Reaction of Phenyllithium with 3,5-Di-*tert*-butyl-*o*-benzoquinone (TBQ) and Structure of $Li^+(TBSQ^{\bullet -})$ in Solution

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Received April 23, 1996[⊗]

Abstract: The reaction between phenyllithium and substituted *o*-quinones (3,5-di-*tert*-butyl-1,2-benzoquinone (TBQ), 1,2-naphthoquinone, 9,10-phenanthrenequinone) results in the oxidation of $C_6H_5^-$ to $C_6H_5^\bullet$, with the subsequent formation of biphenyl. Metathetical reactions yield M(TBSQ) (M = Li, Na, K; $TBSQ^-$ = 3,5-di-*tert*-butyl-1,2-benzosemiquinone) and the adduct Li(TBSQ)bpy (bpy = 2,2′-bipyridine). Solutions of Li(TBSQ) + pyridine in toluene contain triradical species, and analysis of the EPR spectra leads to values for the spin−spin parameters. Similar results have been obtained for Na(TBSQ). An ideal structure has been calculated for $[Li(C_6H_4O_2^\bullet)]_3$; the magnetic properties for the resultant model are in good agreement with the experimental values, and the bond distances and angles with those for known oligomeric lithium complexes.

Introduction

Reactions between main-group organometallic compounds and substituted *o*-quinones, which have been the subject of recent work in this laboratory,[1−3] may involve the oxidation of the metal itself and/or reaction between the quinone and the organic ligand. It therefore seemed reasonable to investigate what is in principle the simplest example of the latter process, namely, the reaction between phenyllithium and an *o*-quinone, using in the main the much studied 3,5-di-*tert*-butyl-1,2-benzoquinone (TBQ). The reaction scheme for this system, in which the primary product is the corresponding $Li^+(TBSQ^{\bullet -})$ ($TBSQ^{\bullet -}$ = 3,5-di-*tert*-butyl-*o*-semiquinonate anion), has been established.

During these investigations, in which electron paramagnetic resonance (EPR) spectroscopy was an important tool, we found evidence for the aggregation of Li(TBSQ) species in toluene solution. In analyzing these results and those for the analogous sodium and potassium systems, we used the methods successfully applied in previous work on $M(TBSQ)_2$ species (M = Mg, Zn, Cd, Ba).[4] These allowed us to establish both the state of association and the distance between the $TBSQ^{\bullet -}$ ligands. The results are compared with earlier work on $M(TBSQ)_2$ and on the stereochemistry of other related complexes of the alkali metals. Molecular orbital calculations allowed the prediction of a likely structure for a trimeric species which is present in solutions of Li(TBSQ) in toluene.

Experimental Section

General Data. Metals (Li, Na, K) were cut into small pieces from the commercially available material. Phenyllithium, TBQ, and *N,N,N′,N′*-tetramethylethanediamine (tmed) were used as supplied (Aldrich). All solvents were dried, redistilled, and degassed before use. Microanalysis was by Canadian Microanalytical Services. Mass spectrometry was carried out with a Shimadzu 14-B instrument operating in the E.I. mode, with Sun Sparc software.

All reactions were carried out in an atmosphere of dry nitrogen, using conventional vacuum line techniques.

Electron Paramagnetic Resonance Spectrometry. A Bruker ESP-300E spectrometer was used to record EPR spectra in the X-band region and a Bruker nuclear magnetometer and a Hewlett-Packard microwave frequency counter served for calibration purposes. Low-temperature spectra were measured with the help of a cooled (liquid nitrogen Dewar) cavity insert. The relevant operating frequencies were ca. 9.80 GHz (room temperature) and 9.44 GHz (77 K). Simulations of the spectra of frozen solutions involved both in-house programs and Bruker's Symphonia Program.

Preparative Methods. *(i) PhLi/TBQ reaction*: When a solution of PhLi (0.42 g, 5 mmol) in cyclohexane/diethyl ether (5 mL, 70/30/v/v) was added dropwise to a solution of TBQ (1.0 g, 4.5 mmol) in toluene (30 mL), the characteristic deep blue color of the $TBSQ^{\bullet -}$ radical was immediately apparent. Partial evaporation of the solvent in vacuo, followed by the addition of cyclohexane until the solution turned slightly cloudy, and cooling, caused the deposition of a blue solid which was characterized analytically as Li(TBSQ). Anal. Calcd for $C_{14}H_{20}O_2Li$: C 74.0, H 8.87. Found: C 74.3, H 8.70. Samples of the solution phase from this reaction were subjected to mass spectrometric analysis.

