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Electrochemical Reactions at Sacrificial Electrodes. VII. Synthesis of Some Unique Mercury(II) Alkoxides and Glycolates and Their Coordination Compounds

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The electrochemical oxidation of malononitrile, diethyl malonate, ethyl cyanoacetate, cyanoacetamide, ethyl acetoacetate, and acetylacetone has been carried out in acetonitrile at sacrificial mercury anode using tetrabutylammonium chloride as supporting electrolyte. The products of these reactions have been identified by elemental analysis and IR spectral studies and are found to be mercury(II) alkoxides/glycolates. Electrochemical oxidation of these compounds in the presence of ligands like 1,10-phenanthroline and 2,2′-bipyridyl yields coordination compounds of these alkoxides/glycolates. All these reactions have been found to proceed with a very high current efficiency.

Recently in our laboratories, eleotrochemical reactions of carboxylic acids, polyhedric alcohols, and monohydric alcohols have been conducted at sacrificial copper,[1-3] mercury,[4] and cadmium[5] anodes. It has been observed that the acidic proton in these compounds has been replaced by the anode metal through these electrochemical reactions. The present paper reports the electrochemical reactions of malononitrile, diethyl malonate, ethyl cyanoacetate, cyanoacetamide, ethyl acetoacetate, and acetylacetone (H_2R) at sacrificial mercury anode. These compounds have no acidic proton but can loose protons to yield carbanions under suitable experimental conditions. Adducts of these products of the above reactions with ligands such as 1,10-phenanthroline and 2,2′-bipyridyl have also been prepared by the electrochemical technique.

Experimental

Material and Equipment. Acetonitrile was dried over phosphorus pentaoxide and distilled. Freshly distilled acetonitrile was used as solvent in all these electrochemical reactions.

Tetrabutylammonium chloride was crystallized from conductivity water and dried under reduced pressure at 100 °C and used as supporting electrolyte.

Mercury was distilled in before use. Other organic compounds (Reidel Pure) were used as supplied.

Electrolysis was carried out in an H-type cell[1-3] made of Pyrex glass. The cathode and anode compartments were separated from each other by a sintered disc of G-3 porosity. Volume of the anode compartment (ca. 200 cm^3) was almost three times as large as that of cathode compartment (ca. 65 cm^3).

Platinum foil (1×1 cm^2) was used as a cathode and mercury pool (surface area 25 cm^2) as anode.

Direct current was obtained with the help of a Toshniwal electrophoresis power supply.

Procedure. A solution of tetrabutylammonium chloride (0.5×10^{-2} mol dm^{-3}) in acetonitrile (250 cm^3) was taken in the electrolysis cell. Two grams of the organic compound (H_2R) was also added to this solution. Necessary connections were then made with the power supply and potential accross the electrodes was adjusted so that a current of about 20 mA passed through the cell. The other experimental details were essentially the same as reported earlier.[1] White/grey colored solids separated in the anode compartment after a prolonged electrolysis of about ten hours. The products were collected by filtration, washed several times with dry acetonitrile in an all glass filtration unit and dried in vacuum.

Coordination compounds of the products of the above electrolytic processes were prepared through the electrolysis of the solution of tetrabutylammonium chloride (0.5×10^{-2} mol dm^{-3}) in acetonitrile containing 2.0 g of the organic compound (H_2R) and 1.0 g of the ligand at the sacrificial mercury anode. The details of the experimental procedure are the same as above.

Current efficiencies were determined from the ratio of actual and theoretical amounts of mercury dissolved when a current of 20.0 mA was passed for 2 h through the cell in the given system.

Infrared spectra of the products in Nujol were recorded with Beckman IR-20 spectrophotometer using sodium chloride plates in the region of 4000 to 600 cm^{-1} and polyethylene plates in the region of 600 to 200 cm^{-1}.

Mercury contents in the electrochemical products were estimated potentiometrically.[6]

Results and Discussion

Products of the electrochemical reactions of malononitrile, diethyl malonate, ethyl cyanoacetate, cyanoacetamide, ethyl acetoacetate, and acetylacetone are not affected much by moisture and air and are quite stable. All these compounds are insoluble in the common organic solvents. The product of acetylacetone, however, is soluble in most of the polar solvents.

