ELECTROCHEMICAL OXIDATION OF ACETYL-N-DIPHENYLAMINE ACETYL-N-PHENOTHIAZINE AND THEIR CHLOROACETYL DERIVATIVES

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The anodic oxidation of four selected organic amides, [viz. acetyl-N-diphenylamine (I), chloroacetyl-N-diphenyl amine (II), acetyl-N-phenothiazine (III) and chloroacetyl-N-phenothiazine (IV)] was carried out. The effect of the nature of anode, structure of the compounds under investigation and the media of electrolysis on the oxidation products was studied and supported by the galvanostatic polarization measurements. A mechanism for the formation of the oxidation products was suggested.

Electrochemical oxidation of formamide was studied by Schneider[1]and Couch[2]. They reported that the anodic oxidiation product was cyanuric acid ($C_3H_3O_3N_3$). The mechanism of oxidation of the aliphatic amides was reported by many authors [3-5], who pointed out that a free radical or cation radical intermediate species are formed in the oxidation processes.

Anodic oxidation of phenothiazines and their derivatives was the subject of study in different conditions [6-8]. The reported mechanism suggested, that the cation radical or di-cation (in case of N-sutituted derivatives) intermediates in the oxidation process, either reacted with the medium or lost their protons to form the corresponding products.

Some work in this field is done by the authors earlier [6]. In this article results of more extensive work has been given which would throw light on the mechanism of these oxidations and the intermidiate species involed in the process.

EXPERIMENTAL

Diphenylamine and phenothiazine were commercially available. Acetyl-N-diphenylamine (I), chloroacetyl-N-diphenyl amine (II) [7], acetyl-N-phenothiazine(III) and chloroacetyl-N-phenothiazine(IV) [9] were prepared according to the. literature procedures.

The cell consisted of anode compartment of 65 ml and cathode compartment of 35 ml capacity separated by diaphragm of sintered glass No.4. Graphite, platinum and metallurgical copper of 4.5 cm^2 surface area were used. The desired temperature was maintained at 30 ± 1°C using an ultrathermostat. The oxidation was carried out under controlled current density of 10 mA/cm^2 for 10 hrs.

Procedure

A 65 ml solution containing 0.01 M of the investigated compounds (I-IV) dissolved in ethanol-water mixture (1:1) and 0.1 M supporting electrolyte (H_2SO_4, or NaOH and/or NaCL) was placed in the anode compartment. The cathode compartment was filled with 35 ml solution of supporting electrolyte. The mixture was electrolyzed for 10 hrs at controlled anodic current density of 10 mA/cm^2 . At the end of the electrolysis, the mixture of the anodic compartment was distilled and the residue was extracted three times with 50 ml portions of ether. The ether extract was dried over anhydrous Na_2SO_4, filtered and the filtrate evaporated using rotory evaporator. The residue was analyzed using GLC, TLC, IR and GC/MS techniques. GLC analysis was performed on a pye Unicam gas chromatograph (model 24, series 104). IR analysis was carried out using a Beckman spectrophotometer (KBr disk). GC/MS analysis were obtained using MAT 4033 spectrophotometer with an Incos

TABLE 1

THE OXIDATION POTENTIAL VALUES OF COMPOUNDS I TO IV AT PLATINIUM ANODE IN ACIDIC MEDIUM (0.1 M H_2SO_4) AT 30 ± 1°C

Exp.	Compound	Oxidation potential, V vs SCE	Concentration g./L
1	Acetyl-N-diphenylamine	+ 0.35	2.11
2	Chloroacetyl-N-diphenylamine	+ 0.66	2.455
3	Acetyl-N-phenothiazine	+ 0.68	2.41
4	Chloroacetyl-N-phenothiazine	+ 0.73	2.755

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data system using J & W scientific Inc. 50-m DBI bonded phase capillary column (0.25 micron film thickness).

RESULTS AND DISCUSSION

Polarization curves of the compounds at platinum anode in presence of 0.1 M H_2SO_4 supporting electrolyte, gave one wave for the anodic oxidiation processes. From the oxidation potential values (Table 1), it is evident that, the oxidation potential of acetyl-N-diphenylamine (I) is lower than that of chloracetyl-N-diphenylamine (II). The measured value is in harmony with the effect of chloro group in compound(II) for attracting the lone pair of electrons from the nitrogen atom, and consequently the oxidation process takes place at higher positive potential. Acetyl-N-phenothiazine and its chloro derivative gave the same behaviour.

The different products obtained and their yields under different conditions are given in Table 2. The products are identified by GC/MS as detailed in Table 3.