(ii) TBQ/M (M = Li, Na, K): Samples of M (TBSQ) were prepared by the direct reaction of metal with a toluene solution of an equimolar quantity of TBQ (ca. 5 mmol of each). The solids which precipitated on partial removal of solvent were the appropriate M(TBSQ) compounds. Anal. Calcd for $C_{14}H_{20}O_2Li$: C 74.0, H 8.80. Found: C 74.2, H 8.70. Anal. Calcd for $C_{14}H_{20}O_2Na$: C 69.1, H 8.29. Found: C 69.0, H 8.40. Anal. Calcd for $C_{14}H_{20}O_2K$: C 64.8, H 7.77. Found: C 64.7, H 7.70. These solids were used in the EPR studies described below.

(iii) PhLi/phenanthrenequinone and naphthoquinone: Solutions of phenyllithium were treated with equimolar quantities of either 1,2-naphthoquinone or 9,10-phenanthrenequinone, following the procedures outlined in (i) above. The addition of *n*-hexane, followed by cooling at ∼0 °C, led to the deposition of crystals identified as the appropriate Li(SQ) product, solvated by toluene.

1,2-Naphthoquinone. Anal. Calcd for $C_{10}H_6O_2Li\cdot 0.5C_7H_8$: C 76.8, H 4.77. Found: C 76.9, H 5.00.

9,10-Phenanthrenequinone. Anal. Calcd for $C_{14}H_8O_2LiC_7H_8$: C 82.1, H 5.25. Found: C 82.3, H, 5.40.

Solutions of these compounds were also studied by EPR spectroscopy, with results very similar to those discussed below.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Annan, T. A.; Ozarowski, A.; Tian, Z.; Tuck, D. G. *J. Chem. Soc., Dalton Trans*. **1992**, 2931.

(2) Tian, Z.; Tuck, D. G. *J. Organomet. Chem*., **1993**, *462*, 125.

(3) Brown, M. A.; Tuck, D. G., unpublished results.

(4) Ozarowski, A.; McGarvey, B. R.; Peppe, C.; Tuck, D. G. *J. Am. Chem. Soc*. **1991**, *113*, 3288.

S0002-7863(96)01346-7 CCC: $12.00

(iv) Adducts of Li(TBSQ): The addition of strong nitrogen donors such as pyridine, γ-picoline, tmed, or 2,2′-bipyridine (bpy) caused a considerable improvement in the resolution of the EPR of Li(TBSQ) (see below). The addition of a 3-fold excess of 2,2′-bipyridine to a solution of Li(TBSQ) in toluene, prepared by method (i), gave a solid which was identified as Li(TBSQ)•bpy. Anal. Calcd for $C_{24}H_{28}O_2N_2Li$: C 75.2, H 7.36. Found: C 74.6, H 7.60. This compound failed to yield crystals suitable for crystallographic study, despite many attempts using widely differing conditions; replacement of 2,2′-bipyridine with other bidentate oxygen or nitrogen donors did not improve this situation.

Results

PhLi−*o*-Quinone Reactions. The rapid color changes which are observed on mixing solutions of PhLi and three orthoquinones studied, together with the analytical results and the EPR spectra (see below), show that the primary reaction is (e.g.)

$$\mathrm{PhLi} + \mathrm{TBQ} \rightarrow \mathrm{Li}^{+}(\mathrm{TBSQ}^{\bullet -}) + \mathrm{Ph}^{\bullet} \qquad (1)$$

Each of these orthoquinones is thus a sufficiently strong oxidizing agent to cause the process

$$\mathrm{Ph}^{-} \rightarrow \mathrm{Ph}^{\bullet} \qquad (2)$$

to go from left to right, with preparative yields in the order of 60−70%.