The products of these electrochemical reactions do not melt upto a temperature of 250 °C. However, in some of the cases there has been a color change of the product in the temperature range of 230 to 250 °C.

Elemental analysis (Hg, C, H, and N) of these compounds have been carried out and the data are listed in Table 1 alongwith the electrolysis characteristics. Perusal of Table 1 reveals that the elemental analysis of the products corresponds to a general formula of $Hg(HR)_2$

Table 1. Electrolysis Characteristics, Analytical and Other Relevant Data of the Electrolysis Processes of H_2R at Mercury Anode

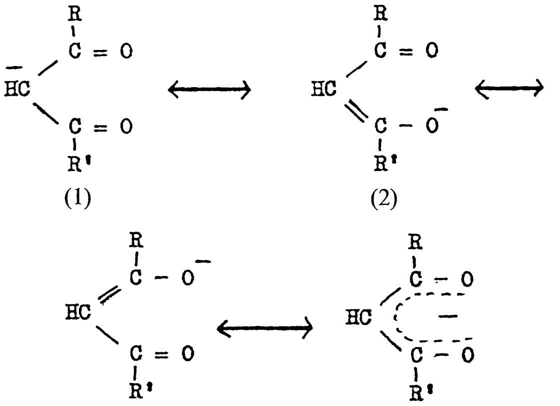
H_2R	Potential applied	Electricity passed	Product	Color	Elemental analysis[a)] / %				Current efficiencies
	V	Coulombs			Mercury	Carbon	Hydrogen	Nitrogen	%
Malononitrile	30	650	$C_6H_2N_4Hg$	White	59.6 (60.7)	23.9 (21.8)	0.5 (0.6)	15.8 (16.9)	88
Diethyl malonate	20	710	$C_{14}H_{22}O_8Hg$	Grey	35.0 (38.7)	33.0 (32.4)	3.3 (4.2)	—	78
Ethyl cyanoacetate	30	680	$C_{10}H_{12}O_4N_2Hg$	Grey	47.1 (47.2)	31.1 (28.3)	2.5 (2.8)	6.9 (6.6)	72
Cyanoacetamide	20	720	$C_6H_6O_2N_4Hg$	Grey	51.8 (53.7)	18.3 (19.6)	0.9 (1.1)	14.2 (15.3)	78
Ethyl acetoacetate	30	640	$C_{12}H_{18}O_6Hg$	White	42.9 (43.7)	30.4 (31.4)	2.9 (3.9)	—	71
Acetylacetone	30	680	$C_{10}H_{14}O_4Hg$	Grey	51.3 (50.3)	30.0 (30.1)	3.2 (3.5)	—	75

a) Results in parenthesis are the theoretical values.

which shows that a proton from the organic molecules (H_2R) has been replaced by the mercury anode.

Infrared spectral data of the electrochemical products recorded in the region of 4000 to 200 cm^{-1} reveal that the characteristic bands of all the products except that of malononitrile appear in the regions of 1020 to 1060 and 450 to 460 cm^{-1}. Survey of literature[7,8] reveals that the ν(C–Hg) stretching band appears in the region of 515 to 554 cm^{-1} and no such band has been observed in the infrared spectra of the present products.

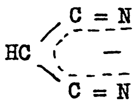
The carbanions formed by the abstraction of proton from the present organic molecules have been reported to exist in different resonance forms:



(1) (2) (3) (4)

Absence of ν(C–Hg) absorption band in the infrared spectra of the electrochemical products indicate that these products may have formed through the resonance form (4). Survey of literature[9,14] reveals that the ν(C–O)M and ν(M–O) absorption bands in various metal alkoxides appear in the regions of 1000 to 1150 cm^{-1} and 400 to 500 cm^{-1} respectively. Infrared spectra of some mercury(II) alkoxides have been reported recently from our laboratories.[4] The absorption bands in the regions 1000 to 1060 cm^{-1} and 450 to 460 cm^{-1} have been assigned to ν(C–O)Hg and ν(Hg–O) respectively. Thus the infrared studies support the formation of these products through the resonance form (4).

