Electrochemical Reactions at Sacrificial Electrodes : Part-XI. Synthesis of Zinc(II) Chelates

J.S. Banait and Baljit Singh

Chemistry Department, Punjab University, PATIALA - 147002

Electrochemical reactions of malononitrile, diethylmalonate, ethylcyanoacetate, cyanoacetamide, ethylacetoacetate and acetylacetone (RH_2) in acetonitrile solvent and tetrabutylammonium chloride as supporting electrolyte at sacrifical zinc anode and inert platinum cathode give solid products in the anode compartment. These are identified as zinc(II) chelates ($Zn(RH)_2$) by elemental analysis and infrared spectral studies. Current efficiencies of these reactions are quite high.

Electrochemical methods have been applied extensively in synthetic organic chemistry [1-3]. This technique, however, has rarely been used for the synthesis of inorganic compounds. Direct electrochemical synthesis of metal alkoxides have been reported from our laboratories [4-6]. In continuation of our interest in this area, we report the electrochemical synthesis of zinc chelates in this communication.

EXPERIMENTAL

Acetonitrile was dried over phosphorus pentoxide and then distilled. Freshly distilled acetonitrile was used as solvent in these electrochemical reactions. Tetrabutylammonium chloride (Reidel Pure) was crystallised from conductivity water, dried under reduced pressure at 100° and was used as supporting electrolyte in these systems. Malononitrile, diethylmalonate, ethylcyanoacetate, cyanoacetamide, ethylacetoacetate and acetylacetone (RH_2) (all BDH) were used as supplied.

H-Type cell made of pyrex glass was used for the electrochemical reactions. The anode and cathode compartments were separated from each other by a sintered glass disc of G-3 porosity. Each compartment was provided with two openings one for the guard tube and the other for the electrode. Platinum foil, 1x1x0.005 cm^3 and zinc foil 10x2x0.02 cm^3 were used as cathode and anode respectively.

Solution of tetrabutylammonium chloride (0.005M) and 2.0g of the organic compound (RH_2) in 250 ml of acetonitrile was taken in the electrolysis cell. The electrolytic solution was stirred efficiently using a magnetic stirrer. Direct current from Toshniwal electrophoresis power supply was used for electrolysis. Potential across the electrodes was then adjusted so that a current of about 20 mA pass through the cell. As the electrolysis proceeded, solid products started separating in the anode compartment. After conducting the electrolysis for about ten hours, the products were filtered, washed repeatedly with acetonitrile followed by dry ether and dried under reduced pressure.

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The products were analysed for zinc content. A weighed amount of the product was heated to dry mass with fuming nitric acid four times. The dry mass was then dissolved in a few drops of dilute hydrochloric acid and zinc in the solution was estimated volumetrically with oxine. Infrared spectra of the products were obtained in nujol using sodium chloride plates and polythene film in the regions of 4000-600 cm^{-1} and 600-200 cm^{-1} respectively.

Current efficiencies (gram equivalent of zinc dissolved per Faraday of electricity passed) of these systems were determined by conducting the electrochemical reactions with a current of 20 mA for exactly two hours. The solution of the anode compartment was taken out, solvent distilled off and mass evaporated to dryness. The amount of zinc in the dry mass was then estimated as detailed above. Current efficiencies were then calculated from the ratio of the amount of zinc in the dry mass to the theoretical amount of zinc dissolved.

RESULTS AND DISCUSSION

Electrochemical reactions of malononitrile, diethylmalonate, ethylcyanoacetate, cyanoacetamide, ethylacetoacetate and acetylacetone have been carried out at sacrificial zinc anode and inert platinum cathode. As the aim of the present studies

Table 1

Electrolysis Characteristics, Analytical and other related data of RH_2 at the Zinc anode.

System RH_2	Potential V	q (Coul)	Product (Colour)	% Composition Found (Calc) Zn	C	H	N	Current effi g.eq.F^{-1}
Acetyl Acetone	20	640	$C_{10}H_{14}O_4Zn$ White	24.00 (24.83)	46.00 (45.55)	5.35 (5.31)	- -	0.85
Malono monitrile	25	720	$C_6H_2N_4Zn$ Light Brown	32.80 (33.47)	37.00 (36.84)	0.95 (1.02)	29.00 (28.65)	0.82
Cyano acetamide	20	680	$C_6H_6O_2N_4Zn$ White	29.50 (28.26)	32.02 (31.11)	3.05 (2.59)	23.80 (24.20)	0.80
Ethylcyano acetate	20	700	$C_{10}H_{12}O_4N_2Zn$ White	21.00 (22.59)	40.00 (41.46)	4.30 (4.14)	9.85 (9.67)	0.75
Diethyl malonate	25	720	$C_{14}H_{22}O_8Zn$ White	17.00 (17.05)	43.00 (43.81)	5.55 (5.73)	- -	0.75
Ethyl aceto acetate	25	720	$C_{12}H_{18}O_6Zn$ White	20.00 (20.22)	44.80 (44.52)	5.02 (5.56)	- -	0.73

is to explore the use of electrochemical methods as a synthetic tool for inorganic compounds. The electrolysis has been conducted at sufficiently high potential so that sufficient amount of the product may be produced. Literature [8] records that the solvent and supporting electrolyte remain unaffected as long as highly electroactive species (RH_2 and Zn) are present in the solution. The electrolysis characteristics are recorded in Table 1.

The products are quite stable as these are not much affected by moisture and air. These products (except that from acetylacetone) are insoluble in common organic solvents. Melting point determination of the products reveal that these do not melt upto a temperature of 250°C. However, these decompose in the temperature range of 200-250°C as is evidenced from the colour change of the product.

