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VOLTAMMETRIC STUDIES OF THE INDIRECT ELECTROCHEMICAL OXIDATION OF SOME ALKYL HETEROCYCLIC COMPOUNDS USING TRIARYLAMINES AS ORGANIC MEDIATORS

M . Abdel Azzem

Chemistry Department, Faculty of Science, El-Menoufia University

Egypt.

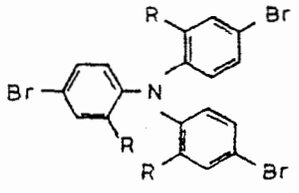
ABSTRACT

Electroanalytical studies were carried out using cyclic voltametric method to examine the indirect electrochemical oxidation of some alkyl substituted heterocyclic compound using triarylamines. The technically important side-chain oxidation of three heterocyclic compound, namely 4-Picoline, 4-methyl-imidazol and 2-methlyl-4, 5-dihydromethylimidazol, can be performed electrochemically at low potentials in CH_3CN / MeOH / $LiClO_4$ system. Catalytic amounts of electro- generated and regenerated triarylamine cation radicals are used as organic mediators.

INTRODUCTION

The applicability of triarylamines as redox catalyst was first demonstrated in the oxidation of cyanide ions by electro-generated trianisylamine cation radicals. The advantage of triarylamine as mediator is the possibility to adjust their oxidation potential by the selection of the ortho and para substituents. A large spectrum of substituted triarylamine has been developed and applied as mild and selective oxidizing agents[2]. Electrogenerated and regenerated triarylamine cation radical is used for the sid-chain oxidation of alkyl-substituted aromatic compounds 3, 4 and benzyl alcohol oxidation. The purpose of this investigation is testing the application

of the triarylamines mediator 1 and 2 to the oxidation of some alkyl-substituted heterocyclic compound as 4-picoline (3) 4-methylimidazol (4). and 2-methyl -4.5-dihydromethyl-imidazol (5) using cyclic voltammetry technique.



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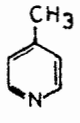
2 R = Br



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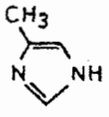

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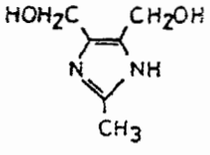

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EXPERIMENTAL

4-Picoline was purified by distillation. 4-Mthylim- idazol, 4, 5-dihydromethylimidazol (Aldrich), methanol (Merck) and $LiClO_4$ (Fluka) were used without further purification. The triarylamines 1 and 2 are prepared as previously describ[6].

Cyclic voltammetry was carried out using a cypress computer measuring system for electroanalytical model CYSY-IB. Current-voltage curves were recorded on Hewlett- Packared model 7440 A X, T-recorder. Analytical cell model C-IA (Bioanalytical) was used together with a glassy carbon electrode (3.0 mmdia) as working electrode, a platium counter electrode and an Ag / AgCL reference electrode. All measurements were carried out at temperature 25°C± 1

RESULTS AND DISCUSSION

Direct electrochemical oxidation of picolins, because of the electron-poor heteroarmotic ring, is only possible under acidic conditions since the used mediator can be applied with potentials which are 600 mV lower than the electrode potenials of the substrate, the triarylamine 2 was used as a medaitor for the indirect oxdation of 4-picoline (3). Fig. 1 shows the cyclic volyammetry (CV) of tris (2.4-dibromophenyl) amine (2) in the absence and presece of 4-picoline as a function of the scan rate in acetonitril containing 0.2 M $LiClO_4$. In the absence of 4-picoline, the typical electrochemically generted and regenerted triarylamine cation $2^{\bullet+}$ is obtained. With increasing the molar ratio of mediator 2 to compound 3 from 1:1 to 1 : 2 the cathodic peak of the reduction of the triarylamine cation $2^{\bullet+}$ is absent at low scan rates and condsiderable dimiution at higher scan rates was observed. Cyclic voltammograms of 4-methylimidazol (4) in CH_3CN containing 0.1 M $LiClO_4$ as supporting electrolyte at variable scan rates are shown in Fig. 2. This compound (4) showed only one irreversible oxidation wave at about 0.8V vs Ag/AgCl electrode. Using tris (p-bromophenyl) amine (1) in absence and presence of different molar ratios of compound 4. The chance of the indirect electrochemical reaction can be evaluated by cyclic voltammetry by which not only values of the redox potenials are measured but also the presence of an electrocatlytic mechanism can be indicated by the so-called cataltic effect. Fig. 3 shows cyclic voltammorgams of the triarylamine 1 in the presence and absence of different molar ratois of compound 5. It is clear that on increasing the molar ratio of the mediator 1 to compound 5 from 1:1 to 1:2, the