Mechanism of Electro-Oxidation

The results in Table 2 show the effect of electrode nature (pt,C and Cu) and the effect of different supporting electrolytes (acidic, alkaline and neutral) on the electro-oxidation of the formamides. The formation of the oxidation products can be explained in terms of the formation of cation radical intermediate species (=N-). Groups like - $COCH_3$, -$COCH_2Cl$, or chorine atom are eliminated from the intermediate to form cation or radical specie s. With abstraction of a hydrogen atom it forms the corresponding amines or the N-acetyl derivatives. Also, the rearrangement of the cation radical intermediates into another

TABLE 2

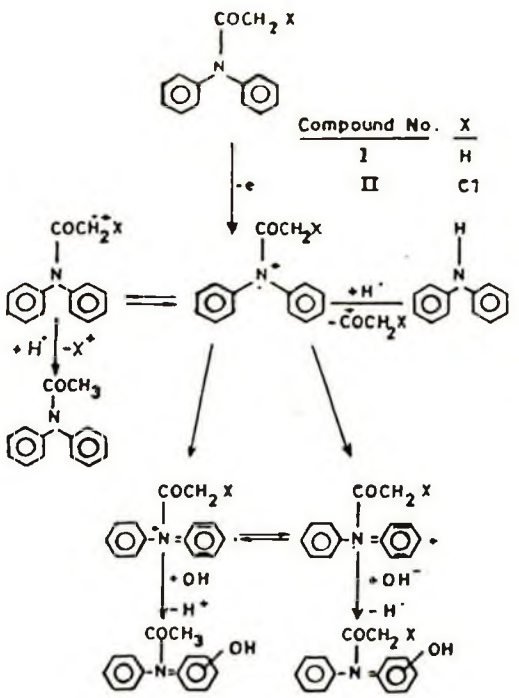
THE CONDITIONS AND PRODUCTS OF THE ANODIC OXIDATION OF COMPOUNDS (I-IV) IN ETHANOL-WATER MIXTURE (1:1) AT CONSTANT CUREENT DENSITY OF 10 mA/cm^2 , at 30 ± 1 °C

Exp.		Electrode	medium	Conversion (%)	Product (yield %)
1	Acetyl--N-diphenylamine	graphite	Acidic	12.0	Diphenylamine (43), Acetyl-N-dihydroxy diphenylamine (52) and acetyl-N-tetra-hydroxydiphenylamine (5).
2	Chloroacetyl-N-diphenylamine	graphite	Acidic	14.0	Diphenylamine (72) and acetyl-N-di-phenylamine (28).
3	Acetyl-N-phenothiazine	graphite	Acidic	20.0	Acetyl-N-dihydroxyphenothiazine (100)
4	Acetyl-N-phenothiazine	graphite	Neutral	21.4	Phenothiazine (13), acetyl-N-mono-hydroxyphenothiazine(62) and acetyl-N-dihydroxyphenothiazine (16).
5	Acetyl-N-pnhenothiazine	graphite	Alkaline	20.0	Phenothiazine (100)..
6	Acetyl-N-phenothiazine	platinum	Acidic	18.0	Monohydroxyphenothiazine (81) and dihydroxyphenothiazine (19).
7	Chloroacetyl-N-phenothiazine	graphite	Acidic	23.0	Phenothiazine (50.4) and acetyl-N-phenothiazine (49.6).
8	Chloroacetyl-N-phenothiazine	graphite	Neutral	14.74	Acetyl-N-phenothiazine(81) and chloro-acetyl-N-monohydroxyphenothiazine (19)
9	Chloroacetyl-N-phenothiazine	graphite	Alkaline	100.00	Phenothiazine (100).
10	Chloroacetyl-N-phenothiazine	Platinum	Acidic	12.00	Acetyl-N-phenothiazine (100).
11	Chlroacetyl-N-phenothiazine	Copper	Acidic	18.50	Acetyl-N-phenothiazine (100).
12	Phennothiazine	graphite	Acidic	-	Phenothiazine (100).

TABLE 3

Compound	M/e	M/e of fragments
Diphenylamine	169	169
Acetyl-N-dihydroxy diphenylamine	245	203
Acetyl-N-Tetra hydroxy diphenylamine	275	198
Acetyl diphenylaine	211	169
Phenothiazine	199	167
Acetyl -N-monohydroxy phenothiazine	257	198
Acetyl-N-dihydroxy phenothiazine	273	231
Acetyl-N-phenothiazine	211	169
Monohydroxy phenothiazine	225	198
Dihydroxy phenothiazine	231	43

resonance form by transferring the cation or radical charge to the adjacent phenyl groups, and subsequent abstraction of hydroxy group from the medium produced mono-, di-, and tetra- hydroxy isomers of diphenylamine and phenothiazine derivatives. This mechanism can be visulalized as follows (e.g. compound 1 and 2).



It was found that, the yield of diphenyl amine produced from the oxidation of compound II (72 %) is higher than that of compound (1) (43 %) under the same conditions. Also the yield of phenothiazine produced from the anodic oxidation of compound IV (50.4 %) is higher than that from compound III (exp. 7 and 3 respectively). This is due to the presence of electron attracting chlorine in the acetyl group, which facilitates the cleavage of carbon-nitrogen bond.

The yield of phenothiazine is much higher in alkaline medium than that in acidic one for compounds(III) & (IV). This can be explained in terms of the higher concentration of reactive OH ions at the anode surface in alkaline medium compared with that in acidic one, which in turn, encourage the cleavage of the carbon-nitrogen bond. On the other hand, the presence of mono-, di- and tetra-hydroxy products indicate the rearrangement of the cation radical intermediate species which are formed during the andodic oxidation processes.

It is worth noting that dehalogenated products were only formed at Pt and Cu anodes in acidic and neutral media (exp. 10 & 11), where hydrogen, protons or radical, are present in high concentration.

Generally, the results obtained give an indication that, the oxidation products and their percentages depend to a great extent on the nature of anode, media and finally on the chemical structure of the investigated compounds.

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