SYNTHESIS OF LEAD CATECHOLATE BY THE DIRECT OXIDATION OF METAL

Stanislav V. Maslennikov*[1], Olga Y. Chekhonina[1], Irina V. Spirina[1],
Alexandr V. Piskounov[2] and Vladimir K. Cherkasov[2]

[1] Chemistry Research Institute at Nizhny Novgorod State University, 23/5 Gagarin av., 603600 Nizhny Novgorod, Russia, <masv@uic.nnov.ru>
[2] G.A. Razuvaev Organometallic Chemistry Institute, 49 Tropinina str., 603600 Nizhny Novgorod, Russia

ABSTRACT

3,5-Di-*tert*-butyl-1,2-benzocatecholate of lead (II) of formula $[Pb(TBCat)]_n$ (where TBCat is 3,5-di-*tert*-butyl-1,2-benzocatecholate) was obtained by the direct oxidation lead metal. The reaction proceeds in both polar and non-polar solvents with the maximum of the reaction rate in THF. The signal of a free radical-anion bonded to a metal was observed in the ESR spectra during the course of the reaction. Due to the low solubility of lead the equilibrium of semiquinolate with quinone and catecholate is shifted to the lead catecholate. The kinetic regularities of lead oxidation by 3,5-di-tert-butyl-1,2-benzoquinone were obtained.

INTRODUCTION

Quinone derivatives of metals are well known in the literature. One of convenient methods of their synthesis is reacting of compact metals with quinones. Metals that tend to form single-charged cations (Li, Na, K, Cu) most easily react with 3,5- and 3,6- di-tert-butyl- 1,2 -benzquinone [1,2]. Non-transition metals of the groups II-IV do not react with quinones in non-polar solvents at the temperatures below 100°C and using their amalgams has been suggested to make them react with quinones [3]. Tuck et al have used boiling in toluene for obtaining quinone derivatives of non-transition metals of groups II-IV [4-10]. Using coordinating donor solvent significantly accelerates the reaction and allows it to proceed it under the normal conditions [11-13]. Kinetic regularities of the reaction of Mg, Zn, Cd, Sn, Cu with 3,5 - di- tert-butyl- 1,2 - benzoquinone in polar coordinating solvents have been described in [11-13]. The only known method of obtaining lead catecholate has been the decomposition of diethyllead catecholate [14]. Hereby we report a novel method of obtaining 3,5 - di- tert-butyl- 1,2 lead catecholate by reacting metallic lead with the oxidizer as well as kinetic particularities of this reaction.

MATERIALS AND METHODS.

3,5-di-tert-butyl-1,2-benzoquinone (TBQ) was prepared by the method described in [15]. Solvents used for the reaction (heptane, toluene, acetonitrile, methylacetate, ethylacetate, THF, diglyme, dimethylformamide DMFA, dimethylacetamide DMAA, DMSO, pyridine, hexamethylphosphortriamide HMFTA) were purified and dried as described in [16]. All reactions of 3,5 - di-tert-butyl-1,2- benzoquinone were carried out under vacuum or anhydrous and oxygen free argon. Lead (99.8% purity, TU 6-09-1490-75) was used as a wire without additional treatment of surface.

Lead catecholate was obtained as following. To a mixture of lead (311 mg, 1.5 mmol) and TBQ (845 mg, 4 mmol) a solvent (10 ml) was added under vacuum. The reaction mixture was stirred at 50°C for 24-72 hours depending on the solvent used. By the end of the reaction the mixture became pale-yellow and a massive precipitate was formed which was isolated by washing with heptane and consequent drying under vacuum. The product yield was 81%. Elemental analysis: Calc. for $PbC_{14}H_{20}O_2$: C, 39.33%; H, 4.72%; O, 7.48%; Pb, 48.47%; found: C, 39.44%; H, 4.67%; O, 7.57%; Pb, 32.81%. The compound obtained was insoluble in both polar and non-polar solvents, sensitive towards the air.

The rate of lead reaction with 3,5-di-tert-butyl-1,2-benzoquinone was measured by controlling the electric resistance of the lead wire put in the reaction mixture [17]. This method was modified for performing experiments in inert atmosphere.

ESR spectra were recorded on a Bruker ESR-2000-SRC spectrometer with a standard double resonator ER-4105-DR with a frequency of 9.5 GHz. Diphenylpicrylhydrazyl was used as a reference for determining g-factor.

RESULTS AND DISCUSSION

The reaction of lead with TBQ leads to the formation of the lead (II) catecholate. The composition of the compound was confirmed by the elemental analysis. Unfortunately, due to the very low solubility of lead catecholate obtaining NMR spectrum or X-ray suitable crystals wasn't possible.

The reaction proceeds in both polar and non-polar solvents. The dependence of the reaction rate on the donor number of the solvent used has an extremis in THF (table I). Similar regularities were observed for the reactions of Mg, Zn, Cd, In and Sn with quinones [11-13, 20].

