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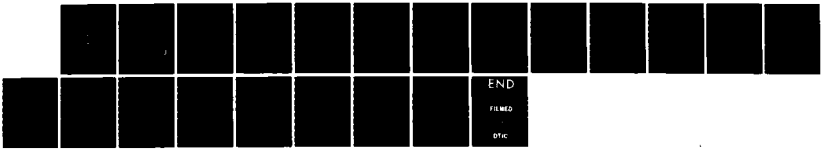

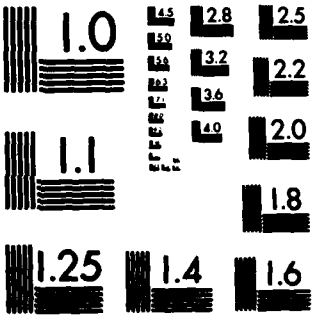

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Electrochemistry at Very High Potentials: The Use of Ultramicroelectrodes in the Anodic Oxidation of Short Chain Alkanes

By

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ELECTROCHEMISTRY AT VERY HIGH POTENTIALS: THE USE OF ULTRAMICROELECTRODES IN THE ANODIC OXIDATION OF SHORT CHAIN ALKANES

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ABSTRACT

The use of ultramicroelectrodes in aprotic solvent containing no purposefully added support electrolyte allows the observed anodic oxidation limit in acetonitrile to be considerably extended. The anodic oxidation of methane, butane, and other aliphatic alkanes is clearly observed under steady state conditions at potential up to about 3.8V (Ag^+ reference). The oxidation of the solvent occurs significantly at potentials greater than 4.0V and appears to result in radical coupling reactions forming both soluble and insoluble polymers.

INTRODUCTION

The electrochemical oxidation of alkanes (chain lengths greater than 5 carbons) was first accomplished by Fleischmann and Pletcher (1-4) in the late 1960's and early 1970's. In very dry aprotic solvents and various support electrolytes, it was possible to observe part of the voltammetric wave of the oxidation of n-pentane, isopentane, n-hexane, 2-methylpentane, 3-methylpentane, n-heptane, 2,2-dimethylpentane, and n-octane. It was shown that anodic oxidation of these substrates led to the formation of the corresponding carbenium ion which reacted rapidly with the electrolyte system. These studies were extended to strongly acidic systems to stabilize the carbenium species by the same workers (5,6) and later by Fritz, et. al. (7) and Pitti, et. al. (8).

The anodic oxidation limit in the solvents used has clearly been shown to be a function of the support electrolyte anion added, and follows the order ClO_4^- > BF_4^- > PF_6^-. The question of the contribution of the oxidation of the solvent to the current at the anodic limit has not been fully explored. Tourillon, et. al. (9) have observed the formation of polymeric acetonitrile/electrolyte films at the platinum/solution interface in, for example, the acetonitrile/perchlorate system at +2.6V. Whether the solvent itself is catalytically activated or whether it reacted with oxidized electrolyte is not entirely clear. The films are obviously conductive and allow the continued passage of current after their formation and surface precipitation. We shall see that with no purposefully added support electrolyte the voltammetric limit of the system is greatly extended. Under these conditions it becomes possible to study the anodic reactions of substrates with extremely high oxidation potentials.

It is clear that because of the high resistance of most pure solvents

that added support electrolyte is necessary to carry the charge passed at the electrode/solution interface through the bulk solution. The electrolyte also reduces the total solution resistance so that the measured or intended interfacial potential is reasonably accurate. At extremely low currents, however, these deleterious effects are circumvented, or are at least quantitatively predictable (10,11). The use of ultramicroelectrodes in solutions containing little or no purposefully added support electrolyte has been demonstrated previously (12,13,14). It is also pointed out that many other interfering processes are also eliminated in electrochemical experiments where support electrolytes are absent; these include ion-pair association reactions of the substrate and its electrogenerated intermediates and intermediates with the support electrolyte, specific adsorption of the electrolyte leading to double layer corrections and other considerations, and problems associated with the isolation and characterization of the products of the electrochemical reaction.

