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ELECTROSYNTHESIS OF ORGANIC COMPOUNDS XIII ELECTROCHEMICAL OXIDATION OF BARBITURIC AND 2-THIOBARBITURIC ACIDS*

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Electrochemical oxidation of barbituric and 2-thiobarbituric acids was carried out in different nonaqueous solvents (N,N-dimethylformamide, dimethyl sulfoxide and methanol) containing different electrolyte (LiCl, NaOH and $NaOCH_3$) on platinium anode at controlled potential of + 1.4 ± 0.03 V vs SCE at 20°C, for a period of 70-112 hrs. The electrosynthesised compounds were the corresponding dimers, methoxy derivatives and some polymerized products. Suitable mechanisms invoiving the formation of cation and free radical intermediates are suggested.

Also, the anodic oxidation behaviour of the investigated compounds was studied in different solvents containing different electrolytes. The current-potential curves were drawn and one wave for the anodic oxidation processes was observed. The anodic discharge potentials were determined.

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The heterocyclic compounds barbituric acid, 2-thiobarbituric acid and their derivatives have a special interest in the medical chemistry [1-2]. A polarographic, a voltametric and an amperometric studies for barbiturates in aqueous solutions were performed [1,2,3,4]. Electrochemical oxidation of some heterocyclic compounds was carried out by many authors and several reviews are available[3-8]. Anodic oxidation of phenothiazine derivatives [5-6], nitromethane anions and malononitrile anions [7-8] (containing active methylene group) was carried out in our laboratory.

This work presents the anodic behavior and the electrosynthesized products as well as the anodic reaction mechanisms for the investigated barbituric and 2-thiobarbituric acids.

EXPERIMENTAL

Electrolytic cell and analytical methods as given in the preceeding paper [6]. Lithium chloride (Prolabo), absolute methanol (Fluka), dimethylformamide (Merck), dimethyl sulfoxide (Merck), were obtained commercially and were subjected to further purification before using. The purity was checked by boiling point and chromatography.

Barbituric acid, 2-thiobarbituric acids and their corresponding dimers were prepared as described in the literature procedures [4,14].

TABLE 1

THE OXIDATION POTENTIAL VALUES OF BARBITURIC, 2-THIOBARBITURIC ACIDS AND THEIR ANIONS*

Compound	Solvent	Electrolyte	Oxidation ** Potential V vs SCE	Con. mol/l
Barbituric acid	DMF	LiCl	0.99	0.15
Barbituric anions	MeOH	NaOMe	1.43	0.15
2-Thiobarbituric acid	DMF	LiCl	1.06	0.15
2-Thiobarbituric anions	MeOH	NaOMe	1.28	0.07

** Determined from the polarization curves.

General Procedure

Polarization Measurements: A 60 ml dimethyl formamide and/or absolute methanol containing barbituric (0.05 mol/l, 0.10 mol/l and 0.15 mol/l) and/or 2-thiobarbituric acids (0.05 mol/l, 0.06 mol/l and 0.07 mol/l) and 0.1 mol/l LiCl and/or 0.2 gm atom/l sodium metal respectively was placed in the anode compartment. The cathode compartment was filled with 30 ml of the same solutions. The potential is scanned from zero to + 2.0 V vs SCE (0.05 V/30 Sec.) and the resulted current is recorded. The current-potential curves were drawn (Figures 1,2,3 and 4), and the oxidation potentials were determined (Table 1).

For Electrolytic Oxidation: Barbituric acid (2.56 gm, 0.02 mol) or 2-thio-barbituric acid (2.88 gm, 0.02 mol) were dissolved in 60 ml of the anhydrous solvents (methanol, dimethylformamide and dimethyl sulfoxide) containing 0.1 mol/l lithium chloride, or 0.3 gm atom/l sodium metal and/or 0.3 mol/l sodium hydroxide and placed in the anode compartment. The cathode compartment was filled with 30 ml of the same solutions. The anodic mixture was electrolyzed for periods of 72 - 112 hrs at controlled potential value of + 1.4 ± 0.03 V at 20°C. During electrolysis, the colourless anodic solution became brown-red colour and no gas evolution was observed on the surface of the anode. The changes of the current with time was recorded and/the current-time curves drawn and the total charge passed was calculated (Table 2).

