# Chemistry Experiments for Instrumental Methods

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## EXPERIMENT 4-2

Study of Electrode Mechanism by Cyclic Voltammetry†

**Purpose**

Cyclic voltammetry is used to study the electrode mechanism of acetaminophen oxidation, which involves coupled chemical reactions.

**References**


1 J. J. Van Benschoten, J. Y. Lewis, W. R. Heineman, D. A. Roston, and P. T. Kissinger, *J. Chem. Ed., 60,* 772 (1983).

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**Apparatus**

Instrument for cyclic voltammetry (such as Bioanalytical Systems, CV-1B, CV27 or Electrochemical Analyzer; Princeton Applied Research 173/175; IBM EC/225)
*x-y* Recorder (oscilloscope can also be used)
Electrochemical cell
Platinum auxiliary electrode
SCE or Ag/AgCl reference electrode
Carbon paste working electrode (such as the MF 2010 from Bioanalytical System, Inc., West Lafayette, Ind.; instructions for preparing the electrode are available from the manufacturer)

**Chemicals**

McIlvaine buffers with 0.5 *M* ionic strength:
pH 2.2, 500 mL
pH 6, 200 mL
1.8 *M* sulfuric acid [$H_2SO_4$], 200 mL

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Stock solution of 0.070 *M* acetaminophen in 0.05 *M* perchloric acid [$HClO_4$] (store in refrigerator)
Tylenol tablet

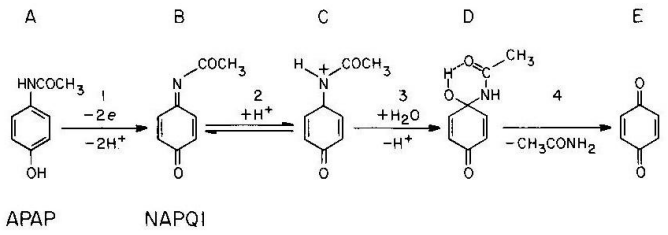
## Theory

There are inorganic ions, metal complexes, and a few organic compounds that undergo electron transfer reactions without the making or breaking of covalent bonds. The vast majority of electrochemical reactions involve an electron transfer step that leads to a species that rapidly reacts with components of the medium via so-called *coupled chemical reactions.* One of the most useful aspects of cyclic voltammetry (CV) is its application to the qualitative diagnosis of these homogeneous chemical reactions that are coupled to the electrode surface reaction. CV provides the capability for generating a species during the forward scan and then probing its fate with the reverse scan and subsequent cycles, all in a matter of seconds or less. In addition, the time scale of the experiment is adjustable over several orders of magnitude by changing the potential scan rate, enabling some assessment of the rates of various reactions.

Acetaminophen (*N*-acetyl-*p*-aminophenol, APAP), the active ingredient in Tylenol, is commonly used as an aspirin substitute. However, unlike aspirin, it is known to cause liver and kidney damage when administered in large amounts. It is suspected that a metabolite of APAP is the actual hepatotoxic agent, thus APAP and its metabolites have been extensively investigated (Ref. 2).

Voltammetric studies in aqueous solution have revealed chemical as well as electrochemical steps (Ref. 3). The APAP system therefore is useful in demonstrating the mechanistic information that can be obtained from CV's.

The oxidation mechanism of APAP is as follows:




APAP is electrochemically oxidized in a pH-dependent, two-electron, two-proton process to *N*-acetyl-*p*-quinoneimine (NAPQI) (step 1). The occurrence of follow-up chemical reactions involving NAPQI is pH-dependent. By varying the pH of the media and the scan rate of the cyclic voltammetry experiment, chemical reactions involving NAPQI can be "mapped-out."

At pH values $\geq 6$, NAPQI exists in the stable unprotonated form (B). Cyclic voltammograms recorded for APAP at pH 6 are shown in Fig. 4-7. Reasonably well-defined anodic and cathodic waves are evident. The anodic current represents step 1 in the mechanism detailed above while the cathodic current represents the reverse of this step. The similarity in appearance of the pH 6 cyclic voltammograms observed with 40- and 250-mV/s scan rates indicates that the involved species are stable in the time domain of the cyclic voltammetry experiment. The large separation between the anodic and cathodic peak currents in the pH 6 cyclic voltammograms is a manifestation of sluggish heterogeneous electron transfer kinetics.

