

Electrochemical reactions at sacrificial electrodes: Part VI-Synthesis of cadmium alkoxides and their coordination compounds

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Cadmium alkoxides [Cd(OR)₂; R=methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl], have been synthesised by the electrolysis of alcohols at a cadmium anode. These alkoxides do not form coordination compounds when refluxed with the ligands like 2, 2'-bipyridine, 1, 10-phenanthroline, dimethylsulphoxide and acetone. However, coordination compounds with the general formula, Cd(OR)₂.L, have been prepared when the solutions of these ligands in alcohols are electrolysed at a cadmium anode. The products have been characterised by elemental analyses and IR data. Current efficiencies of all these systems are quite high.

Direct electrochemical synthesis of metal carboxylates, alkoxides and glycolates by the oxidation of a sacrificial anode in the solutions of carboxylic acids, alcohols, aldehydes and ketones have been the subject of recent papers from this laboratory¹⁻⁶. The most important advantages of this technique are the simplicity and high product yield. Electrochemical synthesis of cadmium alkoxides forms the subject of this paper.

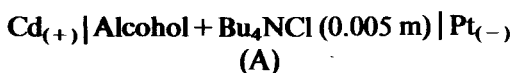
The tendency of metal alkoxides to undergo auto-association in order to achieve the favourable coordination number of the central metal atom is responsible for their poor acceptor properties^{7,8}. Coordination compounds of only a few metal alkoxides are reported^{7,9,10} and that too if a strong electron-withdrawing group is introduced in the alkoxide group. We also report herein direct electrochemical synthesis and characterization of coordination compounds of cadmium alkoxides.

Experimental

Alcohols were purified by the usual methods¹¹. Tetrabutylammonium chloride (Reidel, pure) was crystallized from conductivity water and dried under reduced pressure at 100°C and was used as the supporting electrolyte.

An H-type cell of the type (A) made of pyrex glass was used for the electrolysis reactions. The cathode

and anode compartments were separated from each other by a sintered disc of G-3 porosity.



Platinum foil (1 × 1 cm²) was used as cathode and cadmium plate (2 × 10 × 0.2 cm³) was used as the anode. Direct current was obtained with the help of Toshniwal electrophoresis power supply.

Procedure

Alcohol containing tetrabutylammonium chloride (0.005 mol) as supporting electrolyte was taken in the electrolysis cell. Cadmium plate and platinum foil were dipped in the anode and cathode compartments respectively. Necessary connections were made with the power supply and potential across the electrodes was adjusted so that a current of about 20 mA passed through the cell. Electrolysis was carried out for 6 hr with continuous and efficient stirring at room temperature. The white solid which separated out in the anode compartment was filtered, washed repeatedly with dry ether and dried under reduced pressure.

For the synthesis of the coordination compounds, ligand (1 g) was also added in the anode compartment in addition to the supporting electrolyte before starting electrolysis. The other details are essentially the same as discussed above for the synthesis of cadmium alkoxides.

Current efficiencies were determined from the ratio of actual and theoretical amounts of cadmium dissolved when a current of 20 mA was passed for 2 hr through the cell in the given system.

Cadmium in the products was estimated volumetrically¹².

Results and discussion

Electrochemical reactions of methanol, ethanol, *n*-propanol, *n*-butanol and *n*-pentanol at cadmium anode yield the corresponding cadmium alkoxides [Cd(OR)₂] as white solids in the anode compartment (Table 1). The electrolysis characteristics are given in Table 1. The products of these electrochemical reactions are not affected much by air or moisture and are quite stable. These compounds do not melt upto 250°C and are insoluble in common organic solvents such as benzene, chloroform, carbon disulphide, carbon tetrachloride, acetone, nitromethane, N, N-dimethylformamide etc.

Table 1—Electrolysis characteristics, analytical and other related data of the electrolysis products of alcohols at cadmium anode

Alcohol	Potential (V)	Product*	Found (Calc.), %			Current efficiencies (g eq faraday ⁻¹)
			Cd	C	H	
Methanol	20	C ₂ H ₆ O ₂ Cd	64.0 (64.4)	13.22 (13.76)	2.90 (3.44)	0.90
Ethanol	20	C ₄ H ₁₀ O ₂ Cd	56.2 (55.5)	22.5 (23.72)	4.51 (4.94)	0.89
<i>n</i> -Propanol	25	C ₆ H ₁₄ O ₂ Cd	48.5 (48.8)	30.60 (31.25)	4.85 (6.08)	0.75
<i>n</i> -Butanol	25	C ₈ H ₁₈ O ₂ Cd	41.2 (43.5)	36.00 (37.15)	5.67 (6.97)	0.82
<i>n</i> -Pentanol	30	C ₁₀ H ₂₂ O ₂ Cd	37.8 (39.2)	41.2 (41.90)	6.43 (7.68)	0.87

* All the products were obtained as white solids, m.p. > 250°C.

