Electrochemical Generation and Oxidation of Mercaptan Anions using rotating Ring-Disc Platinum Electrode Method

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THE study of the electrochemical behaviour of some organomercury sulfur compounds $(RS)_2Hg$, using the rotating ring-disc platinum electrode (RDR) method was carried out in acetonitrile containing 0.05M Bu_4NBF_4 as supporting electrolyte. The redox mechanism was suggested. The disc electrode (cathode) process was found to involve the consumption of two electrons, giving $[(RS)_2Hg]^{2-}$ and RS^- anions, while the ring electrode (anode) process involves the oxidation of the disc products, forming $(RS)_2Hg$ and RSSR. The effect of the alkyl or aryl groups on the half-wave potentials was demonstrated.

The electrochemical oxidation of anions of mercaptans in aqueous medium has been carried out by Ucatenko[1], who suggested that the anodic oxidation involves two single-electron processes. The first was the elimination of one electron, forming the corresponding radical (RS), which dimerized into the correspoding disulfides (RSSR). The second involves the removal of two electrons from the disulfide compounds forming other products.

$$2\ RS^- \xrightarrow{-2e} RSSR \xrightarrow{-2e} \text{Products}$$

Davis and Bianco[2] showed that oxidation of mercaptans in aqueous medium on platinum anode gave disulfide and other products, such as sulfonic acids. The authors proposed the following mechanism :

$$RSH \xrightarrow{-e} RS^* + H^+$$

$$2\ RS^* \longrightarrow RSSR$$

$$RS^* + 3H_2O \xrightarrow{-5e} RSO_3H + 5H^+$$

As an extension to our interest on the electrochemical generation and oxidation of anions[3,4] using tha rotating ring-disc electrode (RDR)[5,6], the present work concerns with the electrochemical generation and oxidation in addition to the investigation of the electrode process of anions resulted from organomercury sulfur compounds $(RS)_2Hg$.

EXPERIMENTAL

The electrode (RDR) consisted of a platinum cathode (disc, radius 2.53 mm) a platinum anode (internal and external ring radius were 2.66 and 3.66 mm respectively). Two helping platinum electrodes were used (net-form of surface area 10 × 10 mm). The theoretical and experimental values of N were 0.43 + 0.03, using ferrocene in acetonitrile-tetrabutylammoniumperboroflourate system.

Electrochemical Cell : The electrolysis cell consisted of a central cylindrical compartment of 40 ml capacity, surrounded by a jacket and four side arms of 10 ml capacity each. Two of these side arms were isolated by sintred glass No. 2 as a diaphragm. The other two arms ended in two capillary tubes. One of the capillary tubes was placed at 1 mm distance of the surface of the disc electrode and the other capillary was at 1 mm distance from the ring. Two electrolytic bridges were placed in the two other compartments to connect to two SCE as reference electrodes. The entire cell was placed in an ultrathermostat.

The experiments were performed, using two potentiostats model π 5848, two galvanometers model M−254, two SCES as a references electrodes and a stirrer of 800-3600 rpm.

Chemicals Used : n-Tetrabutylammoniumperboroflourate was prepared by mixing equimolecular amounts of aqueous solution of Bu_4NOH and HBF_4 with continuous stirring. The white ppt was filtered, washed throughly with cold water, dried, recrystallized from ethyl acetate–ether mixture (1:1) and dried in vacuum over P_2O_5 for one day m.p. 162° (Lit.[7] 162–162.5).

Acetonitrile was stirred over CaH_2 for 20 hrs. (10 g/L), decanted and distilled over new P_2O_5 at atmospheric pressure. The fraction of b.p. 81.5° was collected.

The compounds chosen for this work were :

1 – $(RS)_2Hg$ where $R = (CH_3)_2CH$, C_2H_5, C_5H_{11}

2 – $(P-XC_6H_4S)_2Hg$ where $X = OH$, CH_3, NO_2.

3 – $(\beta - C_{10}H_7S)_2$ Hg.

All these were prepared and purified conventionally[8].

Procedure : The surface of the RDR electrode was polished using 5 μm alumina powder, filter paper, wased thoroughly with H_2O; acetone, and finally dried with medical cotton. The mercury metal formed during the measurements on the disc surface electrode was demercurated, by electrolysing in a saturated solution of KCl at 1.5 A for 20 min.

A stream of pure argon was passed through the acetonitrile solution (30 ml) containing 0,05 Mn-Bu_4NBF_4 as supporting electrolyte for 40 min. at 25°C. The calibration curves were drawn for RDR electrode. A 2×10^{-3}M of the investigated materials were added (compounds 5,6 and 7 were poorly soluble in acetonitrile, therefore their saturated solutions were used). The measurements were carried out on the disc only, the polarization curves were drawn, the limiting currents and $-E_{\frac{1}{2}}$ were determined. The measurements on the ring electrode alone were carried out (see results and discussion).. Results of the anodic polarization curves at the ring were obtained when the disc is maintained at the $E_{\frac{1}{2}}$ of the cathode reaction (see Table 1).

RESULTS AND DISCUSSION

In the present investigation, the electrochemical behaviour of seven organomercury sulfur compounds has been studied using the rotating ring-disc platinum electrode method (RDR) to determine the multi-electronic steps in redox reaction of these compounds. The measurements were carried out in acetonitrile containing 0.05 M n-Bu_4NBF_4 as supporting electrolyte vs. SCE as a reference electrode.