At the end of the electrolysis the anodic solution was transfered into a distillation flask and the excess of methanol or DMSO was distilled (using rotatory evaporater) under atmospheric or reduced pressure respectively (in case of dimethylformamide, the anodic solution was diluted with 250 ml H_2O). The product mixture was extracted three times with 150 ml ether. The ether extracts were dried over anhydrous megnesium sulfate, filtered, distilled under atmospheric pressure and the residue was subjected to analysis. The mother liquor was acidified with 0.1 N HCl and the precipitated materials were filtered, dried at 110°C for 4 hrs and analyzed. Analysis of the products was carried out using thin layer chromatography (1:1 methanol-benzene mixture), column chromatography (silica gel neutral, 100% benzene; 80% - 20%, 50% - 50%, 20% - 80% benzenemethanol mixtures; 100% methanol and 100% 1,4-dioxane), I.R spectroscopy and elemental analysis teohniques.

RESULTS AND DISCUSSION

The kinetic studies for different concentrations of barbituric and 2-thiobarbituric acids were carried out in nonaqueous dimethylformamide and methanol containing LiCl and NaOMe as supporting electrolyte at 20° C on platinum anode. The polarization curves (current-potential curves) were drawn for barbituric (Figure 1), 2-thiobiorbituric acids (Figure 3) and their anions (Figure 2 and 4 respectively). These curves showed single oxidation step for the investigated compounds. In addition a linear current concentration relationship at a constant potential for the compounds were obtained (Figure 1a,2a, 3a and 4a). Increasing concentration of the investigating compound resulted in lowering of anodic polarization. This indicates that these compounds depolarize the electrodes and get oxidized. The oxidation potentials of the barbiturates were determined from their polarization curves and are shown in Table 1. The oxidation potential values were in the order; barbituric anions > 2-thiobarbituric anions > 2-thiobarbituric acid > barbituric acid (1.43 > 1.28 > 1.06 > 0.99 V vs SCE, respectively). Thus the acids are oxidised easier than the corresponding anions. This can be interpreted in terms of formation of the free radical intermediate species (Scheme 1 B), which are more stable (by resonance) than the corresponding cation radical intermediates (Scheme 1 A).

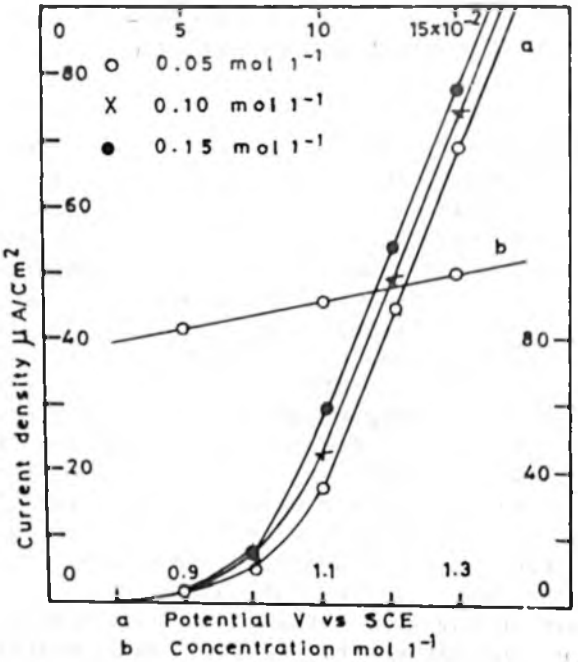


Fig. 1a Anodic oxidation of barbitur c acid in DMF at 20° C.
1b Concentration vs anodic current at + 1.2 V vs SCE

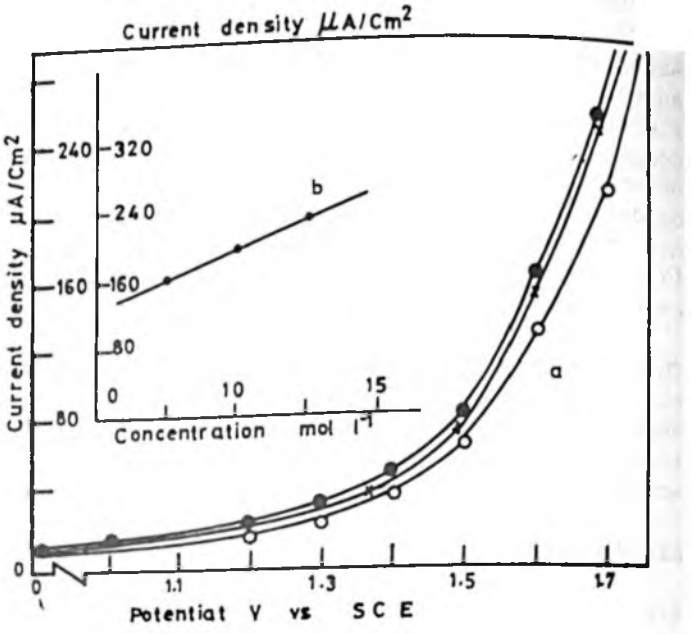


Fig. 2a Anodic oxidation of barbituric anions in absolute methanal at 20° C
2b Relation between concentration and anodic current at + 1.65 V vs SCE