EXPERIMENTAL

Full details of the preparation of platinum microdisk and gold microring electrodes has been described previously (13). The platinum disk electrodes used in this work had diameters from 6000 Å to 25 μm. These were mounted in soda glass tubes. The exposed cross sectional disks were polished immediately before use. The gold ring electrode used was 100 μm in diameter and 9000 Å in thickness. The secondary electrode was either a platinum wire (1 mm diameter, 5 mm long) or a pseudo reference composed of an Ag wire in a 0.01 M Ag^+ solution separated from the working solution by a fine glass frit and a modified short Luggin arrangement. In each case the secondary system was placed about 1 mm from the working electrode.

The cell consisted of a small pear shaped flask with a small elongation pulled down in the tip to accommodate about 5 mL solution. The electrodes were inserted through joints in the top of the flask which were aligned so that the electrode tips would approach to within 1 mm in the bulb at the bottom of the flask. The bulb contained a U-tube in the bottom for gas purging or for the adding of reactants, etc. The cell and electrodes were thoroughly cleaned immediately before use by immersion in a boiling solution of 50% sulfuric acid in nitric acid (v/v). They were then thoroughly rinsed in triply distilled water, steamed in the same solvent, and dried at 100°C in a vacuum oven.

The solvent was acetonitrile (Burdick and Jackson, Distilled-in-Glass, nominal water content 0.003%) and was used as received.

Tetra-n-butylammonium tetrafluoroborate (TBAF) was prepared by the method of Lund and Iversen (15), and was dried at 80°C in a vacuum oven 8 hours before use. The hydrocarbon substrates were obtained from Matheson (gases) or Aldrich and were used as received.

The cell was rigidly mounted in a large 1/4" thick solid aluminum Faraday cage. Electrical connection through the cage was made with triaxial bulkhead connectors. Leads from the connectors to the cell and to the potential sources and the picoammeter were coaxial or triaxial, and were rigidly mounted to prevent the generation of triboelectric noise. Potentials were developed by a Hi-Tek PPR1 waveform generator, added when necessary to a bias obtained at an appropriately divided large capacity 12V battery. Currents were measured through a Keithly Model 616 Electrometer, and the polarization curves were plotted directly on a Hewlett-Packard Model 7015 analog recorder.

RESULTS AND DISCUSSION

Solvent Reaction

Typical voltammetric responses for acetonitrile backgrounds are shown in Figure 1 and 2. In Figure 1a, it is seen that breakdown of the system begins at about +2.5V. (The curves in the Figures all represent first scans at new electrode surfaces. Typically, slight depression of the current is observed on subsequent scans, presumably due to some blocking of the surface to electroactive species by the formation of polymeric film (9)). In this experiment, a platinum wire macroelectrode was used in a conventional three electrode configuration utilizing a high gain potentiostat setup. It was observed that the use of perchlorate electrolytes gave rise to system breakdown at potentials about 400 mV more cathodic, while use of hexafluorophosphates allowed the window to be extended to about 2.7 V. These results are in agreement with those reported previously (1). The process in perchlorate is known to be:

$$ClO_4^- \rightleftarrows ClO_4^{\cdot} + e^- \qquad [1]$$

$$ClO_4^{\cdot} + CH_3CH \rightleftarrows CH_2CN^{\cdot} + HClO_4 \qquad [2]$$

$$2\ CH_2CN^{\cdot} \rightleftarrows (CH_2CN)_2 \qquad [3]$$

Voltammetry of the same system at a 10 μm diameter platinum microdisk electrode is shown in Figure 1b and that at a 1 μm platinum microdisk is shown in Figure 1c. At these microelectrodes, the chacteristic relaxation time is less than a second (13) and the system is thus essentially at steady state conditions at the potential scan rates used in the experiments (1-10 mV/s). The results for all three figures (1a-c) may thus be assumed to be essentially

the same and it is assumed that the dominant process is the oxidation of the tetra-fluoroborate anion.

Comparative results for solutions containing no deliberately added support electrolyte are shown in Figure 2. It is impossible to use a conventional three electrode setup with a potentiostat under these conditions due to the magnitude of the solution resistance encountered. Use of the same microelectrodes in this solution, however, leads to the results in Figure 2a and 2b. The very small currents passed result in extremely small ohmic corrections to the potential. It is pointed out here that the oxidation of a small amount of the solvent, water, or any impurities in the system will simulate conditions of extremely dilute support electrolyte. The theory of the behavior of such systems at microelectrodes has been developed (10).