Under more acidic conditions, NAPQI is immediately protonated (step 2), yielding a less stable but electrochemically active species (C) which rapidly yields (step 3) a hydrated form (D) that is electrochemically inactive at the examined po-

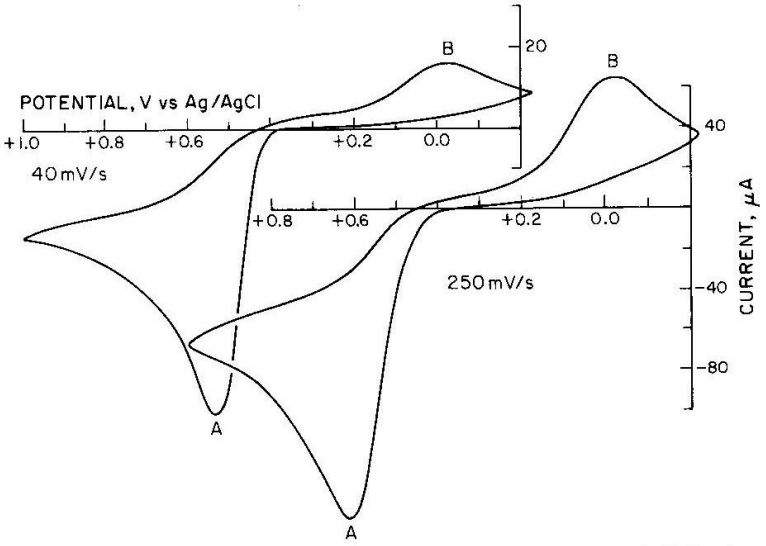



**Figure 4-7 / Cyclic voltammograms of 3.6 m*M* APAP in pH 6 McIlvaine buffer. Carbon paste electrode.** [***Reprinted with permission from J. J. Van Benschoten, J. Y. Lewis, W. R. Heineman, D. A. Roston, and P. T. Kissinger, J. Chem. Ed., 60, 772 (1983). Copyright © 1983, Division of Chemical Education, American Chemical Society.***]

tentials. Cyclic voltammograms shown in Fig. 4-8 are consistent with this mechanism. The pH of the media is 2. A small cathodic wave due to the reduction of protonated NAPQI (C) is evident when the scan rate of 250 mV/s is employed. This wave is even more pronounced when faster scan rates are employed; however, faster scan rates require the use of an oscilloscope to record the voltammogram. With a slower scan rate of 40 mV/s, a cathodic wave for the reduction of protonated NAPQI is not observed. All of the protonated NAPQI (C) is converted to the inactive hydrated form (D) before sufficiently negative potentials are reached during the reverse scan of the cyclic voltammetry experiment.

Hydrated NAPQI (D) converts (step 4) to benzoquinone; however, the medium has to be extremely acidic for the rate of the process to be significant enough that reduction of benzoquinone is observed during the cyclic voltammetry experiment. The medium for the cyclic voltammograms detailed in Fig. 4-9 is 1.8 *M* $H_2SO_4$. A poorly defined cathodic wave for the reduction of benzoquinone (E) is observed when a scan rate of 250 mV/s is employed. The reduction wave is broad because the formation of benzoquinone (E) from hydrated NAPQI (D) occurs during the reverse scan. When the scan rate is 40 mV/s, the increased length of time required to reach negative enough potentials during the reverse scan allows for the accumulation of benzoquinone (E). Consequently, a well-defined reduction wave is observed for benzoquinone (E) when the slower scan rate is employed. The second scan in the positive direction yields an anodic wave, in addition to that of APAP, which corresponds to the oxidation of hydroquinone, the reduction product of benzoquinone.

## Procedure

Prepare the carbon paste electrode according to the manufacturer's instructions. The electrode surface should be polished to a shiny finish. Care must be taken not to scratch the carbon paste surface once it has been polished.

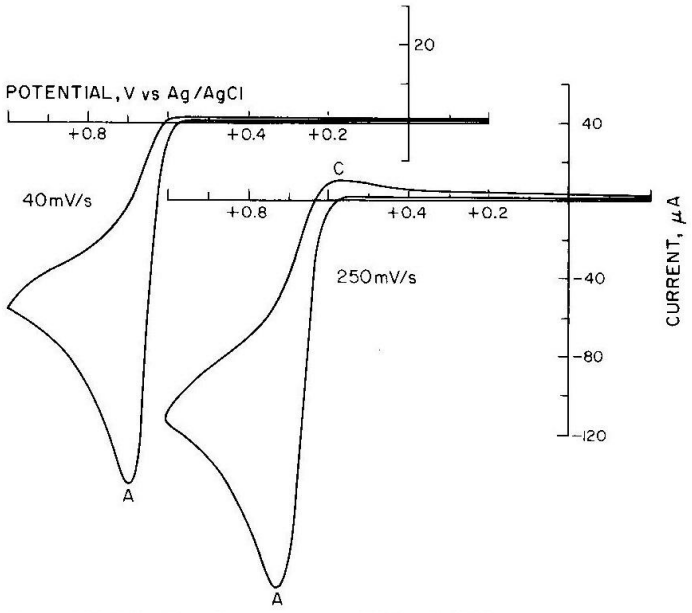



**Figure 4-8 / Cyclic voltammograms of 3.6 m*M* APAP in pH 2 McIlvaine buffer. Carbon paste electrode.** [***Reprinted with permission from J. J. Van Benschoten, J. Y. Lewis, W. R. Heineman, D. A. Roston, and P. T. Kissinger, J. Chem. Ed., 60, 772 (1983). Copyright © 1983, Division of Chemical Education, American Chemical Society.***]