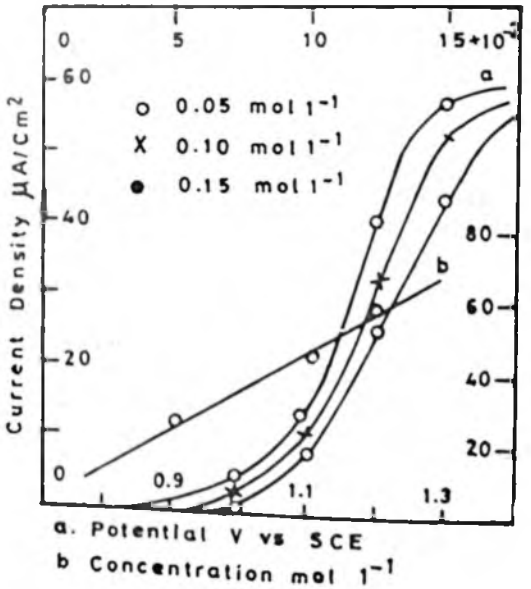


Fig. 3a Anodic oxidation of 2-thiobarbituric acid in DMF at 20° C
3b Concentration vs anodic current at + 0.69 V vs SCE at 20° C

The electrolysis of barbituric and 2-thiobarbituric acids was carried out in different nonaqueous solvents (dimethyl formamide, dimethyl sulfoxide and methanol) containing

TABLE 2

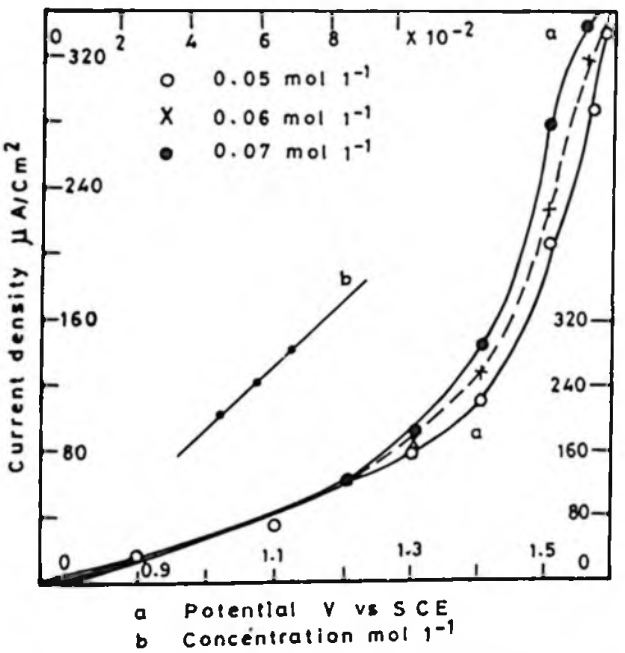
CONDITIONS AND PRODUCTS OF THE ANODIC OXIDATION OF BARBITURIC AND 2-THIOBARBITURIC ACIDS AT 20 C

Exp	Solvent	Electrolyte	Time	Curvent	Charge*	Conversion**	Products*** (Yield %)		
				(A)	(F)	%	Dimer	Methoxy	Polymer
Barbituric acids									
1.	DMF	LiCl	72	0.036 - 0.003	0.044	71	79.2	-	8.7
2.	DMF	NaOH	112	0.007 - 0.003	0.012	14	21.6	-	2.8
3.	MeOH	NaOMe	24	0.080 - 0.003	0.034	87	73.3	7.8	12.3
4.	DMS	LiCl	96	0.015 - 0.003	0.024	64	68.7	-	6.5
2-Thiobarbituric acid									
5.	DMF	LiCl	72	0.035 - 0.003	0.036	74	85.2	-	10.4
6.	DMF	NaOH	96	0.020 - 0.003	0.034	52	37.3	-	3.5
7.	MeOG	NaOMe	72	0.025 - 0.003	0.031	92	72.1	12.4	10.1
8.	DMS	LiCl	76	0.013 - 0.003	0.016	59	66.4	-	9.4

* Calculated from the current-time curves at ± 1.4 + 0.03 V

** Conversion = 100 X total yield of products, mole/amount of starting anions, mole).

*** By weight from column chromatographic separation.



a Potential V vs S C E

b Concentration mol l^{-1}

Fig. 4a Anodic oxidation of 2-thiobarbituric anions in absolute methanol at 20 C

4b Concentration vs anodic current at + 1.5 V vs SCE at 20 C

different electrolytes (LiCl, NaOMe) at controlled anode potential of + 1.4 ± 0.03 V vs SCE on platinum anode at 20° C for a periods of 72-112 hrs.

