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Thermal and Photochemical Reactions of Organotin with Aminophenols. ESR and Other Spectroscopic Study of a Novel Organotin Radical Complex of 2-Amino-4-*tert*-butylphenol

Sandip K. Sur*[†] and J. P. Colpa[‡]

Departments of Chemistry, University of Oregon, Eugene, Oregon 97403, and Queen's University, Kingston, Ontario, Canada K7L 3N6

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The thermal and photochemical reactions of organotin compounds with the 2-amino-4-*tert*-butylphenol have been studied by ESR and other spectroscopic methods at room temperature. The free radical complex generated from the ground-state reaction of the aminophenol with hexaphenylditin is very stable and shows a characteristic ESR with 15 hyperfine lines and tin satellite hyperfine splittings. The complex has been characterized by UV–visible and near-IR absorption spectroscopies. Tin is probably coordinated in this radical complex to the oxygen and nitrogen of the aminophenol. Hexamethylditin and tri-*tert*-butyl tin hydride also produce similar radical complexes.

Introduction

Aminophenols are well-known as intermediates in the manufacture of many important dyes[1] and photographic materials. Although hydroxyl radicals are known to react with aminophenols in neutral aqueous media producing phenoxyl radicals,[2,3] the interactions of organometals with aminophenols generating a new class of radical complexes have not been studied in detail.[4] Additionally, coordination of tin to two oxygen atoms in close proximity in many of its radical complexes has been investigated by electron spin resonance (ESR) and CIDEP[5,6] but coordination to two different heteroatoms such as oxygen and nitrogen is relatively sparse.[7-9] To our knowledge, there has been no report on the observation of organotin radical complex of 2-amino-4-*tert*-butyl phenol by ESR in which tin coordinates to both oxygen and nitrogen atoms in the ortho position.[9]

The thermal and photochemical reaction of organotins with quinones have been shown to take place with an initial charge transfer in the donor–acceptor complexes.[5] Organometals themselves have been recognized as highly effective electron donors in a variety of charge-transfer interactions.[5,6,9-12] Initial electron polarizations of the radicals have been studied in detail by ESR and time-resolved CIDEP, and in these systems, an unified mechanism for thermal and photochemical reactions have been suggested.[5,10]

In this paper, we report the first ESR characterization of a new class of stable organotin–*o*-aminophenol radical complexes obtained by thermal and/or photochemical reactions. As a specific example, the reaction of hexaphenylditin with 2-amino-4-*tert*-butylphenol will be discussed. These radical complexes of tin are very stable at room temperature. They also exhibit resolution of the fairly strong tin satellite hyperfine couplings in solution.

Results and Discussion

No ESR signal was observed during the continuous photolysis of aminophenols alone in benzene or in ethanol

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[†] University of Oregon.

[‡] Queen's University.

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Table I. ESR Parameters of the Radical Complex IV in Benzene at Room Temperature (See Text)

	hyperfine splittings,[b] G							
g factor[a]	$a_{^{119}\mathrm{Sn}}$	$a_{^{117}\mathrm{Sn}}$	$a_{\mathrm{N(NH)}}$	$a_{\mathrm{H(NH)}}$	$a_{\mathrm{H(3)}}$	$a_{\mathrm{H(5)}}$	$a_{\mathrm{H(6)}}$	$a_{\mathrm{H(tBu)}}$
2.0025	56.76	54.32	5.16	6.88	1.72	3.44	1.72	<0.10

[a] Accuracy ±0.0001. [b] Accuracy ±0.02.

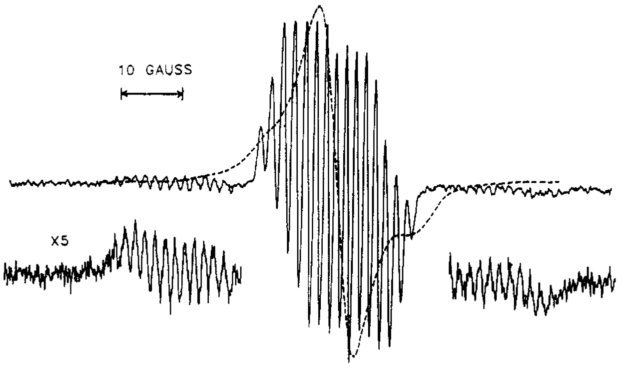
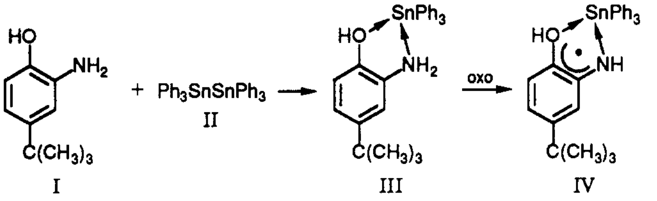


Figure 1. The X-band ESR spectrum of the radical complex IV obtained by ground-state reaction of 2-amino-4-*tert*-butylphenol with hexaphenylditin in benzene at room temperature (~296 K). The inset shows the vertically magnified portions of the wing lines with tin satellite splitting. The dotted line is from the powder sample of the same complex recorded under similar conditions except at a gain 20 times less (see text). Instrumental parameters are as follows: modulation amplitude 0.02 G, scan time 16 min, time constant 0.128 s, microwave power 2 mW.

solutions at room temperature. However, intense ESR signals were obtained when such solutions were irradiated in the presence of di-*tert*-butyl peroxide. The formation of their respective phenoxyl radicals in these aminophenol systems have been identified by their ESR spectra.[2,3] Although radicals from 2- and 4-aminophenols decay as soon as irradiation is stopped, the 2-amino-4-*tert*-butyl phenoxyl radicals are persistent at room temperature for up to 12–15 h.

