Electrochemical Synthesis of Zinc(II) Phenoxides and their Coordination Compounds

J.S. Banait,[*] B. Singh, H. Kaur

Chemistry Department, Punjabi University, Patiala, 147 002, India

Abstract

Electrochemical oxidation of phenol, 4-aminophenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2-hydroxybenzoic acid, 2-tert-butylphenol and 2-tert-butyl-4-methoxyphenol has been carried out at sacrificial zinc anode. The products of these reactions have been identified by elemental analysis and infrared spectral data and are found to be zinc(II) phenoxides. Though these compounds do not form coordination compounds on refluxing with 1,10-phenanthroline or 2,2'-bipyridyl, yet the coordination compounds of these phenoxides with these ligands have been synthesized electrochemically. Current efficiencies of these systems are quite high.

Keywords: electrochemical synthesis, sacrificial zinc anode, phenoxides, coordination compounds and current efficiencies.

Introduction

Electrochemical synthetic technique has been extensively used for the synthesis of organic compounds [1-7], since it provides a single step, direct and pollution free route [8-9] to carry out oxidation and reduction. In order to explore the use of this technique for the synthesis of inorganic compounds, the electrolysis at sacrificial electrodes has been reported from our laboratory [10-15]. In continuation to our interest in synthetic electrochemistry, we report the synthesis of zinc(II) phenoxides and their coordination compounds in the present paper.

Experimental

Double distilled acetonitrile was used as solvent, and tetrabutylammonium chloride crystallized from conductivity water and dried under vacuum at 100 ºC was used as supporting electrolyte in all these reactions. The phenols (AR grade) were used as supplied. The reactions were carried out in a H-type pyrex glass cell having two compartments separating from each other by sintered glass disc of G-

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[*] Corresponding author. E-mail address: js_banait@yahoo.com

3 porosity. Zinc plate $(2 \times 10 \times 0.2 \text{ cm}^3)$ was used as anode, and platinum foil $(1 \times 1 \text{ cm}^2)$ was used as cathode. The necessary connections were made with Toshniwal direct current power supply. The solutions of 2.0 g of phenols, 1.0 g of tetrabutylammonium chloride in 250 mL of acetonitrile were electrolyzed. Potential across the electrodes was adjusted so that a current of 20 mA passed through the solution. The reaction mixture was stirred with the help of magnetic stirrer during the progress of the reaction. The electrolytic cell can be represented as:

$$\text{Zn}_{(+)} \quad \left| \quad \begin{array}{l} \text{Phenol +} \\[6pt] \text{tetrabutylammonium chloride} \quad \text{Pt}_{(-)} \\[6pt] \text{+ Acetonitrile} \end{array} \right.$$
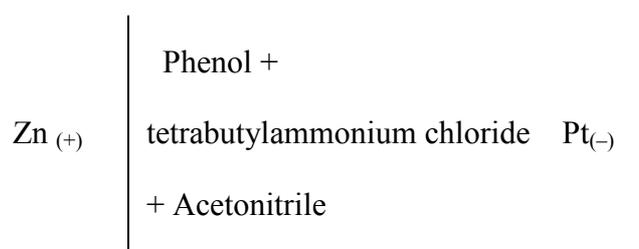
where, $\text{Zn}_{(+)}$ and $\text{Pt}_{(-)}$ represent zinc anode and platinum cathode, respectively.

The solid products started separating in anode compartment within half an hour of starting the reaction. After ten hours of electrolysis, the solid products from anode compartment were filtered, washed with hot acetonitrile and dry ether and then dried under vacuum.

In order to prepare the coordination compounds of these phenoxides, electrolysis was conducted as above except that 1.0 g of ligand was also added to the reaction mixture in addition to the phenol and supporting electrolyte.

Melting points of these products were determined by using an electrical device, which was adjusted so that the temperature rose by five degrees per minute during melting point measurements.

For the determination of zinc contents, a known amount of the product was heated to dryness with fuming nitric acid four times. The dry mass obtained was dissolved in 5.0 mL of water and three drops of hydrochloric acid. The solution was boiled and diluted to a volume of 25.0 mL. Zinc contents in this solution were determined volumetrically by oxine method [16]. Microanalyses for carbon and hydrogen in these products have also been conducted. Infrared spectra of these products have been scanned in potassium bromide pellets by using Perkin-Elmer spectrophotometer, RXI, in the region of $4000 - 450 \text{ cm}^{-1}$.

