Short Communication

Anodic oxidation of some phenothiazine derivatives on pretreated platinum and ruthenium electrodes*

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Introduction

The phenothiazine class of drugs are major tranquilizers. Because of their frequent use their metabolism and pharmacokinetics have been studied. Ring-S-oxidation is an important step in the metabolism of phenothiazine drugs in man.

The aim of this study is to investigate the effect of the electrode material and the electrode surface state on the electro-oxidation of some of the members of the phenothiazine class, namely, thioridazine hydrochloride and promazine hydrochloride.

There is a great interest in modifying the properties of solid electrodes to achieve stabilization and a reproducibility in the electrochemical response of solid electrode surfaces. In the present study two techniques have been applied for this purpose, one of them is to produce an oxide film on platinum and ruthenium electrodes by the application of an anodic potential, the other technique is to treat the electrode by the application of very fast repetitive potential scan under carefully selected potential perturbation conditions as reported in the literature [1].

Experimental

A Tacussel PRG 3 polarographic potentiostat with an EPL 2 recorder was used to record the voltammograms. A platinum wire, 1 mm dia and 14.8 mm length, welded onto the glass (Tacussel), and a ruthenium wire, 1 mm dia and 21.1 mm length (Engelhard), were used as working electrodes. The ruthenium electrode was constructed in our laboratory by welding the ruthenium wire onto a Pyrex glass by means of a platinum joint [2]. A platinum wire was used as a counter electrode. The potential was measured with reference to a saturated calomel electrode, but the potentials were given relative to the standard hydrogen electrode.

Wenking Model 70 HP 10 potentiostat and type 250 Exact function generator were employed for applying fast periodic potential perturbations. All the chemical and standard substances were of analytical grade. All the solutions were prepared with doubly distilled water. Pure nitrogen gas was bubbled through the electrolytic solution to remove dissolved oxygen before each experiment.

Pretreatment of the electrodes

To obtain reproducible results the ruthenium electrode was reduced at -100 mV for 5 min, and was then oxidized at 400 mV for 15 min in 0.5 M H_2SO_4 before each experiment (non-oxidized electrode). The pretreatment of the ruthenium electrode had been given elsewhere [3].

The platinium electrode was pretreated in three different ways in 1 M H_2SO_4: (1) the electrode was oxidized at 1350 mV for 5 min and then a potential of 300 mV was applied until the current became zero (non-oxidized
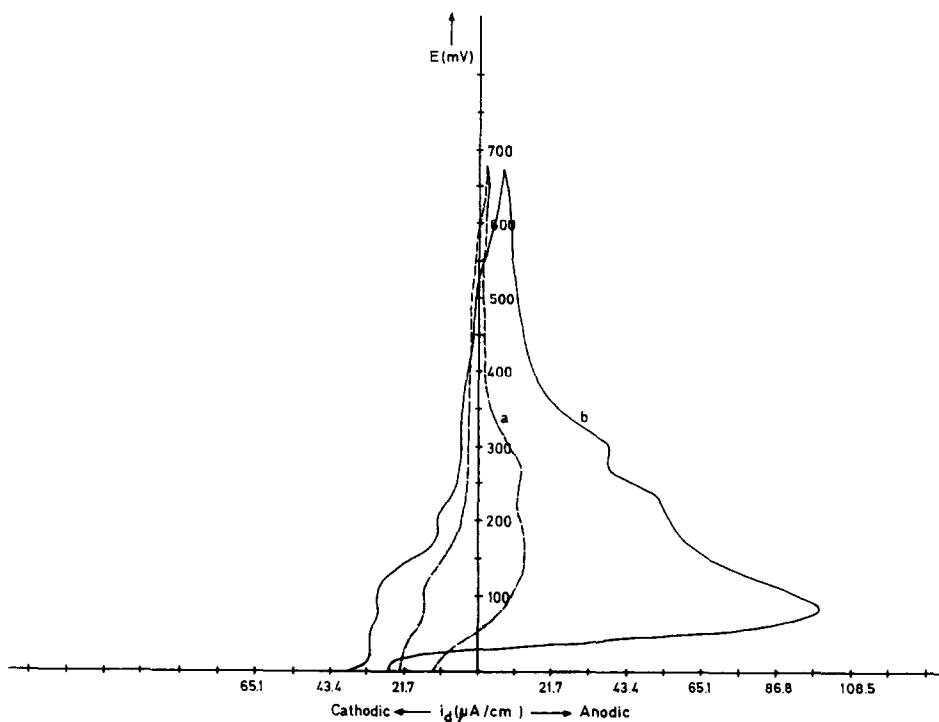