In case of malonitrile, a strong absorption band appears at 2180 cm^{-1}. Generally, ν(C≡N) bands appear in the region of 2240 to 2260 cm^{-1} in alkanenitriles.[15] Appearance of ν(C≡N) stretching modes in the lower region also supports the formation of the product of the electrochemical reaction of malononitrile through the resonance form (5):



(5)

Absorption bands at 2200 and 2150 cm^{-1} have also been observed in the product of ethyl cyanoacetate and cyanoacetamide respectively in addition to the absorption bands in the regions 1010 to 1020 and 450 to 460 cm^{-1}. This also supports the formation of these products through the resonance forms of the type (4) and (5). Thus all these organic compounds except malononitrile yield mercury(II) alkoxides/glycolates through the present electrochemical reactions.

Survey of literature[9–11,16–18] reveals that the metal alkoxides, generally exist as polymers by forming bridged structure through alkoxide groups. Appearance of ν(C–O)Hg absorption bands in the lower region and comparatively broad peaks indicate the polymer structure of these compounds through alkoxyl groups. Insoluble behavior of these compounds in almost all organic solvents also supports this fact. Molecular weight of these compounds, however, could not be determined because of their insolubility in various solvents having convenient melting point.

Current efficiencies of all these reactions have been determined and are listed in Table 1. Reactions of alcohols at sacrificial anodes[2–4] reveal that the metal alkoxide is the only product containing metal atom. The present electrochemical reactions are similar to those of alcohols as in both the cases a proton from the organic molecule is replaced by the sacrificial metal anode. Current efficiencies have, therefore, been evaluated on the basis of equivalents of metal dissolved per Faraday of electricity passed. Perusal of Table 1 reveals that crrrent efficiencies of all these reactions are quite close to 100% showing thereby that the reactions leading to the formation of mercury(II) alkoxides/glycolates are the predominant reactions of these systems. The reaction scheme may be written as:

At the cathode:

$$2\,H_2R + 2e^- \longrightarrow 2\,HR^- + H_2$$

At the anode:

$$2\,HR^- + Hg_{(+)} \longrightarrow (HR)_2Hg + 2\,e^-$$

Coordination Compounds. The electrochemical products of ethyl cyanoacetate and diethyl malonate have been refluxed with 1,10-phenanthroline and 2,2′-bipyridyl in solvents like methanol, ethanol, acetonitrile, and benzene for more than 48 h. However, the elemental analysis showed that the donor molecules could not rupture the alkoxide bridges to form their coordination compounds. It is, therefore, considered worthwhile to add the ligand molecules to these compounds before these are polymerized. Electrolysis of the organic compounds has therefore, been carried out in the presence of sufficient amount of 1,10-phenanthroline or 2,2′-bipyridyl.

The products of these electrochemical reactions are also insoluble in the common organic solvents. This indicates that these may also be polymer in nature like the parent alkoxides/glycolates. Melting points of these products are above 250 °C. Some of these compounds, however, show slight color change in the temperature range of 200 to 250 °C. These compounds are not affected by moisture or air and are quite stable.

Elemental analysis (Hg, C, H, and N) has been carried out and the data are recorded in Table 2. The analytical data of these compounds agree with the molecular formula, $Hg(HR)_2\cdot L$.

Infrared spectral data of these compounds show the characteristic ν(C–O)Hg stretching vibrations[9–14] between 1030 and 1120 cm^{-1}. The absorption bands are slightly broad, appear in a slightly higher region as compared to the parent mercury(II) alkoxides/glycolates and distinct two or three absorption bands are observed in this region. Increase in the number of bands in this region indicates the presence of both the terminal and bridged alkoxide groups in these compounds. The presence of terminal alkoxyl groups may be attributed to the coordination of the ligand molecules and the presence of bridged alkoxyl groups shows that the present coordination compounds of mercury(II) alkoxides/glycolates have still polymeric structure. Insoluble behavior of these compounds also supports the polymeric structure of these compounds. Many such metal alkoxides in which in addition to the ligand