Current efficiencies (gram equivalent of metal dissolved per Faraday of electricity passed) of all these products were determined by electrolyzing the above solutions under similar manner at a constant current of 20 mA for two hours. Zinc contents in the anode compartment were then determined volumetrically. The ratio of experimental to theoretical zinc contents gives the current efficiency.

Results and discussion
Zinc(II) phenoxides
Solid products obtained from the anode compartment are insoluble in different organic solvents like benzene, carbon tetrachloride, dimethyl sulphoxide N,N-

dimethyl formamide and methanol. These products do not melt up to 220 ºC but show a distinct colour change around this temperature, thereby indicating that the products were decomposed around this temperature.

Analytical data of the products are summarized in Table 1. The data correspond to 2:1 stoichiometry of phenol and zinc, respectively.

Table 1. Electrolysis characteristics, analytical and other related data of electrolytic products of various phenols at zinc anode.

Phenol	Potential applied (V)	Electricity passed (C)	Product	Colour	Elemental analysis found (calc.) %			Current efficiency (gram eq. Faraday^{-1})
					Zn	C	H	
phenol	30	680	$C_{12}H_{10}O_2Zn$	dirty white	22.5 (26.0)	55.9 (57.3)	3.7 (4.0)	0.93
2-hydroxybenzoic acid	30	680	$C_{14}H_{10}O_6Zn$	pinkish white	18.9 (19.3)	46.7 (49.5)	1.9 (2.9)	0.88
4-aminophenol	35	700	$C_{12}H_{12}N_2O_2Zn$	brownish black	20.0 (23.2)	49.0 (51.2)	1.3 (2.8)	0.69
4-nitrophenol	30	680	$C_{12}H_8N_2O_6Zn$	brown	19.8 (19.3)	40.1 (42.2)	1.8 (2.3)	0.72
2-nitrophenol	30	720	$C_{12}H_8N_2O_6Zn$	dark brown	18.1 (19.3)	41.9 (42.2)	1.1 (2.3)	0.73
2,4-dinitrophenol	30	720	$C_{12}H_6N_4O_{10}Zn$	dark brown	13.6 (15.1)	30.1 (33.4)	0.9 (1.4)	0.70
2-tert-butylphenol	35	720	$C_{20}H_{26}O_2Zn$	greyish brown	20.4 (18.0)	64.9 (66.0)	6.4 (7.2)	0.62
2-tert-butyl-4-methoxyphenol	35	700	$C_{22}H_{30}O_4Zn$	greyish brown	15.0 (15.4)	60.4 (62.4)	5.7 (7.1)	0.54

Infrared spectra of these products have been obtained in the region of 4000 - 450 cm^{-1}. All the products (except that of 2-hydroxybenzoic acid) do not show any absorption band in the region of 3600 - 3200 cm^{-1} attributed to ν(O - H) group. But show characteristic bands in the regions of 1153 –1000 cm^{-1} and 470 – 460 cm^{-1}.

Survey of literature reveals that ν(M - O) [14,15,18-25] and ν(C - O)M [22-25,26] absorption bands in metal alkoxides appear in the regions of 470 - 450 cm^{-1} and 1150 - 1000 cm^{-1}, respectively. Adam et al. reported [18] the ν(Zn - O) bands at 465 cm^{-1} in zinc(II) methoxides . Banait et al. reported [15] the ν(Zn - O) and ν(C - O)Zn absorption bands at 470 – 450 cm^{-1} and 1160 – 1000 cm^{-1} in zinc(II) alkoxides, respectively. Thus the bands in the region of 470 – 460 cm^{-1} and 1153 –1000 cm^{-1} in the present studies may be attributed to ν(Zn - O) and

ν(C - O)Zn modes, respectively. Presence of these bands and absence of bands due to ν(O - H) group indicate that proton of these phenols has been replaced with anodic zinc.

Metal alkoxides generally exist as polymers through alkoxy bridging. Survey of literature reveals [22-24,26] that bands due to terminal and bridged alkoxide groups in metal alkoxides appear in the regions of $1060 - 1000$ cm^{-1} and $1150 - 1060$ cm^{-1}, respectively. In the present studies one band appears in both these regions in all the products, showing thereby that these products also exist as polymers through phenoxy bridging.