The diffusion controlled limiting current at a microdisk electrode embedded in an insulator, is given by (13) the expression:

$$i_d = 4nFDCr \qquad [4]$$

where n is the number of electrons transferred, F is the Faraday, D is the diffusion coefficient of the electroactive species, C its concentration, and r the radius of the microdisk electrode. It is observed that the current at progressively smaller electrodes in pure acetonitrile solution becomes anomalously small with respect to equation [4] (assuming the shape of the polarization curves for a reversible reaction is unchanged upon varying the electrode size). The steady state background current for acetonitrile in fact decreases to zero when a very small (6000 Å) electrode is used. These results suggest passivation of the surface by film formation by a product of the anodic oxidation of the solvent. The product must be formed by a chemical

reaction following the electron transfer since if it were precipitation of the product due to electron transfer it would passivate electrodes of any size. It is thus likely that the product is acrylonitrile:

$$CH_3CN \rightleftarrows CH_3CN^{+}\cdot \quad [5]$$

$$CH_3CN^{+}\cdot \rightleftarrows CH_2CN\cdot + H^{+} \quad [6]$$

$$2\ CH_2CN\cdot \rightleftarrows (CH_2CN)_2 \quad [7]$$

$$CH_2CN\cdot + (CH_2CN)_2 \rightleftarrows (CH_2CN)_3\cdot \quad [8]$$

The mass flux of any of the species that are electroactive in this sequence (the radical species will be more readily oxidizable than acetonitrile) will be increased at the small electrodes (16). When this flux is fast enough, the coupling polymeric reactions will occur in the kinetic layer which will be small compared to the size of the diffusion layer boundary (17) and insoluble polymer may be deposited at the surface. At larger electrodes, assuming fast electron transfer, the coupling reactions will occur in the kinetic layer, which, due to the decreased rate of mass flux will be larger than the diffusion layer boundary. Polymeric material thus formed will remain in the bulk of the solution and the electrode will not be passivated. The polarization curve of a 6000 Å diameter microdisk electrode is shown in Figure 3. The steady state current is seen to remain essentially zero to extremely high values of applied potential. Periodically the film ruptures either through ionization of parts of the film or mechanical failure and more acetonitrile can access the electrode. (Alternatively, charge may penetrate the membrane.) When this occurs, oxidation of the solvent occurs. The rate of electron transfer to the solvent is reflected by the shape of the envelope of the current pulses appearing through (or across) the membrane. This shape

is seen to track the shape of the normal curves at larger electrodes. These transient oxidations terminate either by "plugging" of the film rupture by electrogenerated polymer in close proximity to the electrode or by discharge across the film (if oxidation is occurring at the outside of the membrane). The study of electrode reactions at very high potentials in systems where polymerization will occur must thus be performed with carefully chosen electrode sizes. In acetonitrile, this limit seems to be around 1 μm for platinum microdisks. Other microelectrode materials or geometries may extend this limit, but it should be pointed out that the ultimate useful limit is always the diffusion controlled solvent oxidation, the value of which is closely approached already in this work. Thus, the extension of the present useful potential range of electrochemical solvents seems imminent; there is, for example, no longer the restriction that electrolyte be soluble in the solvent.

Alkane Oxidation

The ionization potentials of straight chain alkanes are, in general, greater than 10.2 electron volts. From the results of earlier correlation studies (1), we expect the half wave potentials in the acetonitrile system to appear at potentials greater than +3.2V. The results for methane, cyclopropane, butane, pentane, and heptane are summarized in Table 1.

Alkane	I.P./eV*	E/V
n-Methane	12.70	3.87
n-Butane	10.63	3.70
n-Pentane	10.35	3.61
Cyclopropane	10.1	3.41
n-Heptane	9.90	3.50

Table 1. Ionization potentials and half-wave potentials for some alkanes. Acetonitrile solution, no added support electrolyte, 10 μm platinum microdisk electrode, potential scan rate 10 mV/s.
*Photoelectron spectroscopy data from ref 18.