When hexaphenylditin (II) was added to solutions of the respective aminophenols at room temperature, 2-amino-4-*tert*-butylphenol (ABP, I) immediately gave a characteristic ESR spectrum consisting of 15 well-resolved hyperfine lines (see Figure 1). The ESR spectrum of its powdered sample is also included in the figure. It is to be noted that the solution ESR spectrum is sensitive to oxygen and the best resolution is obtained from a dilute oxygen-free solution of the complex.



The assignment of the ESR to a pentacoordinated tin radical complex IV of the ABP has been made by observation of the clear tin satellite hyperfine splittings (^{117}Sn and ^{119}Sn, $I = {}^1/_2$)[5,13,14] and by computer reconstruction of the 15-line ESR spectrum.[15] No further smaller hyperfine couplings could be resolved in these spectra. The initial radical III is probably unstable in solution and immediately oxidized to the more stable species IV.[9] Following Stegmann et al.,[4] the 15 resolvable hyperfine lines may be explained by considering accidental equivalence of protons at positions 3 and 6 and both nitrogen and proton of the NH group have similar splitting. In the organotin complex with 2-amino-4-(triphenylmethyl)-6-*tert*-butylphenol, the unpaired spin density at position 3 is negligible.[4] The smaller splitting of 1.72 G has, therefore, been assigned to protons at positions 3 and 6. The ESR parameters are presented in Table I. The unresolved hyperfine splittings from protons of the $C(CH_3)_3$ group of IV is very small (<0.1 G).

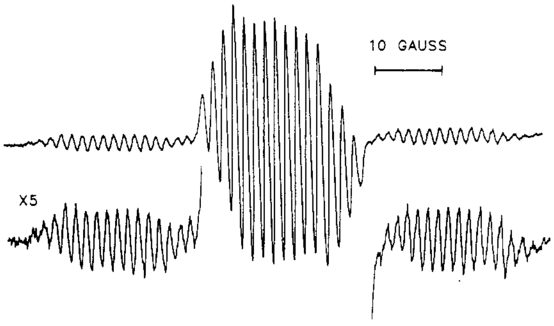


Figure 2. The X-band ESR spectrum of the radical complex obtained by ground-state reaction of 2-amino-4-*tert*-butylphenol with tri-*tert*-butyltin hydride in benzene at room temperature (~296 K). The inset shows the vertically magnified portions of the wing lines with tin satellite splitting. Instrumental parameters are as follows: modulation amplitude 0.05 G, scan time 16 min, time constant 0.128 s, microwave power 2 mW.

Aminophenol I also reacts at room temperature with organogermanium and organolead compounds giving similar 15-line ESR spectra. Reaction of ABP with other tin hydrides produces similar results. The ESR of the complex from tri-*tert*-butyl tin hydride is presented in Figure 2, in which the tin splittings are more prominent. Although g factors are very similar among a series of organotin radical complexes, there is, however, minor differences in the hyperfine splittings and in the resolutions of the spectral lines.

The observed g factor of 2.0025 ± 0.0001 (negative g shift) for the complex of organotin and the isotropic tin satellite splitting ($a_{^{119}\mathrm{Sn}} = 56.8$ G) suggest that the unpaired electron is delocalized onto vacant d orbital of the tin.[16] Increasing the atomic number of the metal in these organometallic radical complexes should, therefore, decrease the g factor. This trend has indeed been observed. Thus although organogermyl and organoplumbyl radical complexes are not formed as efficiently as organostannyl radicals, the resulting isotropic ESR spectra in each case consist of 15 identifiable lines with comparable hyperfine splittings. The g factors of these complexes (for organogermyl, $g_{\mathrm{iso}} = 2.0029$ and for organoplumbyl, $g_{\mathrm{iso}} = 2.0013$) decrease in the series Ge > Sn > Pb presumably due to appreciable metal d orbital participation in the unpaired spin density distribution.

The radical is very stable in nonpolar solvents and in the solid-state. When generated in ethanol solution,

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however, the radical decays within ~2 h. No ESR could be observed in solvents such as acetic acid and pyridine, showing that the radical stability is solvent dependent and it is best produced in a solvent like benzene. The bluish powder[17] of the complex obtained by evaporating a benzene solution of hexaphenylditin(II) and aminophenol(I) in equivalent amounts gives intense ESR signal as shown by solid lines in Figure 1. The stability of the radical is probably in part due to steric reasons associated with the *p*-*tert*-butyl group. Other spectroscopic measurements on this complex will be discussed later.