Figure 1

Curves obtained in 1 M H_2SO_4 between 0–600 mV, scan rate 50 mV s^{-1}: curve (a) with polycrystalline platinum (pretreatment 1); curve (b) with pretreated platinum (pretreatment 3).
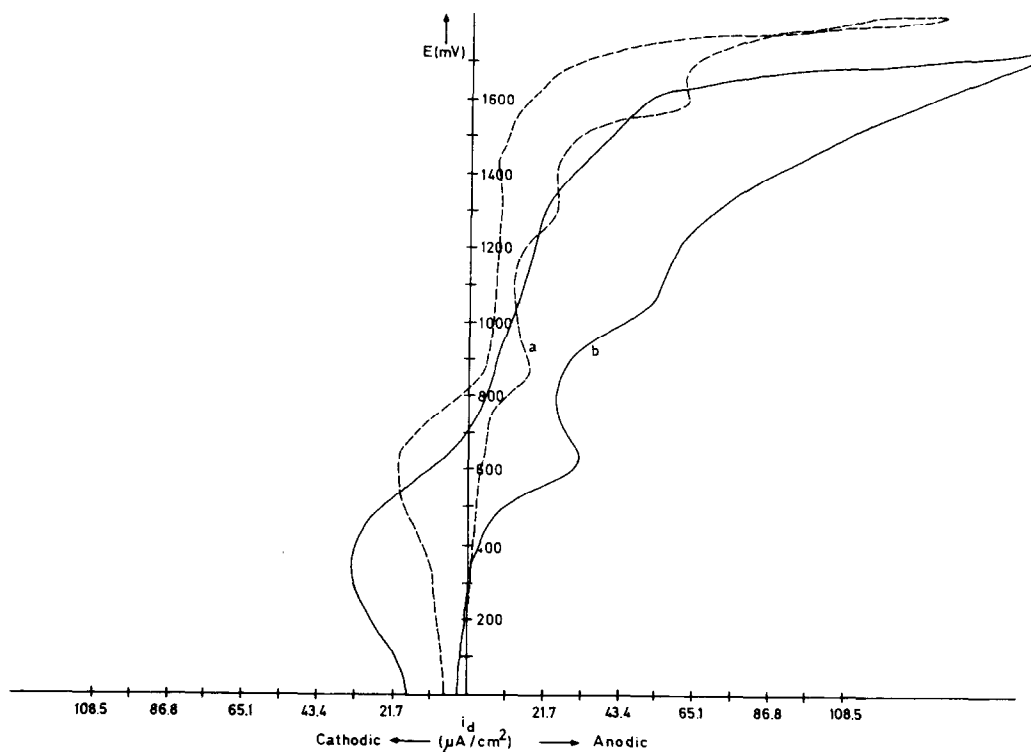

Figure 2

Voltammograms obtained in 8 × 10^{-4} M promazine hydrochloride solutions, scan rate 10 mV s^{-1}: curve (a) using non-oxidized platinum electrode (pretreatment 1); curve (b) using oxide coated platinum electrode (pretreatment 2).

electrode); (2) the electrode was oxidized at 1200 mV for 1 h, and this procedure was repeated more than 10 times until the voltammograms became reproducible; (3) the polycrystalline platinum electrode in 1 M H_2SO_4 was subjected to a repetitive potential sweep by applying a high frequency triangular potential signal (7000 Hz) for 1 h between 400–1600 mV following a procedure explained by Canullo et al. [1].

Results and Discussion

Figure 1 shows the changes in the electrochemical response of the polycrystalline platinum electrode subjected to a repetitive potential signal (pretreatment 3), as reported in the literature [1, 4]. The first voltammogram ran immediately afterwards at 100 mV s^{-1} between 50–1450 mV and the second voltammogram was recorded between 0–600 mV, as shown in Fig. 1 (curve b).

Figure 2 shows the voltammograms obtained in promazine hydrochloride solutions using non-oxidized platinum (curve A) and oxide coated platinum (curve b) electrodes. The

voltammograms obtained in promazine hydrochloride solutions using non-oxidized and oxidized ruthenium electrodes were given in Fig. 3. Figure 4a shows the voltammograms obtained in thioridazine hydrochloride solutions using non-oxidized polycrystalline (curve I) and pretreated platinum electrodes.

From these curves it was concluded that on the thick oxide coated platinum electrode (pretreatment 2), oxidation peaks of promazine hydrochloride shift to more positive potentials, and peak currents decrease in comparison with non-oxidized platinum.