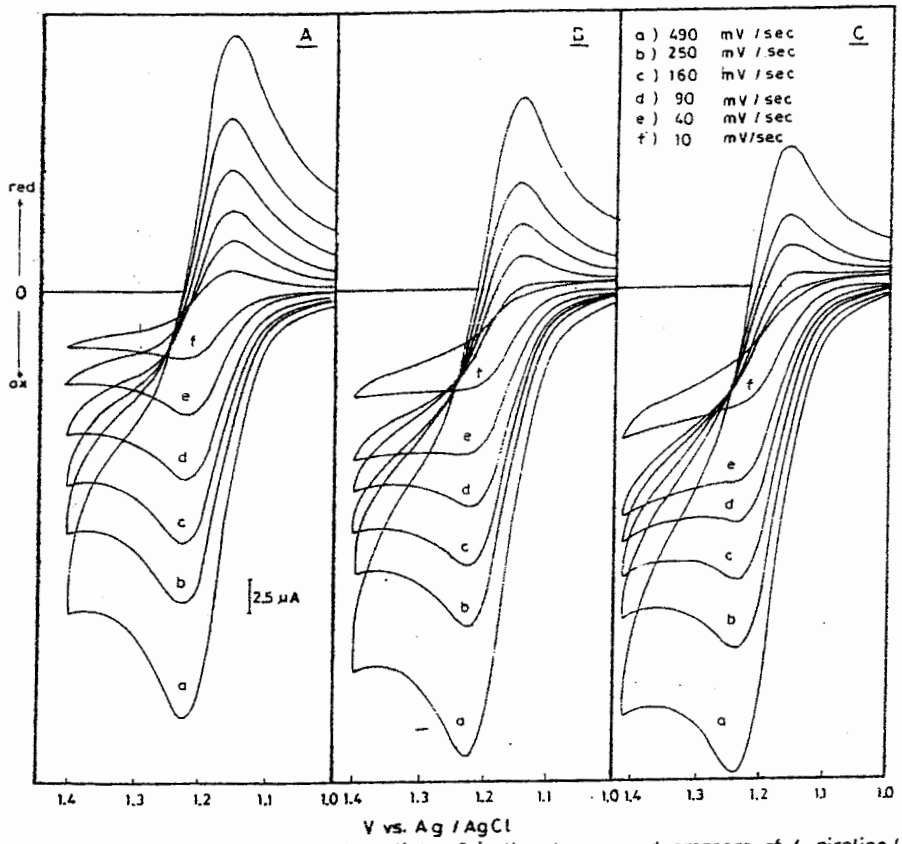

Fig. 1. Cyclic voltammograms of mediator 2 in the absence and presence of 4-picoline (3) in $CH_3CN-CH_3OH-LiClO_4$. A: 1.0 m mol /L mediator 2 . B : 1.0 m mol /L 2 + 1.0 m mol /L 3 . C : 1.0 m mol /L 2 + 2.0 m mol /L 3 .