The product of the electrochemical reaction of 2-hydroxybenzoic acid at sacrificial zinc anode exhibits a band at 3605.6 cm^{-1}, thereby indicating that the phenolic proton of 2-hydroxybenzoic acid is not replaced with anodic zinc. However, the product shows bands at 1608.9 cm^{-1}, 1386.4 cm^{-1}, 1032.5 cm^{-1}, 964 cm^{-1} and 762.4 cm^{-1}. The bands in the region of $1610 - 1556$ cm^{-1}, $1400 - 1320$ cm^{-1} and $780 - 650$ cm^{-1} may be attributed to asymmetric, symmetric and bending modes of zinc carboxylate group [27-29]. Since carboxylic group is easily oxydisable as compared to phenolic group, thus proton of carboxylic group is replaced with anodic zinc and phenolic group remains unaffected.

Literature reveals [30] that the bands present in the region of $1200 - 1000$ cm^{-1} are attributed to ν(M – OH) modes. The presence of band in comparatively lower region (at 1032.5 cm^{-1}) and a weak band at 964 cm^{-1} may be assigned to bridged ν(Zn - OH) mode. The plausible structure is given below:
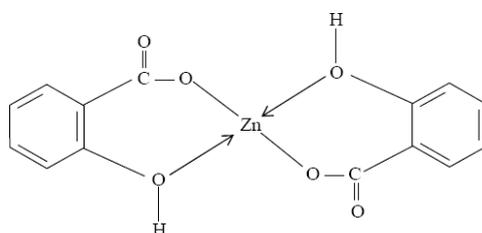
Current efficiencies of all these systems (Table 1) are quite high except in case of 2-tert-butyl-4-methoxyphenol. High current efficiencies of these systems indicate that the reactions leading to the formation of these products are the predominant reactions of these systems. The reaction scheme may be written as:

at cathode
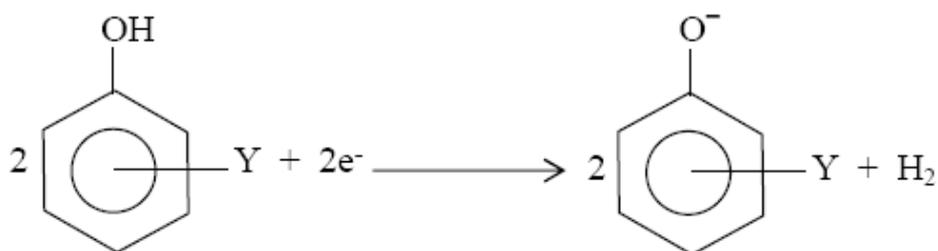
at anode
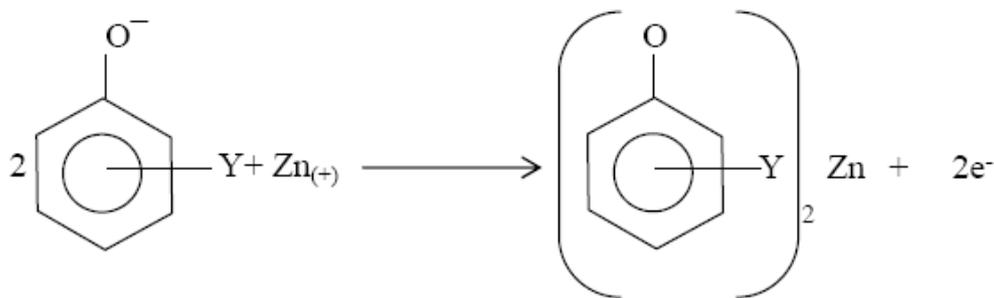
and in case of 2-hydroxybenzoic acid:

