Notes

Anodic Stripping Voltammetry of Uric Acid at Glassy Carbon Electrodes after Pre-Electrolysis in Solution Containing Copper(II)

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The electrochemistry of biologically important compounds has recently been extensively studied. Uric acid is one of the purine derivatives whose oxidation mechanisms have attracted much attention with respect to metabolism *in vivo* as well as analytical applications. Dryhurst and co-workers have reported on the electrochemical oxidation of uric acid at carbon electrodes.^{1,2} Yao and co-workers have applied anodic voltammetry to the determination of uric acid and other purine derivatives.³

In previous studies, we found that the oxidation currents of uric acid and other purine bases at glassy carbon electrodes (GCE) were extremely enhanced by pre-electrolysis with Cu^{II} in solution.⁴ In the case of adenine or guanine, a complex between the base and Cu^{I} , electrogenerated in pre-electrolysis and deposited on GCE, was responsible for the current amplification.⁵ The interaction between uric acid and Cu^{I} was studied in the present work.

Experimental

Chemicals

Uric acid was purchased from Merck & Co., Inc. and used without further purification. A Cu^{II} solution was prepared from copper acetate of analytical grade. Every sample solution was prepared from an analytical-grade reagent in doubly distilled water.

Apparatus

A three-electrode voltammetric cell maintained at 25°C was used throughout. A saturated calomel electrode (SCE) was employed as a reference electrode, and a platinum wire as a counter electrode. GCE was made from a 3-mm ϕ rod of glassy carbon (GC30s, Tokai Carbon Co.); its working surface was polished to a mirror finish.

Anodic stripping voltammograms were recorded with a Fuso potentiostat (Model 311) and a Graphtec x-y recorder. UV spectra were measured on a Shimadzu spectrophotometer (Model UV-240).

Procedure

The anodic stripping of uric acid was carried out as in previous studies.^{4,5} Briefly, a uric acid solution containing Cu^{II} and the background electrolyte was pre-electrolyzed at an initial potential (E_i) on a GCE rotated so as to stir the test solution. After pre-electrolysis the potential of GCE was scanned to positive values so as to obtain the anodic peaks of uric acid.

Results and Discussion

Large oxidation currents were observed on the anodic stripping voltammograms, recorded as mentioned above (Fig. 1a, b). Two oxidation peaks appear in the voltammogram: a sharp peak (i_{p1}) at 0.5 V and a broad

Fig. 1 Influence of the pre-electrolysis potential (E_i) on the anodic voltammogram of uric acid at GCE. Test solution: 4×10^{-6} M uric acid, 0.4×10^{-3} M Cu^{II} . E_i (V): a) -0.10; b) -0.05; c) 0; d) 0.20. Pre-electrolysis period: 180 s.

Fig. 2 Cathodic voltammogram of 2×10^{-4} M copper(II) at GCE. Scan rate, 50 mV/s; broken line, background current.

peak (i_{p2}) at around 0.35 V. The former peak may reflect the oxidation of uric acid since it depends on the uric acid concentration; the latter peak is absent in electrolytes not containing Cu^{II} .

Conditions for the anodic stripping process

The oxidation peaks of uric acid were influenced by the solution pH, the concentration of Cu^{II} , the initial potential (E_i) and the pre-electrolysis period (τ_d). Based on the knowledge acquired in a previous study⁴, a pH value of 3.8 (Britton–Robinson buffer) and a Cu^{II} concentration of 0.4 mM were employed. The effect of E_i on the oxidation current can be seen in Fig. 1. The current (i_{p1}) reached a maximum when E_i was -0.1 V, while no anodic stripping peaks were obtained for $E_i \geq 0.2$ V and $E_i \leq -0.2$ V. The magnitude of i_{p1} for $E_i = -0.2$ V was the same in both the presence and absence of Cu^{II} in the solution. The anodic stripping process is presumably prevented by metallic copper on GCE. For $E_i = -0.1$ V, a large reoxidation peak of metallic copper is seen on the stripping voltammogram; this renders any estimation of the residual current quite difficult. Hence, an appropriate E_i may be -0.05 V, rather than -0.1 V, for obtaining the anodic stripping peak of uric acid for analytical purposes.

When E_i was set at a potential at which Cu^{II} was reduced to metallic copper or not reduced at all, the oxidation current of uric acid was not enhanced. These results indicate that the anodic stripping process is related to the reduction of Cu^{II} .

Reduction of copper(II) during pre-electrolysis

Cu^{II} gave two reduction peaks at GCE (Fig. 2). A cyclic voltammetric study showed that the more positive peak ($E_p = -0.12$ V) reflects the reduction of Cu^{II} to Cu^{I} and the other ($E_p = -0.26$ V) the reduction to metallic copper.⁶ Cu^{I} electrogenerated at GCE is reoxidized reversibly to Cu^{II} , while metallic copper is reoxidized directly to Cu^{II} . In the course of pre-electrolysis, Cu^{II} may be partially reduced to Cu^{I} .

Reaction between uric acid and copper(I)

It is known that uric acid reacts with Cu^{I} , generated by

Fig. 3 Decrease in the uric acid concentration due to its reaction with Cu^{I} . Abscissa: concentration of Cu^{II} added to a mixture of 8×10^{-5} M uric acid and 2×10^{-3} M hydroxylamine. Ordinate: absorbance of uric acid in the supernatant. See text for details.

the addition of hydroxylamine to a Cu^{II} solution⁷, giving a white precipitate. This precipitate may be a Cu^{I} compound, since it is oxidized by passing atmospheric oxygen and is redissolved in solution. UV spectrophotometry of the supernatant solution, obtained by the addition of hydroxylamine to a Cu^{II} solution containing uric acid, confirmed the reaction between Cu^{I} and uric acid. The absorbance of uric acid in the supernatant at 283 nm was decreased by increasing the amount of generated Cu^{I} (Fig. 3). When the concentration of hydroxylamine was higher than 1 mM, the absorbance of uric acid reached zero and uric acid was completely precipitated. Since the absorbances of Cu^{II} , Cu^{I} and hydroxylamine were sufficiently small at 283 nm, a mixed solution of Cu^{II} and hydroxylamine was used as a reference. Presumably, excess Cu^{I} caused the uric acid to precipitate quantitatively as the Cu^{I} complex.

Mechanism of the current enhancement

Based on these pieces of evidence, the anodic stripping of uric acid at GCE may proceed as follows:

1. During pre-electrolysis at E_i , where Cu^{II} is reduced to Cu^{I} , uric acid is accumulated on the surface of GCE as the precipitate of a Cu^{I} compound.
2. When the electrode potential reaches *ca.* 0.3 V on the anodic scan, Cu^{I} of the compound is reoxidized to Cu^{II} and the precipitate is redissolved. The uric acid concentration in the vicinity of GCE is considerably increased by this process, yielding a large oxidation peak at 0.5 V.

This stripping method facilitates the determination of a micromolar concentration of uric acid. Other purine derivatives may also be determined in a similar manner.

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