The fate of the phenyl radicals released by eq 1 can be identified from the mass spectrum of the mother liquor from the reaction. The most prominent peak at *m/e* = 154 corresponds to Ph_2, and this was confirmed by the isotopic distribution (calcd 154, 88.1, 155, 11.9%, ratio 7.42; experimental ratio 5.1) and the exact mass at *m/e* = 154 (calcd 154.0783, found 154.0779). A weaker peak at *m/e* = 182 indicates the formation of dibenzyl, presumably by reaction of $Ph^{\bullet}$ with solvent:

$$\mathrm{Ph}^{\bullet} + \mathrm{PhCH_3} \rightarrow \mathrm{Ph_2\dot{C}H_2} + \mathrm{PhH} \qquad (3)$$

$$2\mathrm{Ph\dot{C}H_2} \rightarrow \mathrm{PhCH_2CH_2Ph} \qquad (4)$$

The other interesting feature of the mass spectra of solution of Li(TBSQ) in toluene are weakly abundant ions corresponding to Li(TBSQ), $TBSQ^{\bullet -}$, $(TBSQ)_2^{\bullet -}$, and $(TBSQ)_3^{\bullet -}$. We do not ascribe any structures to these ions, but the existence of such clusters is interesting in the light of the species identified in the solution phase by EPR spectroscopy (see below).

Electron Paramagnetic Resonance Results

M(TBSQ). The solutions exhibit a moderately broad featureless $S = {}^1/_2$ signal with $g = 2$ for M = Li, Na, and K at room temperature, but frozen solutions show a complex splitting pattern due to spin−spin interactions, indicating the presence of mixture of associated species containing at least two semiquinone free radicals, in addition to the monoradical. The presence of a signal at half the resonant field from the $\Delta M_s = \pm 2$ transition confirms the existence of these aggregates.

M(TBSQ) plus Base. With the introduction of excess base such as pyridine, the resolution improves and hyperfine splitting becomes evident. At higher concentrations a doublet spectrum is observed, with the splitting due to the 4-H proton of the $TBSQ^{\bullet -}$ radical. At lower concentrations and with careful removal of oxygen, the resolution improves. The spectra for the dilute ($\sim 10^{-3}$ M) solutions in toluene containing excess pyridine for M = Na are shown in Figure 1. The spectrum of Na(TBSQ) shows the 2.99 G splitting, due to the 4-H proton, and smaller splittings arising from the 6-H proton and the 5-*tert*-butyl protons. It will be noted that there is a weak series of lines outside the main spectrum, caused by the presence of another magnetic species. The smaller spacing is the same as the hyperfine splitting of the 5-*tert*-butyl group in the $TBSQ^{\bullet -}$ radical, and the separation of the outside patterns is exactly double that of the 4-H proton in the main free radical, leading us to conclude that we have a triplet pattern due to two equivalent protons. This suggests the presence of a biradical containing two semiquinones, with an exchange interaction much larger than the Zeeman interaction. The spectrum for Li(TBSQ) appears mainly to be a broad line exhibiting only a splitting of an approximate 3 G, with a weaker but sharper spectrum superimposed. This highly resolved but weak spectrum is identical with that of the monoradical spectrum of Na(TBSQ) and must be due to the corresponding lithium monoradical. It follows that most of the Li(TBSQ) must be in some form other than the monoradical even at these low concentrations.

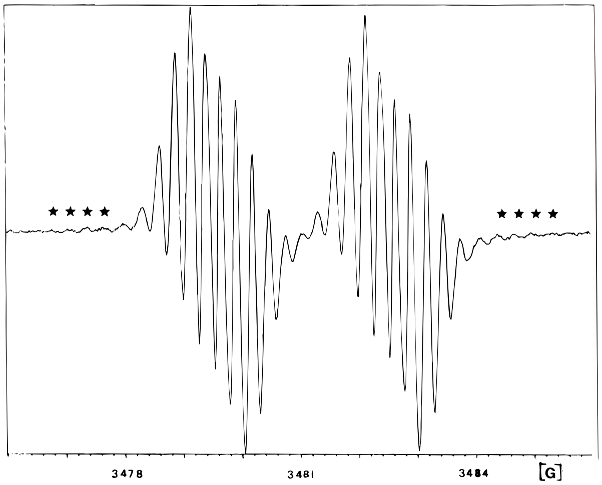

Figure 1. EPR spectrum of a dilute ($\sim 10^{-3}$ M) solution of Na(TBSQ) + pyridine in toluene at room temperature. Asterisks identify weak features due to another species present in the solution.