The oxidation curves of the thioridazine hydrochloride recorded with pretreated platinum (pretreatment 3) showed only one oxidation step when the concentration of thioridazine was less than 4×10^{-4} M. But when the concentration was increased a second oxidation step at more positive potentials formed. The depression of the current in the hydrogen region of the voltammograms of the drugs can be attributed to the blocking of the active sites taking place in the hydrogen adsorption by the adsorbed drugs (Fig. 1 curve b, Fig. 4a curves II and III).
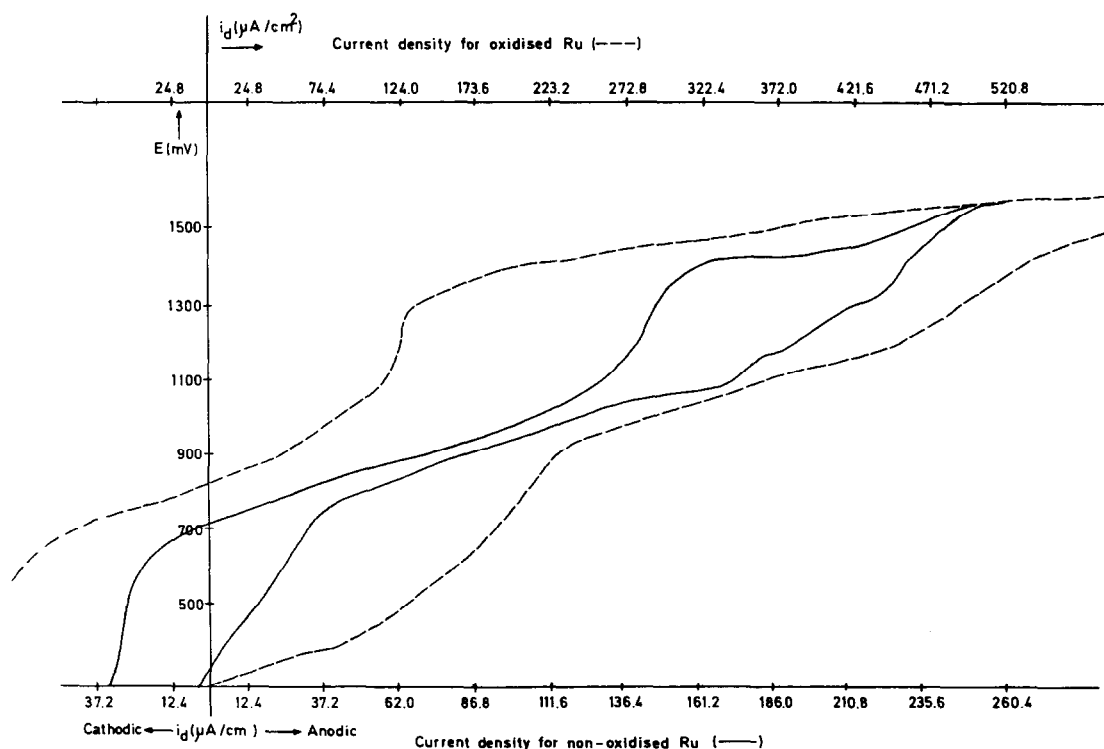