Prepare a 3 m*M* APAP solution in the pH 2.2 buffer. (The concentrations of all APAP solutions should be accurately known.) Set the scan limits of the potentiostat at 1.0 V and −0.2 V vs. Ag/AgCl. Initiate cyclic voltammograms at 0.0 V with a positive scan. Record cyclic voltammograms at scan rates of 40 mV/s and 250 mV/s. (If an oscilloscope is available, record voltammograms at a few faster scan rates.) Stir the solution briefly and then allow 2 min for the solution to quiet between the recording of each voltammogram.

Repeat the above procedure for the following two solutions: 3 m*M* APAP in pH 6 buffer and 3 m*M* APAP in 1.8 *M* $H_2SO_4$.

## Treatment of Data

Write the electrode reaction that is occurring for each peak of the cyclic voltammograms obtained for the three supporting electrolytes.

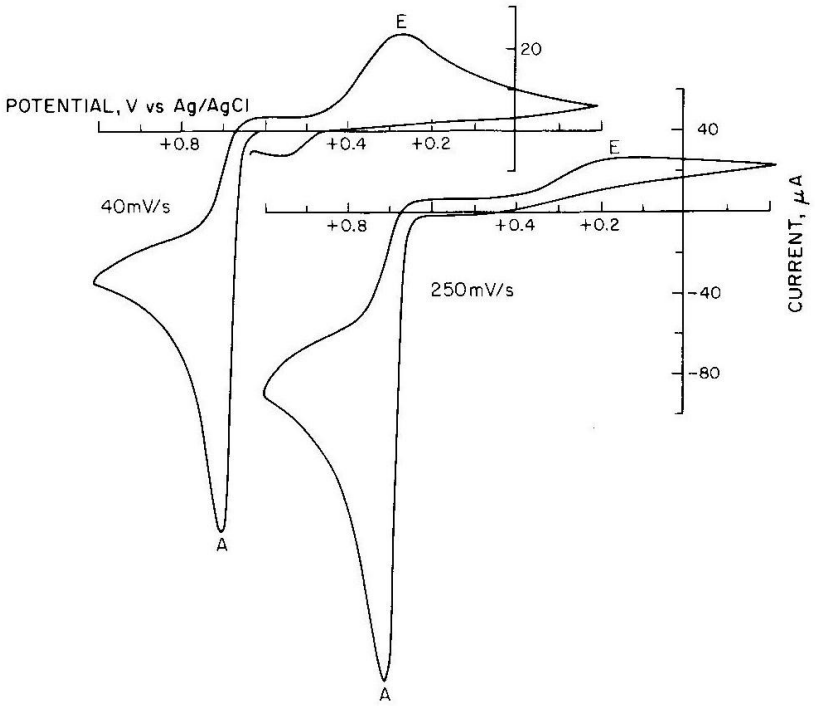



**Figure 4-9 / Cyclic voltammograms of 3.6 m*M* APAP in 1.8 *M* $H_2SO_4$. Carbon paste electrode.** [***Reprinted with permission from J. J. Van Benschoten, J. Y. Lewis, W. R. Heineman, D. A. Roston, and P. T. Kissinger, J. Chem. Ed., 60, 772 (1983). Copyright © 1983, Division of Chemical Education, American Chemical Society.***]

## Questions

1 An electrode mechanism in which the electrogenerated species reacts chemically is termed an EC mechanism and can be described by the following equations:

Electrode reaction, E: $O + ne \rightleftharpoons R$

Chemical reaction, C: $R \xrightarrow{k}$ product

Draw cyclic voltammograms for the following cases. (Assume the electrode reaction to be reversible.)

**a** The rate constant $k$ is zero.

**b** The rate constant $k$ is so large that the chemical reaction is essentially instantaneous relative to the scan rate.

**c** $k$ has an intermediate value between those in **a** and **b.**

2 What effect would lowering the temperatures be expected to have on the voltammograms in Fig. 4-8?

3 Explain why faster scan rates are necessary to study mechanisms involving faster chemical reactions.

4 What problems can you anticipate encountering for very fast scan rates ($>100$ V/s)?