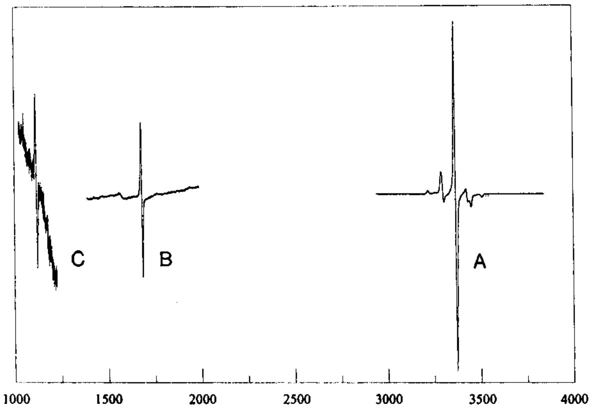

Figure 2. EPR spectra of a dilute ($\sim 10^{-3}$ M) frozen solution of Li(TBSQ) + pyridine in toluene at 77 K. (A) Central region of spectrum. (B) Spectrum at half-field ($\Delta M_s = \pm 2$). (C) Spectrum at one-third field ($\Delta M_s = \pm 3$).

In frozen solutions we find spin−spin splittings identical with those seen in the absence of base, but there is only one aggregate cluster, whose concentration relative to the monoradical is much larger than is the case in the absence of pyridine. The most striking example is that of Li(TBSQ) with excess pyridine, the spectra of which are shown in Figure 2. Not only do we record the signal from the $\Delta M_s = \pm 2$ signal at half-field, but in addition the forbidden $\Delta M_s = \pm 3$ signal at one-third the resonant field is also detected, indicating that the aggregate is likely a trimer

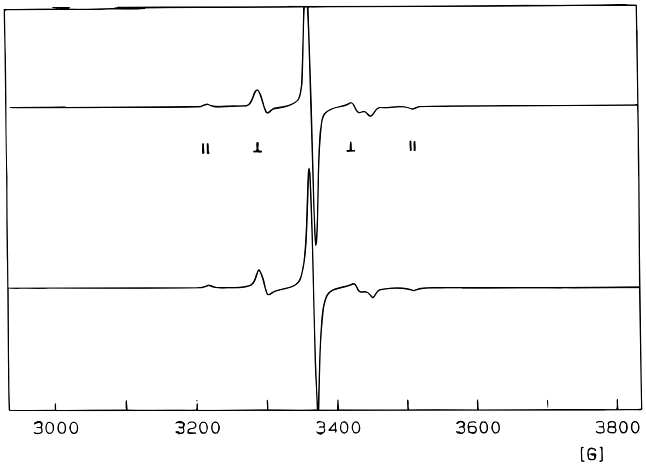

Figure 3. EPR spectrum of a dilute (~10^{-3} M) frozen solution of Li(TBSQ) + pyridine in toluene. Upper trace, experimental; lower trace, simulated spectrum using values given in the text. The ⊥ and II signs identify the region of the spectrum due to molecules with their main axis perpendicular and parallel to the magnetic field.

radical. It should be noted that these different regions of Figure 2 were recorded with differing gain settings.

We have simulated the monoradical region of this spectrum using the spin Hamiltonian

$$H = \beta[g_xS_xB_x + g_yS_yB_y + g_zS_zB_z] + D[S_z^{\,2} - {}^1/_3S(S+1)] + E[S_x^{\,2} - S_y^{\,2}] \quad (5)$$

