, with the aim of obtaining the radicals (V) and (VI) (see Table 1). It was established by analysis of the ESR spectra that in these reactions, the phenyl ligand splits out. This result is consistent with the generally known lability of the phenyl ligand in organotin compounds in comparison with aliphatic substituents [21].

In the example of the interaction of TBQ with triphenyltin, we demonstrated the role of the polarity of the medium in directing the substitution reaction. In nonpolar media, the phenyl ligand is replaced, forming the radical (VII); in DMSO, the ESR spectra of the reaction mixture show the presence of the radical (IV) (Table 2), identified on the basis of the HFI constants of the ring protons and ^{117}Sn and ^{119}Sn. In DMSO, apparently, abstraction of the Cl from the organotin compound becomes thermodynamically favorable because of loosening of the Sn–Cl bond upon complex formation.

CONCLUSIONS

1. For tin-containing complexes of 3,6-di-tert-butyl-o-benzoquinone, the parameters of the ESR spectra (HFI with ring protons and with ^{117}Sn and ^{119}Sn nuclei) and the distribution of spin density in the free-radical ligand depend on the nature of the substituents on the Sn atom.

2. The frequency of "stannotropic" migration in the radicals that we have investigated is determined by the strength of the Sn–O bond, the coordination unsaturation of the Sn atom, and the spin density on the univalent O atom; as these latter factors become more important, pentacoordinated structures appear, with equivalent Sn–O bonds.

3. The polarity of the medium determines the direction of the reaction of ligand substitution in the interaction of the o-quinone with organic monochlorotin compounds; in nonpolar media, the organic ligand is replaced, and in polar media (DMSO), the Cl atom is replaced.

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INVESTIGATION OF LIGAND-SUBSTITUTION REACTIONS IN PARAMAGNETIC o-QUINONE – TETRACARBONYLMANGANESE AND o-QUINONE – TETRACARBONYLRHENIUM COMPLEXES

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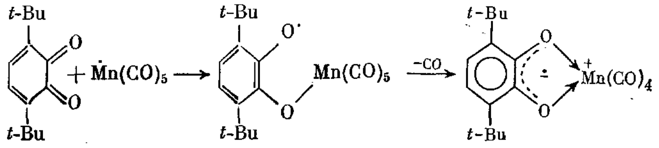
Pentacarbonylmanganese, which is obtained by photodissociation of $Mn_2(CO)_{10}$, reacts with o-chloranil (Cl_4-Q) or with 3,6-di-tert-butyl-o-quinone (3,6-Q) in two steps [1]:



(I) (II)

When we carried out this reaction in the presence of triethyl phosphite, we observed the EPR spectra of substituted derivatives containing one or two molecules of the phosphite, as can be judged from the appearance of additional splittings in the EPR spectra (Figs. 1 and 2).

In the present research in order to ascertain the effect of a paramagnetic ligand on the lability of CO groups we studied the kinetics of ligand substitution in the II radical. For this, a toluene solution of the phosphite or amine of known concentration was added to a solution of radical II in toluene (~ 0.10 mole/liter) at ~ 70°C. The spectral data are presented in Table 1, while the rate constants for substitution of one and two CO groups are presented in Table 2. Substitution of the CO groups is a stepwise process. One CO group is substituted at −40 to 0°C, while a second CO group is substituted at 5-25°C. The difference in the energies of activation for substitution of the first and second CO groups is evidently associated with the manifestation of both steric and polar factors. The decrease in k_2 in the order $P(OEt)_3 > P(OBu)_3 > P(OPr\text{-}i)_3$ is probably associated with the effect of the first factor.

In contrast to complex II, substitution in the chloranil complex takes place at a very high rate even at −80°C. Such significant acceleration is evidently associated with an increase in the acceptor properties of the ligand and with an increase in the effective positive charge on the Mn atom.

Substitution of CO by pyridine and tert-butylamine takes place with considerably greater difficulty, and only one CO group is substituted even at 80°C.

It is known that $Mn_2(CO)_{10}$ undergoes substitution of a CO group by phosphines, phospites, or amines only under the influence of UV irradiation or by heating to ~ 100°C [2] to give $[(R_3P)_2(CO)_3Mn]_2$. In [3] it was assumed that under UV irradiation conditions substitution of CO groups takes place in the more labile $\dot{M}n(CO)_5$ radical, which is formed by photodissociation of the starting dimer. It also follows from the data that we obtained that the lability of CO in the radical complexes of quinones is considerably higher than in the corresponding dimers.

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