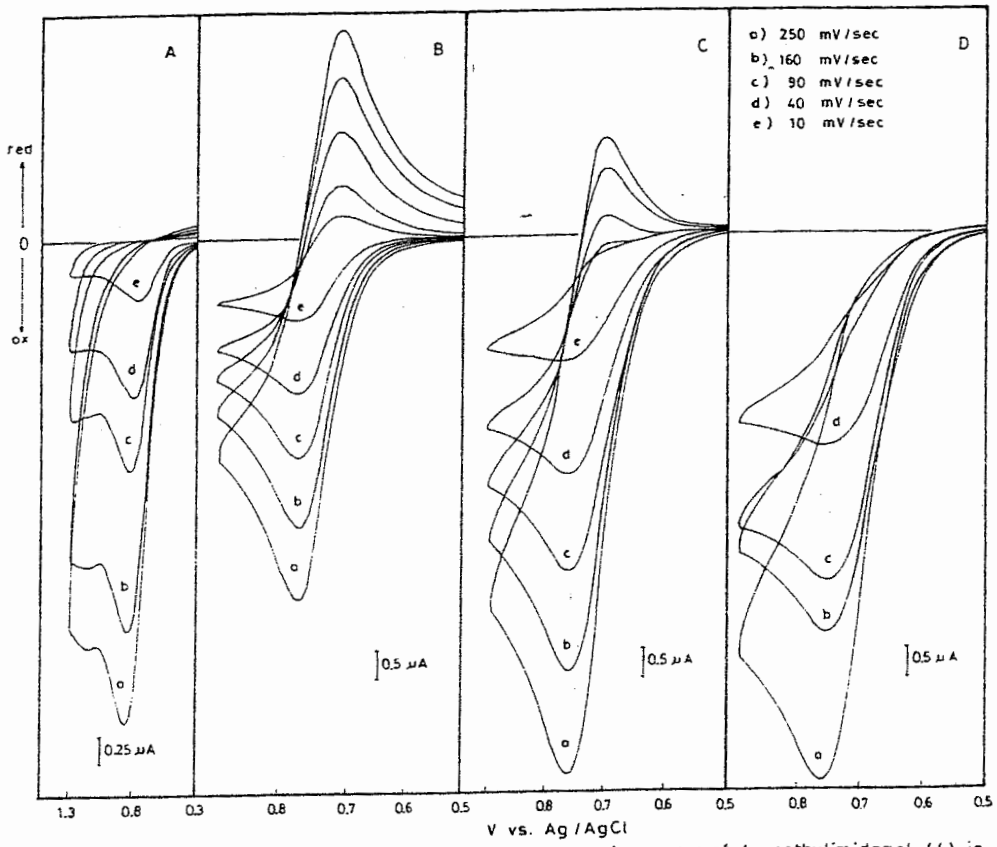

Fig. 2. Cyclic voltammograms of mediator 1 in the absence and presence of 4-methylimidazol (4) in CH_3CN - CH_3OH - $LiClO_4$ · A: 0.11 m mol /L 4 · B: 0.055 m mol /L mediator 1 · C: 0.055 m mol /L 1 + 0.055 m mol /L 4 · D: 0.055 m mol /L mediator 1 + 0.11 m mol /L 4 ·