Table I
The rate of lead oxidation by 3,5 - di-tert-butyl-1,2-benzoquinone (TBQ) in different solvents. T= 293 K. C_{TBQ}=0.1 mol/l

Solvent	DN_{SbCl_5} [21]	$V \cdot 10^{-}$[illegible], $g \cdot cm^{-2} \cdot min^{-1}$
Heptane	0	1.0
Toluene	1.8	1.0
Acetonitrile	60	1.5
Methylacetate	69	2.7
Ethylacetate	72	4.5
THF	84	7
Diglyme	100	1.4
DMFA	111	1.7
DMAA	116	1.7
DMSO	125	1.7
Pyridine	139	1.9
HMFTA	162	2.0

ESR spectra of the reactions carried out in toluene and DMSO were recorded. Almost immediately after the beginning of the reaction doublets with lead satellites appear in the isotropic spectra of the reaction mixtures (g_i=1.9997, A_H=3,4 G, $A_{^{207}Pb}$=65.9 in toluene and g_i=1.9993, A_H=3,4 G, $A_{^{207}Pb}$=51.4 in DMSO). These signals are typical for semiquinolate free radical-ion bonded to the metal ion [18,19]. The coupling constant on lead is in typical for lead (II) [14]. It is likely that the polarity of the solvent influences the coupling constant on lead. Rising the polarity decreases the coupling constant.

No signals corresponding to the biradical particles were detected in the anisotropic spectrum of the reaction mixtures. This could be explained by the very low concentration of the radical particles in the reaction mixture for the reasons discussed below. The final product of the reaction is diamagnetic.

Normally the oxidation of metals by quinones occurs according to the following scheme:

$$n\,\mathrm{TBQ} + \mathrm{M} \longrightarrow \mathrm{M(TBSQ)}_n \qquad (1)$$

$$\mathrm{M(TBSQ)}_n + \mathrm{M} \longrightarrow 2\,\mathrm{M(TBCat)}_{n/2} \qquad (2),$$

where n is the valence of the metal, TBSQ is semiquinolate radical-anion, Cat is catecholate.

Depending on the donor properties of the solvent, the reaction can stop at the formation of $M(TBSQ)_n$ or proceed further to the formation of a catecholate. For example, the interaction of group II metals with 3,5-TBQ in toluene leads to the formation of corresponding TBSQ derivatives [4], while the same reaction in DMFA or DMSO gives rise to metal catecholates [20].

The equilibrium

$$\mathrm{M(TBCat)} + \mathrm{TBQ} \rightleftarrows \mathrm{M(TBSQ)}_2 \qquad (3)$$

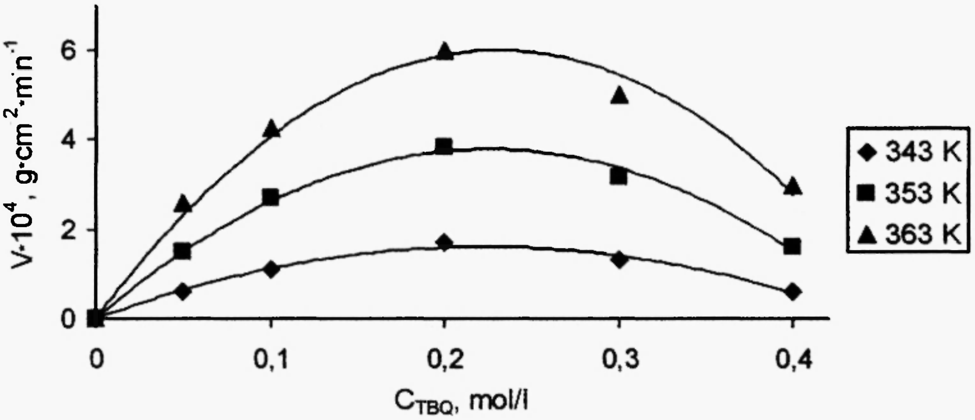
(M=Mg, Zn, Cd), is normally shifted to the right and no metal catecholate is formed as long as quinone is present in the reaction mixture [20]. With the lead the situation is the opposite. When lead and 3,5 TBQ were mixed with the ratio 1:2 in DMSO or THF a precipitate was formed by the end of the reaction which was identified by the elemental analysis as lead catecholate. More than 99% of the lead introduced into the reaction mixture was found in the precipitate. Thus, due to the very low solubility of the lead catecholate the equilibrium (3) in case of lead is shifted to the left. The oxidation of lead by TBQ can be described by the following scheme:

$$2\,\mathrm{TBQ} + \mathrm{Pb} \longrightarrow \mathrm{Pb(TBSQ)}_2 \qquad (4)$$

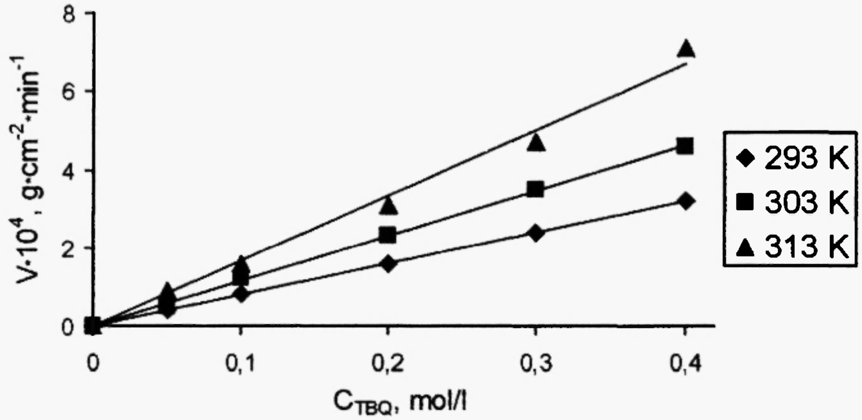
$$\mathrm{Pb(TBSQ)}_2 \longrightarrow \mathrm{Pb(TBCat)} + \mathrm{TBQ} \qquad (5)$$