Figure 3
Voltammograms obtained in promazine hydrochloride solutions, scan rate 10 mV s^{-1}, in 8×10^{-4} M promazine hydrochloride having 0.2 M H_2SO_4 solutions: _____, with the non-oxidized ruthenium electrode; – – – – – –, with the oxidized ruthenium electrode.
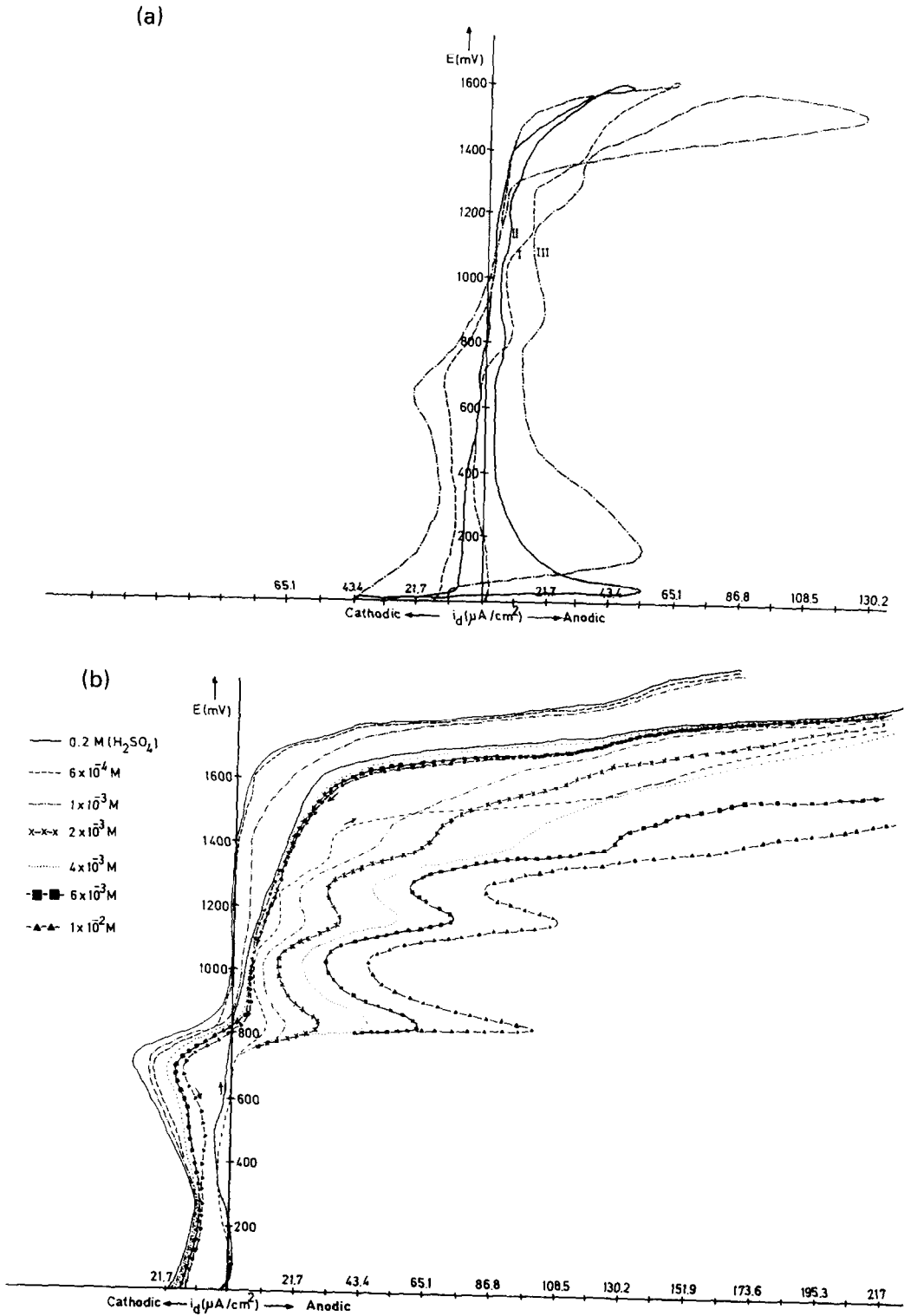
(a)

(b)

Figure 4

Voltammograms obtained in thioridazine hydrochloride solutions. (a) 5 × 10⁻⁴ M thioridazine hydrochloride (1 M sulphuric acid). _____, Using pretreated platinum (pretreatment 3), scan rate 10 mV s⁻¹; ---------, using pretreated platinum (pretreatment 3), scan rate 100 mV s⁻¹; ---------, using platinum polycrystalline (pretreatment 1), scan rate 10 mV s⁻¹. (b) Voltammograms obtained in 0.2 M H₂SO₄ solutions having various concentrations of thioridazine hydrochloride, with platinum electrode (pretreatment 1), scan rate 10 mV s⁻¹. _____, 0.2 M H₂SO₄; ---------, 6 × 10⁻⁴ M thioridazine; ---------, 1 × 10⁻³ M thioridazine; x-x-x-x-x-x, 2 × 10⁻³ M thioridazine; ...., 4 × 10⁻³ M thioridazine; -■-■-■-■-, 6 × 10⁻³ M thioridazine; -▲-▲-▲-▲-, 1 × 10⁻² M thioridazine.

The electro-catalytic effect of RuO_2 on promazine oxidation can be seen in Fig. 3.

The curves obtained with platinum (pre-treatment 1) in 0.2 M H_2SO_4 having various concentration of thioridazine hydrochloride at the scan rate 10 mV s^{-1} showed three oxidation peaks (Fig. 4b). The peak currents are directly proportional to the concentration in the range $6 \times 10^{-4} - 1 \times 10^{-2}$ M. The results of linear regression analysis are given below:

for the first peak at   830 mV $y =$
$4,23 \times 10^3 x + 3,52$; $r = 0.9986$ $(n = 6)$
for the second peak at 1150 mV $y =$
$4,37 \times 10^3 x + 1,97$; $r = 0.9992$ $(n = 6)$
for the third step at 1400 mV $y =$
$6,3x \ 10^3 x + 8,13$; $r = 0.9903$ $(n = 6)$

According to these results it can be seen that the quantitative analysis of thioridazine hydrochloride could be made under the specified conditions.

References

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