Elemental analysis (Zn, C, H and N) of the products has also been carried out and the data are summarised in Table 1. Perusal of the Table reveals that the data correspond to the general formula, $Zn(RH)_2$, which shows that a proton from the organic molecule (RH_2) has been replaced by the sacrificial anodic zinc. The reactions may be represented as:

At the cathode :

$$2RH_2 + 2e^- \longrightarrow 2RH^- + H_2 \qquad (1)$$

At the anode :

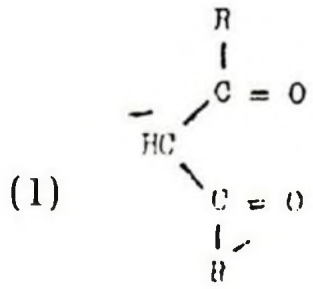
$$2RH^- + Zn_{(s)} \longrightarrow Zn(RH)_2 + 2e^- \qquad (2)$$

Infrared spectra of the products have been recorded in the region of 200-4000 cm^{-1}. The prominent absorption bands are summarised in Table 2. Perusal of Table 2 reveals that the characteristic absorption bands of the products (except that of malononitrile) appear in the regions of 1000 to 1060 cm^{-1} and 400 to 450 cm^{-1}.

The organic compounds (RH_2) yield the carbo-anion (1) on abstraction of hydrogen.

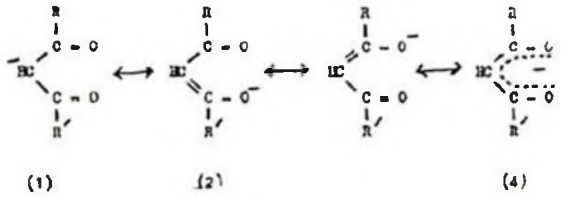
Table 2
Selected IR absorption bands (cm^{-1}) of the product of Electrolysis of RH_2

System	ν(C=N)	ν(C-O)Zn	ν(Zn-O)	ν(C-O)
Malononitrile	2180	-	-	-
Diethylmalonate	-	1025,1060	420	1611
Ethylcyanoacetate	2175	1000,1020	400	1611
Cyanoacetamide	2170	1020	400	1611
Ethylacetoacetate	-	1020	420	1611
Acetylacetone	-	1020	450	1611



(1)

Survey of literature [9] revelas that the ν (Zn-C) stretching vibrations appear in the region of 500 to 510 cm^{-1}. However, no absorption band is observed in this region in the infrared spectra of the products. The carboanion(1) is reported to exist in different resonance forms :

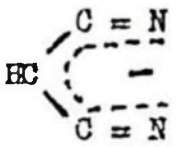


(1) (2) (4)

Absence of ν(Zn-C) absorption band in the infrared spectra of the products indicates that these may have been formed through the resonance form (4).

Survey of literature reveals that the ν(C-O)Zn and ν(Zn-O) absorption bands in zinc alkoxides appear in the region of 1000 to 1130 cm^{-1} and 400 to 450 cm^{-1} respectively [10,11]. Thus the infrared spectral bands observed in the regions of 1000 to 1060 cm^{-1} and 400 to 450 cm^{-1} in the present studies can be assigned to ν(C-O)Zn and ν(Zn-O) stretching vibrations respectively.

In case of the product of malononitrile, a strong absorption band appears at 2180 cm^{-1}. Generally ν(C_N) stretching vibrations appear in the region of 2240-2560 cm^{-1} in alkylnitriles [12]. Appearance of ν(C_N) stretching vibrations in the lower region and absence of ν(Zn-C) absorption band in the infrared spectra of the product of malononitrile also support the formation of the product through a resonance form(5) similar to the resonance form(4):



(5)

Absorption bands at 2175 cm^{-1} and 2170 cm^{-1} have also been observed in the infrared spectra of the electrochemical products of ethylcyanoacetate and cyanoacetamide respectively. These products also exhibit bands in the region of 1000 to 1020 cm^{-1} and at 400 cm^{-1} due to ν(C-O)Zn and ν(Zn-O) stretching vibrations respectively. This also suggests the formation of these products through the resonance form of the type (4) and (5) which is further supported by the appearance of ν(C=O) in a significant lower region (1611 cm^{-1})[12].

Various workers [10,11,13,14] have identified the appearance of two types of ν(C-O)M absorption bands in metal alkoxides, i.e., due to terminal and bridged alkoxide groups. In general, terminal alkoxide groups show absorption bands in the region of 1060 to 1130 cm^{-1} and the bridged alkoxide groups show absorption bands in the region of 1000 - 1060 cm^{-1}. Appearance of ν(C-O)Zn absorption bands in the lower region indicates the existence of the products of the present electrochemical reactions in the polymer form through alkoxide groups. Polymeric

structure of these compounds is also indicated by their insoluble behaviour in various organic solvents.

Current efficiencies of all these electrochemical reactions have also been determined and are recorded in Table 1. Perusal of Table 1 reveals that the current efficiencies of all these systems are quite high. Thus the electrochemical reactions (1) and (2) are the predominant reactions of these systems.

The present studies thus reveal that the electrochemical methods for the synthesis of zinc(II) alkoxides are direct, single-step and simple as compared to the reported multi-step methods for the synthesis of metal alkoxides [15]. The additional advantage of the electrochemical technique is that the zinc(II) alkoxides can be synthesised by using routine laboratory chemicals and equipment.

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