The simulation is shown in Figure 3 assuming $S = {}^3/_2$. The fitting parameters have the values $g_x = 2.0044$, $g_y = 2.0008$, $g_z = 2.0043$, $D = 68.2 \times 10^{-4}$ cm^{-1}, and $E = 2.5 \times 10^{-4}$ cm^{-1}. These g values are good to ±0.0002, and the D and E parameters to $\pm 0.1 \times 10^{-4}$ cm^{-1}. The uneven splitting in the perpendicular region of the spectrum is caused by a combination of E with the anisotropy of g in the xy plane. It is interesting to note that the total signal is very closely simulated and that there is no apparent contribution from any monoradical. We have repeated this experiment at different concentrations of Li(TBSQ) and different ratios of pyridine to Li(TBSQ) and find no evidence of dissociation of the trimer to monomer in any case. At higher concentrations of Li(TBSQ), the line width increases, giving a poorer resolution than that displayed in Figure 2. This trimer appears to quite stable over time in solution.

A similar spectrum is seen in the case of Na(TBSQ), but the central $g = 2$ line is more intense relative to the outside lines, indicating that in such solutions monomer is also present. The fraction of monomer increases as the concentration of Na(TBSQ) is decreased. In this system we easily detected the $\Delta M_s = \pm 2$ transition but were never able to detect the very weak $\Delta M_s = \pm 3$ transition. We presume the spectrum is that of species analogous to those in M = Li system because the spin Hamiltonian parameters are so similar. The fitted parameters are $g_x = 2.0061$, $g_y = 2.0017$, $g_z = 2.0051$, $D = 55.6 \times 10^{-4}$ cm^{-1}, $E = 1.5 \times 10^{-4}$ cm^{-1}. The D value for the sodium compound is smaller than that for the lithium system, which is consistent with the larger radius of the sodium ion, which will place the three semiquinone free radicals further apart from each other than in the lithium complex. In some preparations, we saw evidence of a much less intense spectrum from another species with even larger spin−spin splittings, but we have not been able to identify the origin of this.

For the potassium compound there is evidence of spin−spin bands, but their intensity relative to the strong $S = {}^1/_2$ signal makes it impossible to carry out any simulation. A signal at $\Delta M_s = \pm 2$ indicates that clusters also exist in these solutions.

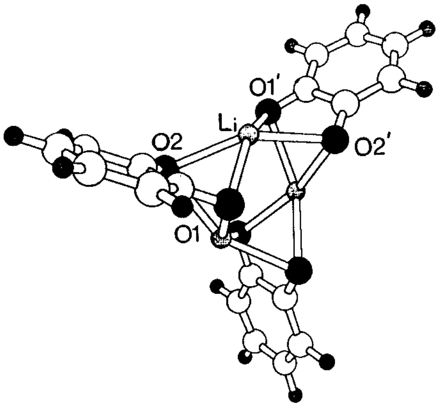

Figure 4. Minimum energy structure of $[\mathrm{Li(C_6H_4O_2^{\bullet})}]_3$ as calculated by MOPAC-6.

Discussion

It is quite apparent that Li(TBSQ) and Na(TBSQ) form a trimer $\mathrm{M_3(TBSQ)_3py}_n$ in the presence of excess pyridine in solution. Our EPR evidence was obtained from frozen solutions, and we therefore have no direct evidence of trimer formation in liquid solutions at room temperature, but the solution EPR does not contradict the existence of trimers or other aggregates since theory[4,5] predicts the same spectrum as that of the monoradical, provided that the spin-exchange interaction between the semiquinones is negligible. The striking difference in resolution between the liquid solution spectrum of Li(TBSQ) and Na(TBSQ) suggests that the trimer still exists for Li(TBSQ) in the solution phase but not for Na(TBSQ), since larger line widths would be likely for the trimer due to the very rapid tumbling motions needed to average out the zero-field splittings.

Repeated attempts to obtain crystals from these solutions for X-ray analysis have been unsuccessful, and we therefore used the molecular orbital program MOPAC 6, installed on the University of Windsor SGI server, to predict the probable structure of the trimer. To keep the number of atoms in this calculation to a reasonable level, we omitted both pyridine and the *tert*-butyls of TBSQ, so that the molecule studied is actually $[\mathrm{Li(C_6H_4O^{\bullet}_2)}]_3$. The calculation identifies the most stable structure by minimizing the energy, and the result is shown in Figure 4; the enthalpy of formation for this form of the trimer is −966 kJ mol^{-1}. This molecule has a C_3 axis, which cannot be valid for the frozen solution species which we detected, since the E parameter would in that case be zero, but this difference may well be the result of using unsubstituted *o*-quinone rings in the calculation, rather than the di-*tert*-butyl system studied experimentally.