at cathode
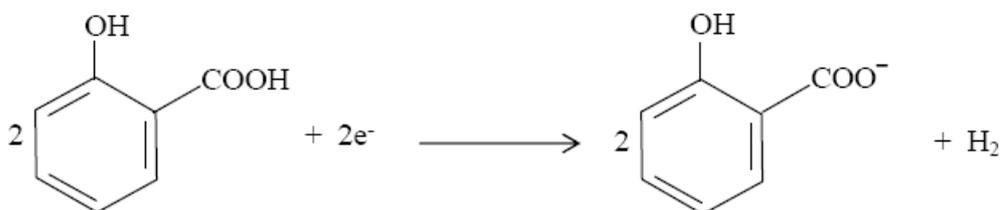
at anode
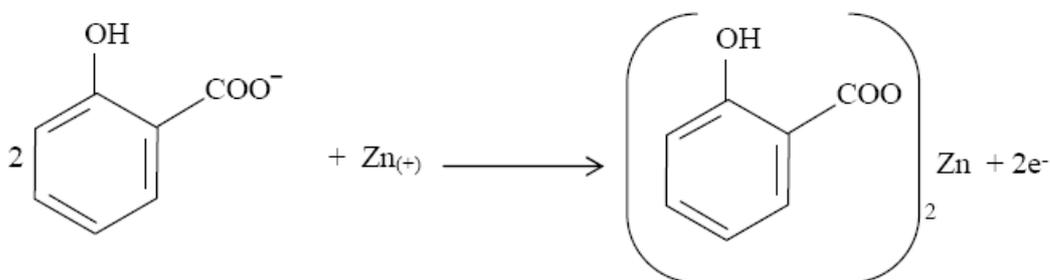
In order to determine the reason for low current efficiency of 2-tert-butyl-4-methoxyphenol system, the electrolysis has been carried out at different intervals of time. The results indicate that current efficiencies are the same at different intervals of time, i.e., product does not act as corrosion inhibitor by forming a protective layer at the zinc anode. Low current efficiency of this system may be due to the presence of two electron-releasing groups on 2-tert-butyl-4-methoxyphenol, which increases the electron density on benzene ring and inhibits the delocalization of negative charge of phenoxide ion. As a result the phenoxide ions become unstable. Thus only a small fraction of phenoxide ions reaches at sacrificial anode resulting in the decrease in the current efficiency of the system.

Table 2. Electrolysis characteristics, analytical and other related data of electrolytic products of various phenol + ligand systems at zinc anode.

System	Potential applied (V)	Electricity passed (C)	Product	Colour	Elemental analysis found (Calc.) %			Current efficiency (gram equiv. F^{-1})
					Zn	C	H	
phenol +1,10-phenanthroline	30	680	$C_{12}H_{10}O_2ZnC_{12}H_8N_2$	light brown	15.5 (15.2)	63.7 (66.8)	3.6 (4.2)	0.81
2-hydroxybenzoic acid + 1,10-phenanthroline	30	680	$C_{14}H_{10}O_6ZnC_{12}H_8N_2$	brown	13.1 (12.6)	57.3 (60.1)	2.9 (3.5)	0.94
4-aminophenol + 1,10-phenanthroline	30	680	$C_{12}H_{12}N_2O_2ZnC_{12}H_8N_2$	dark brown	13.4 (14.2)	60.1 (62.4)	2.9 (4.3)	0.70
4-nitrophenol + 1,10-phenanthroline	30	680	$C_{12}H_8N_2O_6ZnC_{12}H_8N_2$	brown	11.3 (12.5)	54.1 (55.2)	2.2 (3.1)	0.81
2-nitrophenol + 1,10-phenanthroline	30	640	$C_{12}H_8N_2O_6ZnC_{12}H_8N_2$	brown	12.0 (12.5)	54.3 (55.2)	2.1 (3.1)	0.78
2,4-dinitrophenol + 1,10-phenanthroline	35	680	$C_{12}H_6N_4O_{10}ZnC_{12}H_8N_2$	dark brown	9.9 (10.7)	45.3 (47.1)	2.1 (2.3)	0.74
2-tert-butylphenol + 1,10-phenanthroline	30	680	$C_{20}H_{26}O_2ZnC_{12}H_8N_2$	grey	12.7 (12.1)	67.7 (70.7)	4.9 (6.3)	0.98
2-tert-butyl-4-methoxyphenol +1,10-phenanthroline	30	680	$C_{22}H_{30}O_4ZnC_{12}H_8N_2$	brown	11.4 (11.4)	65.3 (71.4)	5.1 (6.7)	0.57
phenol + 2,2'-bipyridyl	30	680	$C_{12}H_{10}O_2ZnC_{10}H_8N_2$	brown	16.1 (16.1)	62.3 (64.8)	4.1 (4.4)	0.93
2-hydroxybenzoic acid + 2,2'-bipyridyl	30	880	$C_{14}H_{10}O_6ZnC_{10}H_8N_2$	light brown	13.2 (13.2)	55.9 (58.1)	3.1 (3.6)	0.82
4-aminophenol + 2,2'-bipyridyl	30	700	$C_{12}H_{12}N_2O_2ZnC_{10}H_8N_2$	dark brown	14.7 (14.9)	58.3 (60.4)	3.9 (4.6)	0.71
4-nitrophenol + 2,2'-bipyridyl	30	680	$C_{12}H_8N_2O_6ZnC_{10}H_8N_2$	brown	12.4 (13.1)	51.9 (53.1)	2.9 (3.2)	0.83
2-nitrophenol + 2,2'-bipyridyl	30	680	$C_{12}H_8N_2O_6ZnC_{10}H_8N_2$	greenish brown	12.9 (13.1)	50.0 (53.1)	2.3 (3.2)	0.78
2,4-dinitrophenol +2,2'-bipyridyl	30	680	$C_{12}H_6N_4O_{10}ZnC_{10}H_8N_2$	dark brown	10.9 (11.1)	42.1 (44.9)	2.1 (2.4)	0.76
2-tert-butylphenol + 2,2'-bipyridyl	30	680	$C_{20}H_{26}O_2ZnC_{10}H_8N_2$	grey	12.3 (12.6)	65.9 (69.3)	4.8 (6.6)	0.98
2-tert-butyl-4-methoxyphenol + 2,2'-bipyridyl	30	680	$C_{22}H_{30}O_4ZnC_{10}H_8N_2$	light brown	11.9 (11.3)	64.1 (66.3)	6.4 (6.9)	0.50