The cathodic polarization curves on the disc for all the compounds showed only one wave corresponding to two electrons with half-wave potential from −0.4 to −1.4 V vs. SCE (see Table 1). The possible product may be the anion complex $[(RS)_2Hg]^{-2}$ which undergoes fragmentation to the corresponding anions (RS^-), and mercury metal which was observed at the end of the measurements on the disc electrode. The cathodic mechanism may be written as follows :

$$(RS)_2\,Hg \xrightarrow[\text{disc}]{+\,2e} [(RS)_2Hg]^{-2} \longrightarrow 2\,RS^- + Hg$$

From Table I, it can be seen that the $E_{\frac{1}{2}}$ of the reduction. $[(CH_3)_2CHCH_2S]_2$ Hg and $(\beta\text{-}C_{10}H_7S)_2Hg$ were −0.40 and −1.14 V vs. SCE respectively, indicating that increasing of the electron density on the reducible centre, decreases the case of reduction and vice versa.

Each of the disc products. $[(RS)_2Hg]^{-2}$ and (RS^-), were simultaneously transferred to the ring

TABLE 1

Results of the electrochemical generation and oxidation of anions of $(RS)_2$ Hg compounds

Compound	$E_{\frac{1}{2}}$ V Ring	I Ring	$E_{\frac{1}{2}}$ V Ring	I Ring	$E_{\frac{1}{2}}$ V Disc	I Disc	Con. M	$N = \frac{I\ ring}{I\ disc}$
$(CH_3CH\ CH_2S)_2Hg\ CH_3$	+0.58	75	+1.10	180	−0.40	460	2×10^{-3}	0.39
$(C_2H_5S)_2Hg$	+0.35	100	+0.80	250	−0.43	580	2×10^{-3}	0 43
$(C_5H_{11}S)_2Hg$	+0 60	100	+1.00	140	−0.55	320	2×10^{-3}	0.44
$(p\text{-}HO\text{-}C_6H_4S)_2Hg$	+0 57	250	+0.67	300	−0.58	550	2×10^{-3}	0.54
$(p\text{-}CH_3C_6H_4S)_2Hg$	+0.80	250	+0 88	350	−0 80	1100	Sat.	0.32
$(p\text{-}NO_2C_6H_4S)_2Hg$	+0.58	40	+1.34	125	−0.80	300	Sat.	0.42
$(\beta\text{-}C_{10}H_7S)_2Hg$	+1.06	20	+1.76	90	−1.14	130	Sat.	0.42

(anode). Polarization curves of all the compounds on ring electrode showed two waves at $E_{\frac{1}{2}}$ + 0.35 to + 1.06 and + 0.67 $F_{\frac{1}{2}}$ + 1.76V vs. SCE, corresponding to the oxidation of $(RS)_2Hg$ and (RS^-) anions to $(RS)_2Hg$ and RSSR respectively. The mechanism of the electrode processes at the ring can be visualized as follows :

$$\text{first wave} \quad [(RS)_2Hg]^{-2} \xrightarrow[\text{ring}]{-2\,e} (RS)_2Hg$$
$$\downarrow$$

$$\text{second wave} \quad Hg + 2RS^- \xrightarrow[\text{ring}]{-2\,e} 2RS \longrightarrow RSSR$$

Experimental data showed a nonlinear relationship between the ring (anode) currents and rotation speed, indicating that the limiting ring current was independent on the rotation speed. On the other hand, the lower pK_a values of mercaptan ions prevented the occurrence of the acid-base reaction between those ions and acetonitrile, i.e. the presence of two anodic waves does not mean the oxidation of two stable cathodic products. This indicates that the limiting ring current has a kinetic values, i.e. depends on the velocity convected diffusion. Thus the first wave represents the oxidation of the complex $[(RS)_2Hg]^{2-}$ to the non oxidizable products $(RS)_2Hg$ and the second wave corresponding to the oxidation of anion RS^- to the disulfides as the final products.

REFERENCES

1. U. N. Uoatenko and F. N. T. U. Tulur, T. R. Trudy *Dnepropetrovckovo Khim-Tekhn. In-te*, 12 (1959) 26.
2. D. Davis and E. Bianco, *J. Electroanal. Chem.*, 12 (1960) 254.
3. K. P. Butin, M. T. Ismail and O. A. Reutov, *Ezv. Akad. Nauk, (SSSR), ser Knim.* (1978) 508.
4. M. T. Ismail, Ph.D., Thesis, *Published by MGU* (Moscow State Univ.) Moscow, (1978).
5. A. N. Frumkin and L. N. Nekrosov, *Dokl. Akad. Nauk. SSSR*, 126 (1959) 115.
6. Yu. V. Plsaskov and V. Yu. Filinoskil, *"The Rotating Disc Electrode"* New York and London, 8, 287 (1976).
7. J. F. Coctree, *Anal, Chem.*, 34, (1962) 1159.
8. L. G. Makarova and A. N. Nesmeyanov, *Metody elementoorganicheskoi Khimii, Mercury*, Nauka, Moscow (1965).