Table 2. Electrolysis Characteristics, Elemental Analysis and Other Related Data of the Electrolysis of H_2R+Ligand Systems at Mercury Anode

System	Potential applied	Electricity passed	Product	Color	Elemental analysis[a]/%				Current efficiencies
	V	Coulombs			Hg	C	H	N	%
Malononitrile+2,2′-Bipy.	30	640	$C_6H_2N_4Hg\cdot C_{10}H_8N_2$	Grey	40.7 (41.3)	37.9 (39.4)	2.0 (2.1)	16.9 (17.3)	80
Diethyl malonate+2,2′-Bipy.	40	510	$C_{14}H_{22}O_8Hg\cdot C_{10}H_8N_2$	Grey	29.1 (29.7)	40.9 (42.7)	4.8 (4.5)	4.9 (4.2)	62
Ethyl cyanoacetate+2,2′-Bipy.	20	720	$C_{10}H_{12}O_4N_2Hg\cdot C_{10}H_8N_2$	Grey	33.6 (34.6)	40.8 (42.1)	3.0 (3.5)	9.2 (9.8)	84
Cyanoacetamide+2,2′-Bipy.	20	700	$C_6H_6O_2N_4Hg\cdot C_{10}H_8N_2$	Light Brown	40.1 (38.4)	35.9 (36.7)	1.9 (2.6)	15.1 (16.1)	76
Ethyl acetoacetate+2,2′-Bipy.	20	720	$C_{12}H_{18}O_6Hg\cdot C_{10}H_8N_2$	Grey	31.9 (32.7)	43.2 (43.0)	3.8 (4.2)	4.5 (4.6)	67
Acetylacetone+2,2′-Bipy.	30	650	$C_{10}H_{14}O_4Hg\cdot C_{10}H_8N_2$	Grey	37.2 (36.2)	41.2 (43.3)	3.7 (4.0)	4.9 (5.1)	82
Diethyl malonate+1,10-Phen.	30	650	$C_{14}H_{22}O_8Hg\cdot C_{12}H_8N_2$	Light Green	28.4 (28.8)	43.6 (44.7)	3.6 (4.3)	3.9 (4.0)	79
Ethyl cyanoacetate+1,10-Phen.	40	500	$C_{10}H_{12}O_4N_2Hg\cdot C_{12}H_8N_2$	White	33.5 (33.2)	42.2 (43.7)	3.3 (3.3)	9.0 (9.3)	83
Cyanoacetamide+1,10-Phen.	20	680	$C_6H_6O_2N_4Hg\cdot C_{12}H_8N_2$	Grey	37.4 (36.9)	38.9 (39.5)	2.0 (2.7)	14.2 (15.3)	60
Ethyl acetoacetate+1,10-Phen.	20	650	$C_{12}H_{18}O_6Hg\cdot C_{12}H_8N_2$	White	30.9 (31.4)	43.7 (45.1)	3.9 (4.1)	4.3 (4.4)	64
Acetylacetone+1,10-Phen.	30	650	$C_{10}H_{14}O_4Hg\cdot C_{12}H_8N_2$	Grey	34.5 (34.7)	43.8 (45.6)	3.2 (3.8)	3.9 (4.8)	82

a) Results in parenthesis are the theoretical values.

molecules, alkoxyl bridging are also present have been reported in literature.[19–21]

Current efficiencies of all these systems are recorded in Table 2. It has been observed that the current efficiencies of most of the systems are quite close to 100% showing thereby that the reactions leading to the formation of coordination compounds of mercury(II) alkoxides/glycolates are the predominant reactions of these systems.

The present methods for the synthesis of mercury(II) alkoxides/glycolates and their coordination compounds are quite simple as compared to the usual multistep methods[10] for the synthesis of such compounds. These methods are associated with quite high values of current efficiencies also. Thus the electrochemical technique presents a new route for the synthesis of metal alkoxides/glycolates and their coordination compounds.

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