Coordination compounds of zinc(II) phenoxides

The solid products obtained from anode compartment are insoluble in different organic solvents and do not melt up to 200 ºC but show a colour change around this temperature.

Elemental analysis of these products (Table 2) conforms to 2:1:1 stoichiometry of phenol, zinc and ligand, respectively.

Characteristic infrared bands in these products appear in the regions of 467 – 452 cm^{-1} and 1160 - 1015 cm^{-1}. These bands can be assigned to ν(Zn - O) [14,15,18-25] and ν(C - O)Zn [22-24,26] modes, respectively. Comparison of the infrared spectra of these products with the parent phenoxides reveals that the bands appear in a higher region in these products, which can be attributed to the coordination of the ligand.

The bands in the region of 1630 – 1420 cm^{-1} are due to ligand molecules [31] as no such bands were observed in the infrared spectra of the parent phenoxides. These bands can be assigned to ν(C --- N) and ν(C --- C) stretching modes. These bands however, appear in slightly lower region as compared to those in the pure ligand.

Appearance of ν(C – O)Zn and ν(Zn – O) absorption bands and absence of bands due to phenolic group in the present products (except in the products of 2-hydroxybenzoic acid + ligand systems) indicate that the protons of the phenol molecules have been replaced by anodic zinc to yield zinc(II) phenoxides. Shift of the ν(C – O)Zn and ν(Zn – O) absorption bands towards the higher region as compared to those in parent alkoxides and appearance of the bands ν(C --- N) and ν(C --- C) due to ligand molecules show that the present products are the coordination compounds of zinc(II) phenoxides.

Presence of the bands due to the bridged phenoxide groups and terminal phenoxide groups in the infrared spectra, insoluble behaviour in various commonly used solvents and high melting point of the present products indicate their polymeric nature through phenoxy bridging.

Infrared spectral data of the products of 2-hydroxybenzoic acid + ligand systems show bands due to ν(COO)Zn [27-29] and ν(Zn - OH) modes [30] at shifted positions. Bands due to ligand molecule are also present at shifted positions, indicating thereby the coordination of the ligand to metal in these cases also.

Current efficiencies of these systems (listed in Table 2) are also quite high except in case of 2-tert-butyl-4-methoxyphenol + ligand systems. High current efficiencies of these systems indicate that reactions leading to the formation of coordination compounds of zinc(II) phenoxides are the predominant reactions of these systems.

The present electrochemical technique thus presents a single step and one pot method for the synthesis of zinc(II) phenoxides and their coordination compounds. The method is further associated with the advantages of high current efficiencies and use of routine laboratory chemicals and equipments.

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