The kinetic regularities of the reaction were studied in DMSO and THF. The dependencies of the rate of the reaction on the oxidizer's concentration are shown at the figures 1,2. In case of THF this dependency is nearly linear while in case of DMSO it proceeds through the maximum which is observed at the concentration of TBQ 0.2 mol/l. The activation energy of the reaction also significantly depends of the solvent. In THF the activation energy is 25.8 kJ/mol while in DMSO its value is 69 kJ/mol.

Figure 1



The dependency of the rate of lead oxidation by TBQ in DMSO



The dependency of the rate of lead oxidation by TBQ in THF

Figure 2

REFERENCES

1 G.A. Abakumov, V.A. Muraev, G.A. Razuvaev, *Doklady Akademii Nauk SSSR*, 1974, **215**, 5, 1113 (in Russian).
2 V.A. Muraev, G.A. Abakumov, G.A. Razuvaev, *Doklady Akademii Nauk SSSR*, 1974, **217**, 5, 1083 (in Russian).
3 M.I. Kabachnik., N.N. Bubnov, A.I. Prokof'ev, S.P. Solodovnikov, *Science Rev.* 1981, Ser. B. **3**, 22, 197.
4 A . Ozarowsky, B.R. McGarvey, C. Peppe, D.G. Tuck, *J. Am. Chem. Soc.* 1991, **113**, 9, 3288.
5 T.A. Annan, D.N. McConville, McGarvey B.R., A. Ozarowsky, D.G Tuck., *Inorg. Chem.* 1989, **28**, 9, 1644.
6 Z. Tian, D.G. Tuck, *J. Chem. Soc. Dalton Trans.* 1993, 1381.
7 A. Ozarowski, B.R. McGarvey, A.A. El-Hadad, Z. Tian, D.G. Tuck, *Inorg. Chem.* 1993, **32**, 841.
8 T.A. Annan, A. Ozarowski, Z. Tian, D.G. Tuck, *J. Chem. Soc. Dalton Trans.* 1992, 2931.
9 A.A. El-Hadad, B.R. McGarvey, B. Merzougui, R.G.W. Sung, A.K. Trikha, D.G. Tuck, *J. Chem. Soc. Dalton Trans.* 2001, 1046.
10 M.A. Brown, A.A. El-Hadad, B.R. McGarvey, R.C.W. Sung, A.K. Trikha, D.G. Tuck, *Inorg. Chim. Acta.* 2000, **300–302**, 613.
11 N.V. Berezina, V.K. Cherkasov, A.V. Kondin, V.P. Maslennikov, *Zhurn. Obsh. Khim.* 1996, **66**, 1, 40, (in Russian)
12 N.V. Berezina, V.K. Cherkasov, V.P. Maslennikov, *Zhurn. Obsh. Khim.* 1996, **66**, 9, 1488, (in Russian)

13 L.I. Modinova, V.P. Sergeeva, V.K. Cherkasov, V.P. Maslennikov, *Zhurn. Obsh. Khim.* 1999. **69**. 12. 2006. (in Russian)

14 G.A. Abakumov, V.I. Nevodchikov, V.K. Cherkasov, G.A. Razuvaev, *Doklady Akademii Nauk SSSR*. 1978. **242**. 3. 609 (in Russian).

15 E. Muller, K. Ley, G. Schecher, *Chem. Ber.* 1957. **b90.** 8. 1530.

16 N. Gordon, R. Ford, Chemist's Companion. Mir: Moscow. 1976; 437 (Russian ed.).

17 S.A. Zhukov, I.P. Lavrentvev, T.A. Nifontova, *React. Kinet. Catal. Lett.* 1974. **4.** 1105.

18 Annan T.A., McGarvey B.R., Ozarowski A., *J. Chem. Soc. Dalton Trans.* 1989. 439.

19 Annan T.A., Chadha R.K., Doan P., McConville P.H., Tuck D.G., *Inorg. Chem.* 1990. **29**. 3936

20 Piskounov A.V., Maslennikov S.V., Cherkasov V.K., Spirina I.V., Maslennikov V.P., *Zhurn. Obsh. Khim.* (in Russian) In press.

21 V. Gutman, Chemistry of coordination compounds in non-aqueous solutions. Mir: Moscow. 1971. 220 p. (in Russian).

Received: November 15, 2001 - Accepted: November 21, 2001 – Accepted in publishable format: November 26, 2001