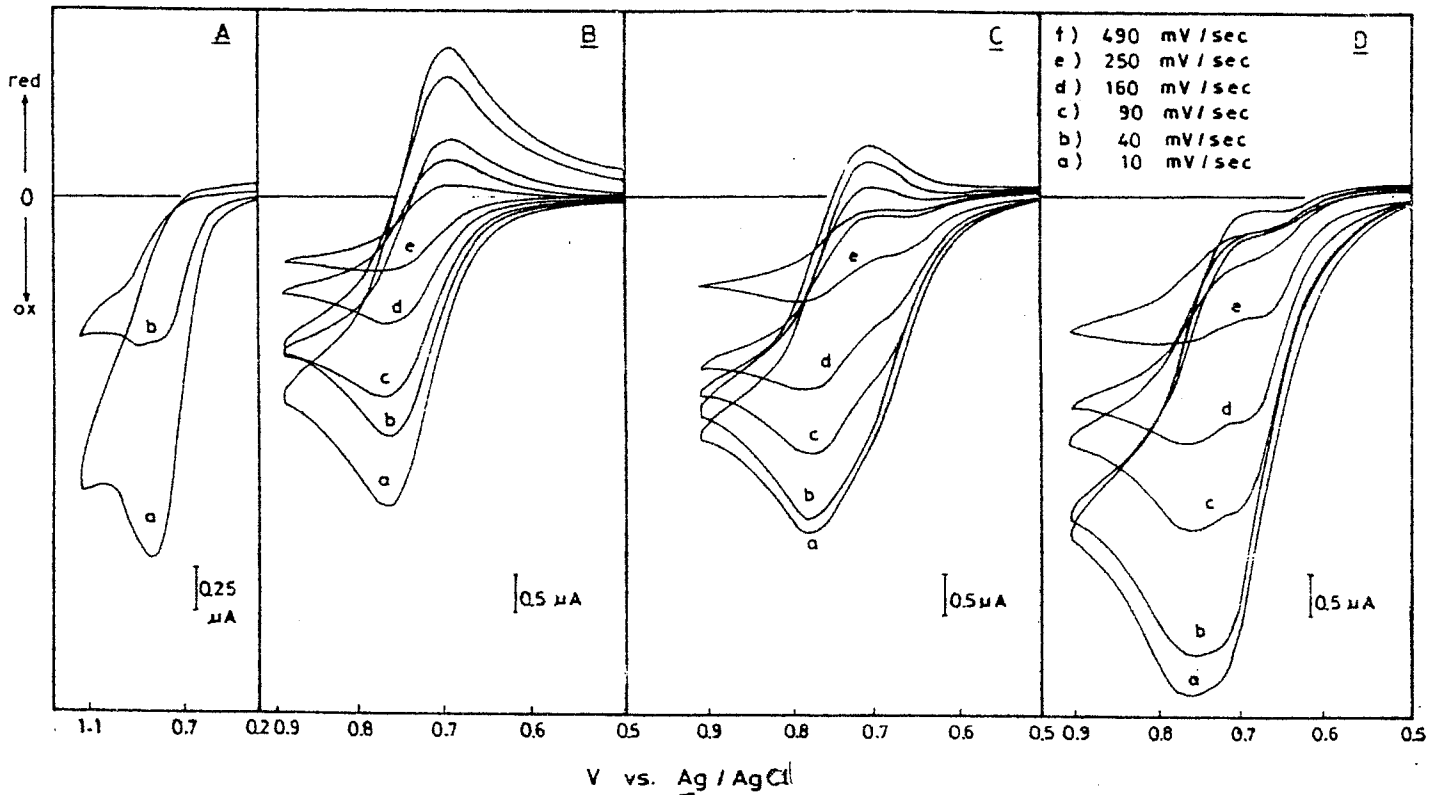

Fig. 3. Cyclic voltammograms of mediator 1 in the absence and presence of 2- methyl- 4,5- dihydromethylimidazol (5) in $CH_3CN - CH_3OH - LiClO_4$. A : 0.05 m mol / L 5
B : 0.05 m mol / L mediator 1 . C : 0.05 m mol / L 1 + 0.05 m mol / L D : 0.05 m mol / L mediator 1 + 0.1 m mol / L 5 .

catalytic effect increas. Based on the foregoing results, one can conclude that the indrect electrochemical oxidation of the 4-methylimidazol and 2-methyl-4.5- dihydromethylimidazol by triarylamine mediator 1 and 4-picoline using triarylamine 2 will be possible in CH_3CN-MeOH-$LiClO_4$ iystem. In correspondance with previously detected similar reaction one can postulate the following mechanism .

$$Ar_3N - e \longrightarrow Ar_3N^{\cdot+}$$

$$Ar_3N^{\cdot+} + R\text{-}CH_3 \rightleftharpoons Ar_3N + RCH_3^{\cdot+}$$

$$RCH_3^{\cdot+} + CH_3OH \rightleftharpoons RCH_2^{\cdot} + CH_3OH_2^{+}$$

$$RCH_2^{\cdot} + Ar_3N^{\cdot+} \rightleftharpoons RCH_2^{+} + Ar_3N$$

$$RCH_2^{+} + CH_3OH \longrightarrow RCH_2OCH_3 + H^{+}$$

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