Typical polarization curves are shown in Figure 4. The anomalously low value for the half wave potential of cyclopropane is probably due to is oxidation by a totally different mechanism than simple two electron transfer, and loss of proton to the carbenium ion (vide infra). If this oxidation leads to the rapid formation of ethylene as does photooxidation of cyclopropane (19), then the anomalous behavior can be explained by the electrooxidation of the electrogenerated ethylene which is observed at similar potentials. It has been shown that the anodic oxidation of other aliphatic hydrocarbons (ethylene is an exception) generally proceeds by the transfer of two electrons and the loss of one proton to give the corresponding carbenium ion:

$$RH = R^+ + H^+ + 2e^- \qquad [9]$$

Slopes of the polarization curves near the half wave potential indicate that there is one electron transferred before the rate determining step so that a short lived cation radical is probably formed first, followed by a relatively slow chemical step in which the proton is lost, and then the final rapid

electron transfer at the electrode or by disproportionation of the radical with the cation radical.

Indeed, Pitti, et. al. proposed the following mechanism at low temperatures [-60°C] in fluorosulfuric acid for cyclopentane (20)

$$RH \rightarrow RH^{+\cdot} + e^- \quad [10]$$

$$RH^{+\cdot} \rightarrow R^{\cdot} + H^+ \quad [11]$$

$$R^{\cdot} \rightarrow R^+ + e^- \quad [12]$$

two waves were obtained and it was presumed $R^{\cdot}$ was weakly adsorbed at the Pt surface.

The highly reactive carbenium ion in these systems will react with nucleophiles of all strengths, even the solvent itself:

$$R^+ + CH_3CN \rightleftarrows \overset{+}{R}NCCH_3 \quad [13]$$

The final products of these reactions depends, therefore, to a large extent on the solvent system and its purity. Alternative reaction paths exist even for the nitrilium ions (reaction [13]), as well as the cation radical and free radical. Thus the concentration of the substrate will also be a factor in the final product distribution. It is anticipated that the hydrocarbon substrates studied in this work (with the possible exception of cyclopropane) will lead to the same types of products by similar mechanisms.

The anodic oxidation of substrates without supporting electrolyte leads to distorted polarization curves due to the extremely high resistance of the solution. Since there are other species always present (H_2O, impurities), there is little doubt that additional ionic species are formed near the

microelectrode. This situation will usually mean that conditions are developed that aproach the conventional electrochemical three-ion problem, the theory of which at microelectrodes has been given '10). In the end, the currents observed approach the theoretical values, and were linearly proportional to concentration. It is concluded that meaningful electrochemical results can be obtained in systems without added supporting electrolytes, and that the useful positive potential limit in acetonitrile is extended by at least one volt. It is anticipated that electrochemistry under such conditions will lead to a variety of important practical uses, such as fast, accurate sensors and detectors in HPLC systems (21) which use solvents of low dielectric constant in which electrolytes cannot be conveniently dissolved (hexane, benzene, carbon tetrachloride, etc.) (22,23).