Under similar conditions, 2-aminophenol and 4-aminophenol failed to produce any radical complex at room temperature. When irradiated, 4-aminophenol gave only its phenoxyradicals, probably by reaction with $^{\bullet}SnPh_3$ radical (Sn–Sn bond dissociation energy is 53 kcal mol^{-1}).[14]

ESR signal obtained by ground-state interactions between ABP and organoditin is enhanced by UV irradiation for a short period of time (~10 s),[18] presumably due to the formation of reactive $^{\bullet}SnPh_3$ radicals which subsequently reacts with ABP. The radical complex is, therefore, produced not only thermally but also photochemically.[5,10]

The optical absorption spectra of the radical complex has been recorded in various solvents. It has characteristic bands with λ_{max} at ~393 and 578 nm in benzene. The λ_{max} of ABP itself in benzene occurs at 292 nm. The broad band at 578 nm is probably due to metal–ligand charge transfer in this complex supporting our ESR observation of appreciable metal d orbital participation in the stability of the radical. The near-IR measurements show overtone bands at 6060 cm^{-1} and two combination bands of the aromatic C–H vibrations at 4650 and 4059 cm^{-1}.

Conclusion

The spontaneous ground-state reaction of the organotin compounds with 2-amino-4-*tert*-butylphenol at room temperature is demonstrated by ESR measurements, taking hexaphenylditin as the model organotin compound. A very stable radical complex, in which tin is probably coordinated to the oxygen and nitrogen of the aminophenol, is formed. 2-Aminophenol and 4-aminophenol do not react under similar conditions. The radical complex has been characterized by UV–visible and near-IR absorption spectrophotometry.

Experimental Section

2-Amino-4-*tert*-butylphenol, 2-aminophenol, and 4-aminophenol were purchased from Aldrich Chemicals and were purified by sublimation. Hexaphenylditin, tri-*tert*-butyltin hydride and other organometallic compounds were supplied by Alfa Inorganics and were used as received. All solvents were purified by standard procedures.[19] The purity of the reagents used in this study were checked by IR using a Nicolet 5DXB FT-IR spectrometer and by NMR using a GE QE-300 FT-NMR spectrometer.

CW-ESR spectra were recorded with 100 kHz magnetic field modulation on a Varian E-109 X-band spectrometer equipped with Varian E-272B Field/Frequency lock assembly and a Nicolet 1280 computer for data acquisition and manipulations.[20] Standard sample of DPPH was used as *g* marker and for magnetic field calibration.

All measurements were carried out at room temperature (~296 K). A standard sample consisted of about 1-mL solution containing 10^{-2} M aminophenol and 5×10^{-3} M organoditin in a 4-mm quartz tubing which was thoroughly degassed with nitrogen and sealed closed. The sample was irradiated in situ in the ESR cavity by using a high-pressure mercury arc lamp.

The UV–visible and near-IR absorption spectra of sample solutions were recorded on a Perkin-Elmer DU-7 and on a Coleman Model EPS-3T spectrophotometers.

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Registry No. I, 1199-46-8; II, 1064-10-4; IV, 123125-63-3; 2-aminophenol, 95-55-6; 4-aminophenol, 123-30-8; hexamethylditin, 661-69-8; tri-*tert*-butyltin hydride, 16216-29-8.

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(17) The solid sample can be stored for days without any indication of decaying as measured by ESR signal intensity.

(18) CIDEP measurements done in the laboratory of Dr. J. K. S. Wan of Queen's University show that the photochemical formation of the radical occurs with weak polarization in the emissive mode.

(19) Particular care was taken to dry solvents used in this study. Benzene was dried over sodium and distilled. The radical complexes are rather unstable in polar solvents.

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Synthesis and Characterization of Dimethyltin(IV) Derivatives of Fluoro- and Oxyfluorochromates

Siva P. Mallela and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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Dimethyltin(IV) fluoride reacts with CrO_2F_2 to yield a $(CH_3)_2Sn$-containing derivative, while with $CrOF_4$ and CrF_5 only $(CH_3)_2SnF$ derivatives are obtained. Anhydrous HF is found to be necessary for the reactions to proceed at room temperature, and, in its absence, $(CH_3)_2SnF_2$ did not react with CrO_2F_2 even at high temperature. The vibrational data are consistent with a linear C–Sn–C group in each of these derivatives. Reaction of CrO_2F_2 with elemental fluorine in the presence of either CsF or NOF provides a one-step direct route to $CsCrOF_5$ or $NOCrOF_5$ salts. Reaction of either CrO_2F_2 or CrO_3 with COF_2 in the presence of CsF is another simple, convenient, new synthetic route to the $CsCrOF_5$ salt.

Introduction

While the dark violet-red crystalline solid CrO_2F_2 (mp 31.6 °C, to yield an orange-red liquid and red-brown vapor) can be obtained in a variety of ways, the most convenient and nearly quantitative synthetic route is the fluorination of CrO_3 with carbonyl difluoride.[1] Salts of the type $M_2CrO_2F_4$ can be conveniently obtained from CrO_2F_2 and alkali-metal fluorides.[2,3] The interesting oxofluoride

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