Table 2—Electrolysis characteristics, analytical and other related data of the electrolysis products of alcohol + ligand systems at the cadmium anode

System	Potential (V)	Product*	Found (Calc.), %				Current efficiencies (g eq faraday ⁻¹)
			Cd	C	H	N	
Methanol + acetone	20	C ₂ H ₆ O ₂ Cd.C ₃ H ₆ O	48.0 (48.4)	24.32 (25.82)	4.27 (5.16)	—	0.80
Ethanol + acetone	25	C ₄ H ₁₀ O ₂ Cd.C ₃ H ₆ O	42.2 (43.2)	30.04 (32.26)	7.40 (6.14)	—	0.85
Methanol + dimethylsulfoxide	30	C ₂ H ₆ O ₂ Cd.C ₂ H ₆ SO	44.1 (44.5)	18.75 (19.02)	4.02 (4.75)	—	0.94
Ethanol + dimethylsulfoxide	30	C ₄ H ₁₀ O ₂ CdC ₂ H ₆ SO	39.5 (40.1)	24.90 (25.68)	5.60 (5.71)	—	0.82
Methanol + 2, 2'-bipyridine	15	C ₂ H ₆ O ₂ Cd.C ₁₀ H ₈ N ₂	33.8 (34.0)	42.00 (43.58)	3.90 (4.24)	8.03 (8.47)	0.84
Ethanol + 2, 2'-bipyridine	20	C ₄ H ₁₀ O ₂ CdC ₁₀ H ₈ N ₂	31.2 (31.3)	45.50 (46.88)	4.90 (5.02)	8.02 (7.81)	0.88
Methanol + 1, 10-phenanthroline	30	C ₂ H ₆ O ₂ Cd.C ₁₂ H ₈ N ₂	29.0 (31.7)	45.90 (47.50)	2.02 (3.95)	6.96 (8.00)	0.80
Ethanol + 1, 10-phenanthroline	35	C ₄ H ₁₀ O ₂ Cd.C ₁₂ H ₈ N ₂	28.6 (29.4)	48.80 (50.20)	3.95 (4.70)	6.82 (7.30)	0.76

* All the products were obtained as white solids; m.p. > 250°C; colour change at 200°C.

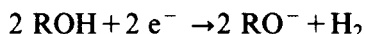
Infrared spectra of the products were recorded in nujol using a Beckman IR-20 spectrophotometer and sodium chloride plates for the region 4000 to 600 cm⁻¹ and polythene plates for the far IR region (600 to 200 cm⁻¹). The products do not show any absorption corresponding to the hydroxylic group¹³ but do exhibit slightly broad¹⁴⁻¹⁶ ν(C-O) modes between 1000 and 1030 cm⁻¹. Two types of ν(C-O) modes are observed in metal alkoxides¹⁴⁻¹⁸. Terminal alkoxide groups show ν(C-O) between

1060 and 1130 cm⁻¹ and the bridged alkoxide groups between 1000 and 1060 cm⁻¹. Appearance of these bands in the lower region indicates the polymeric structure of these compounds through alkoxy bridges. The weak bands in the region 290 to 310 cm⁻¹ may be assigned to the ν(Cd-O) modes¹⁴⁻¹⁸.

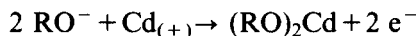
Current efficiencies of all these reactions have also been determined and are listed in Table 1. The current efficiencies of these systems are quite high, thereby showing that the reactions leading to the formation of

cadmium alkoxides are the predominant reactions of these systems. The reaction scheme may be written as:

At cathode:



At anode:



Coordination compounds of cadmium methoxide and ethoxide

The coordination compounds of cadmium methoxide and ethoxide with 2, 2'-bipyridine, 1, 10-phenanthroline, acetone and dimethylsulphoxide could not be prepared by refluxing the reactants in solvents like methanol, ethanol, acetonitrile, benzene etc. for more than 48 hr. The coordination compounds, however, could be prepared easily by the electrochemical processes. The compounds separated in the anode compartment are also insoluble in common organic solvents and are not affected by moisture and air. The products do not melt upto 250°C but show slight colour change at 200°C.

The analytical data correspond to the composition, $\text{Cd}(\text{OR})_2 \cdot \text{L}$; R represents methyl or ethyl group and L is the ligand molecule (see Table 2).

Infrared spectra of these compounds exhibit characteristic $\nu(\text{C}-\text{O})\text{Cd}$ modes¹⁴⁻¹⁸ between 1000 and 1120 cm^{-1} . These bands are slightly broad and distinct two or three absorption bands appear in this region, which indicate the presence of both the terminal and bridged alkoxide groups in these compounds.

Infrared spectra of these compounds also exhibit peaks in the region of 300 to 335 cm^{-1} , assignable to the $\nu(\text{Cd}-\text{O})$ modes¹⁴⁻¹⁷. Shift of this band towards higher region and appearance of more than one band in the region of 1000 to 1120 cm^{-1} show the coordination of the ligand with the alkoxides. Insoluble behaviour of the products and appearance of $\nu(\text{C}-\text{O})\text{Cd}$ band in the lower region (bridged alkoxide group) also show that these compounds have polymeric structure like the parent alkoxides.

Survey of literature¹⁹⁻²¹ reveals that several such metal alkoxides have been reported in which the ligand molecule and alkoxy group both donate electron pairs to the central metal to form coordinate linkages.

Current efficiencies of all these systems have also been determined and are recorded in Table 2. The current efficiencies of these systems are also quite close to 100% showing that the reactions leading to the formation of coordination compounds of cadmium alkoxides are the predominant reactions of these systems.

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