ACKNOWLEDGEMENT

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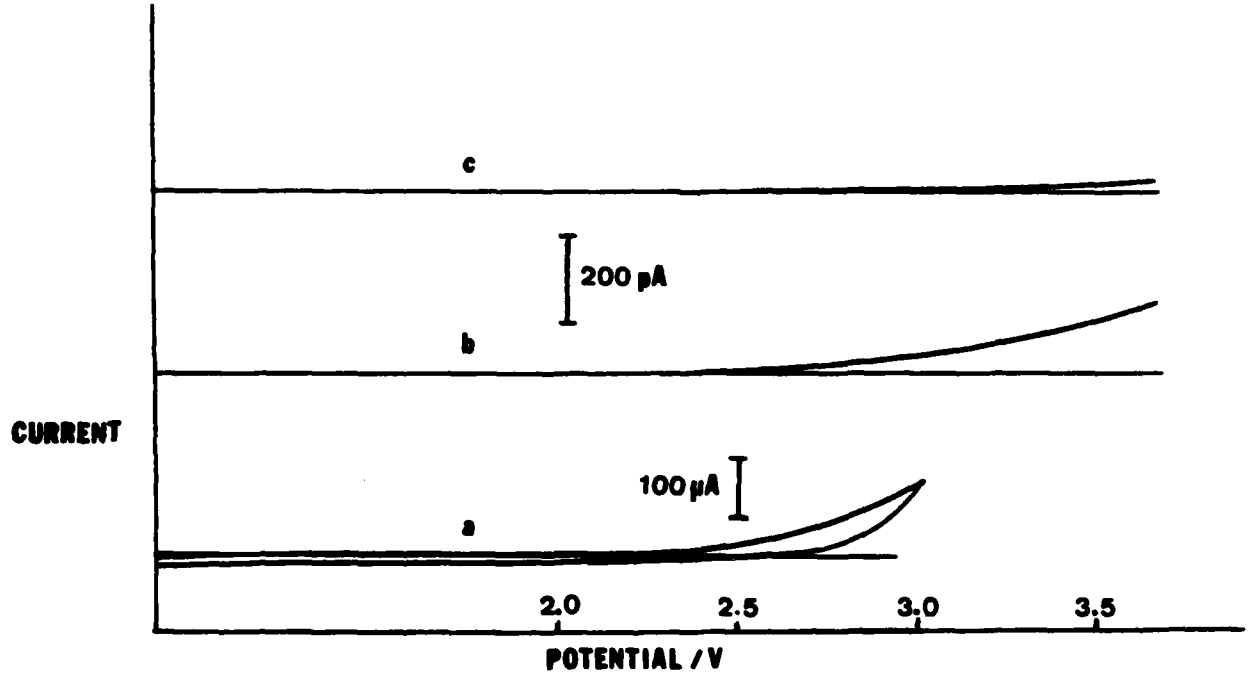
FIGURE LEGENDS

1. Voltammetry of 0.1 M TBAF in acetonitrile, scan rate 10 mV/s. (a) Macro platinum wire electrode, 14 gauge, 1 cm length. (b) 10 μm platinum disk ultramicroelectrode. (c) 1 μm platinum disk ultramicroelectrode.

2. Same parameters as Figure 1 except no deliberately added support electrolyte (pure acetonitrile). (a) 10 μm platinum disk ultramicroelectrode. (b) 1 μm platinum disk ultramicroelectrode.