We have used the positional coordinates determined by the MOPAC program to calculate the D value from the spin−spin interactions. This calculation is essentially identical with that used for the triradical Ga(TBSQ)$_3$, and in this case the electron densities do take account of the asymmetry due to the presence of substituents.[5] The calculated values are $D = 75.4 \times 10^{-4}$ cm^{-1} for Li and 58.8×10^{-4} cm^{-1} for Na, both of which compare favourably with those obtained from the spectral analysis (Li 68.2×10^{-4} cm^{-1}, Na 55.6×10^{-4} cm^{-1}), so that a structure of the form shown in Figure 4 is consistent with the observed EPR spectra.

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(5) Ozarowski, A.; McGarvey, B. R.; El-Hadad, A. A.; Tian, Z.; Tuck, D. G.; Krovich, D. J.; Defotis, G. C. *Inorg. Chem.* **1993**, *32*, 841.

Table 1. Calculated Bond Distances (Å) and Angles (deg) for $[Li(C_6H_4O_2^{\bullet})]_3$

Li−O	2.21	O1−Li−O2	76
C−O	1.29	O2−Li−O1′	89.5
C1−C2	1.52	O1−Li−O1′	139
C2−C3	1.46	Li−O−Li	82
C3−C4	1.38	C−O−Li	95
C4−C5	1.44		
C5−C6	1.38		
C6−C1	1.46		

The reliability of the model structure can also be judged by comparing the calculated bond distances and angles (Table 1) with those obtained by X-ray crystallographic analysis of related compounds. There are several structural determinations of oligomeric lithium complexes, but none is isostructural with that shown in Figure 4. In the hexameric $[Li(t\text{-}C_4H_9(CH_3)CO)]_6$, hexagonal Li_3O_3 planes are linked by Li−O bonds; the range of Li−O bond distances is 1.852(8)−1.976(9) Å.[6] In the cation $[Li(1,2\text{-dimethoxyethane})_3]^+$, the values lie between 2.09(1) and 2.20(3) Å, and in $[Li(dme)_2]Br$, in which lithium is five-coordinate, the range is 2.064(9)−2.112(4) Å.[7] The complex $(LiOAr)_3$, where OAr = 2,6-dimethylamino(methyl)-4-methylphenate, contains an almost perfect Li_3O_3 plane in which Li−O = 1.865(9) Å (av).[8] The Li−O bond distance of 2.21 Å is clearly higher than most of these values, but this may be a consequence of the bonding to bridging and bidentate ligands. Equally relevant are the *r*(C−O) value of 1.29 Å, and the O−Li−O bite angle of 76°, which are very close to those in $Ga(TBSQ)_3$ (*r*(C−O) = 1.29(2), O−Ga−O = 82.4(4)°) and $In(TBSQ)Br_2(pic)_2$ (pic = 4-methylpyridine) (*r*(C−O) = 1.28(2) Å, O−In−O = 74.8(2)°),[9] so that the derived structure is in agreement with the presence of *o*-semiquinone ligands.

Conclusion

The oxidation of phenyllithium by various substituted orthoquinones leads to the formation of the appropriate lithium semiquinone. The EPR spectra of the 3,5-di-*tert*-butylsemiquinone compound shows that the trimer is the predominant species in solution, and molecular modeling of this system gives rise to a structure which is compatible with the EPR results and with crystallographic data on related lithium complexes.

Acknowledgment. This work was supported in part by Research Grants (to B.R.M. and D.G.T.) from the Natural Sciences and Engineering Research Council of Canada.

JA9613466

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[6] Willard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3845.

[7] Atwood, J. L.; Rogers, R. D.; Vann Bynum, R. *Acta Crystallogr. Sect. C* **1984**, *40*, 1812.

[8] van der Schaaf, P. A.; Hogerheider, M. P.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1703.

[9] Annan, T. A.; Chadha, R. K.; Doan, P.; McConville, D. H.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chem.* **1990**, *29*, 3936.