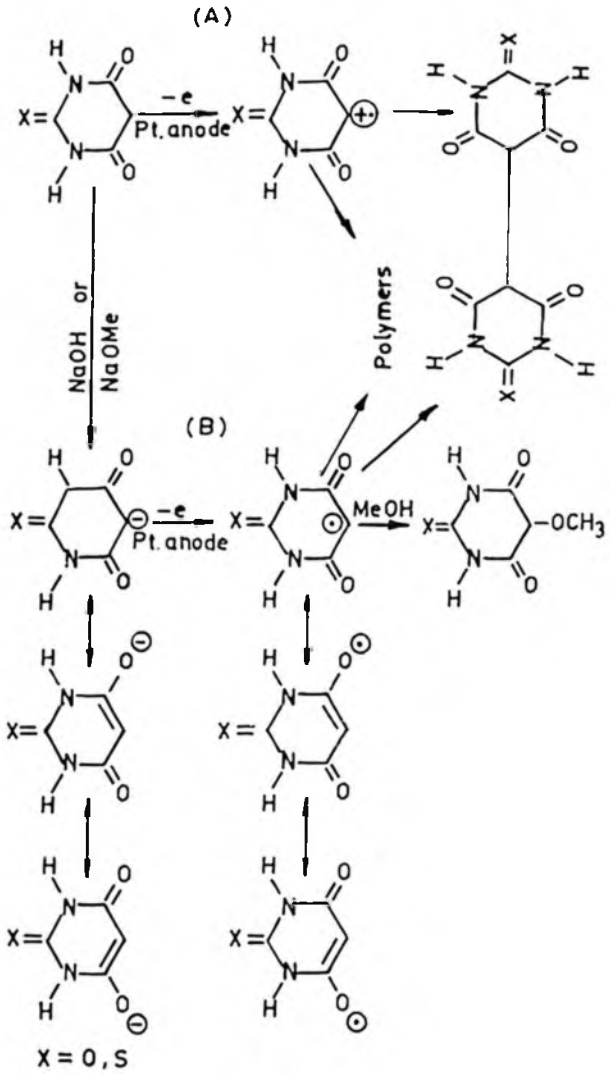
The isolated products were the dimerzation products [(5,5' bis (2,4,6,1H,3H,5H pyrmimidinetrione) 21 - 79.2%, 5,5' bis (2-thio, 4,6 (1H, 3H, 5H) pyrimidinedione) 37 - 85.2%)], methoxy derivatives [(5-methoxy 2,4,6 (1H, 3H, 5H) pyrimindinetrione 7.8%, 5-methoxy 2-thio-4,6-(1H,3H,5H) pyrimidinedione 12.4%)] and some polymerized products (2.8 - 12.3%).

Mechanism of the Anodic Oxidation Processes

Results of the kinetic studies (Table 1) as well as the electrosynthesised products (Table 2) indicate that the oxidation of barbituric and 2-thibarbituric acids (experiment 1,4,5 and 8) without added bases, resulted in the formation of cation radical intermediate species [11-13] which dimerise at C-S to bis (2,4,6 (1H,3H,5H) pyrimidinetrione) bis (2-thio-4 6(1H, 3h, 5H) pyrimidinedion) and/or polymerise to give a polymerised products (Scheme 1 A). In methanol and/or dimethyl formamide solutions containing bases (NaOH or MeONa, experiments 2,3,6,7), the anodic oxidation processes leads to the formations of free radical intermediates [4,7,8] which dimerise at C-S to give the corresponding dimers and/or attack the methanol solvent, forming 5-methoxy 2,4,6 (1H, 3H, 5H) pyimidinetrione, 5-methoxy 2-thio-4,6 (1H,3H,5H) phrimidinedione and/or polymerise to a polymerised products ,(Scheme 1 B).

This method can be used successfully for preparing the dimers of barbitric acid, thiobarbitric acid and their derivatives, for their importance in the medical purposes.

SCHEME 1



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