3. Polarization curve of pure acetonitrile at a 6000 Å diameter platinum disk ultramicroelectrode.

4. Polarization curves for the oxidation in pure acetonitrile (dry, no support electrolyte) for methane and heptane. Concentrations are approximately 5 mM. Scan rate was 10 mV/s.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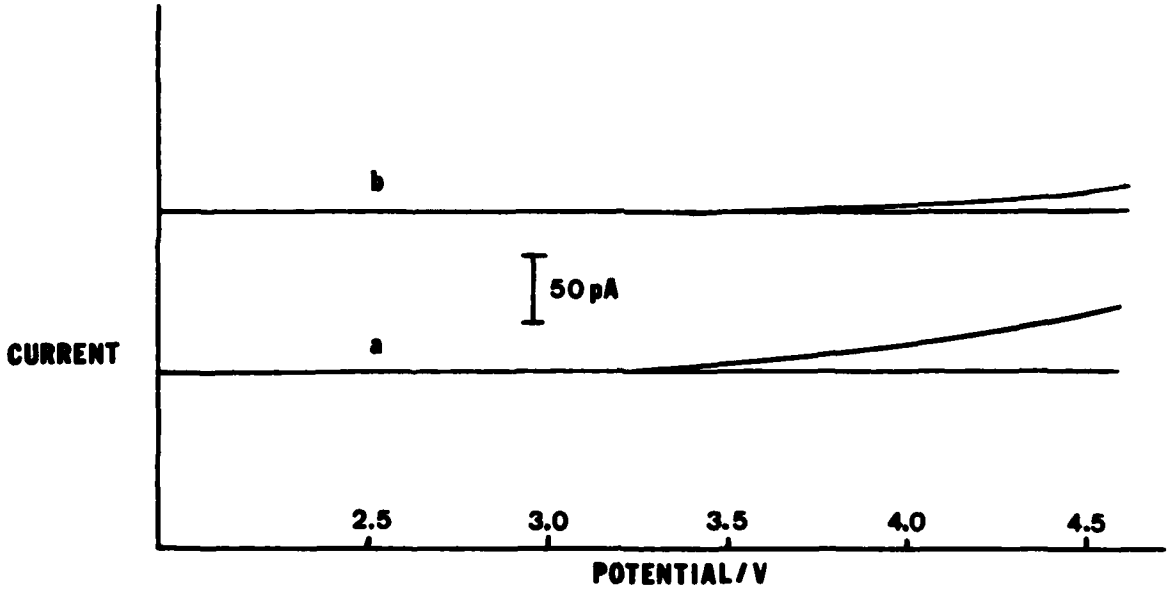
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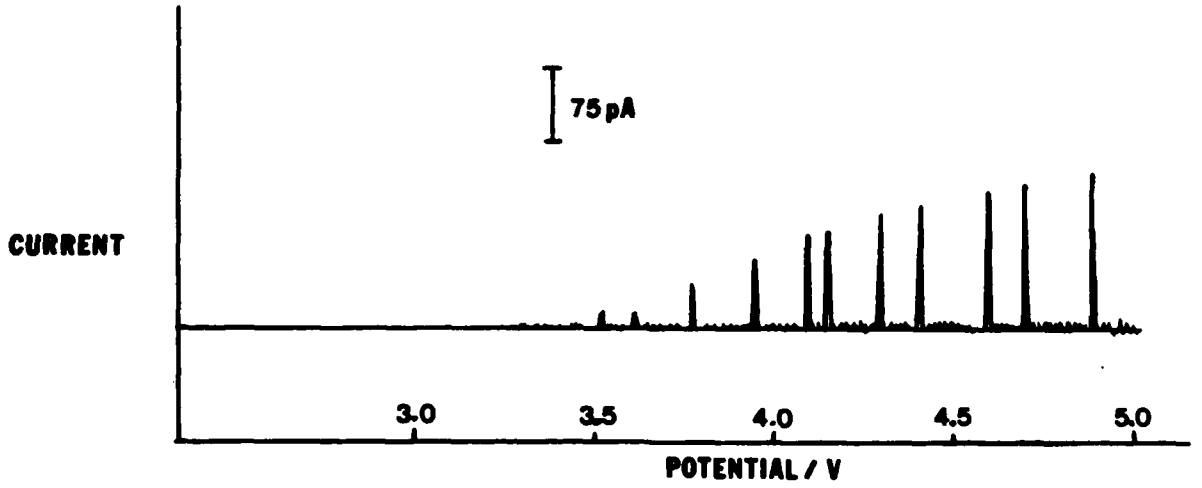
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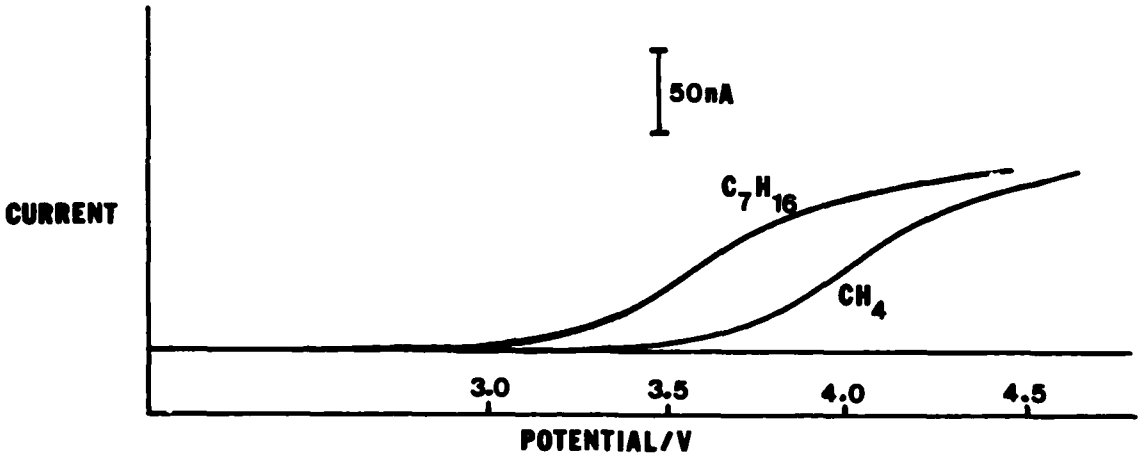
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