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actions. The electron-accepting and -donating properties or the acidity and the basicity of the ion and the solvent for the formation of the solvation bond have been defined in the absolute scales based upon the thermodynamic empirical rules. For convenience the empirical rules and the related correlations developed in the

preceding sections are summarized in Table IX.

It is hoped that these thermodynamic rules are helpful to the further development of the theoretical and experimental approaches to the elucidation of the problems related to the bonding of the monoatomic ions.

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

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The use of ultramicroelectrodes in aprotic solvents containing no intentionally added supporting 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 potentials up to approximately 4.3 V (Ag<sup>+</sup> reference). The oxidation of the solvent occurs significantly at potentials greater than 4.5 V 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, Pletcher, and Clark<sup>1-4</sup> in the late 1960's and early 1970's. In very dry aprotic solvents and various supporting 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<sup>5,6</sup> and later by Fritz and Wurminghausen<sup>7</sup> and Pitti et al.<sup>8</sup>

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<sub>4</sub><sup>-</sup> < BF<sub>4</sub><sup>-</sup> < PF<sub>6</sub><sup>-</sup>.<sup>1-4</sup> 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.<sup>9</sup> have observed the formation of polymeric acetonitrile/electrolyte films at the platinum/solution interface in, for example, the acetonitrile/perchlorate system at +2.6 V. 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.

We shall see that with no intentionally added supporting electrolyte the voltammetric limit of the system is greatly extended. Under these conditions it becomes possible to study the anodic reactions of compounds with extremely high oxidation potentials.

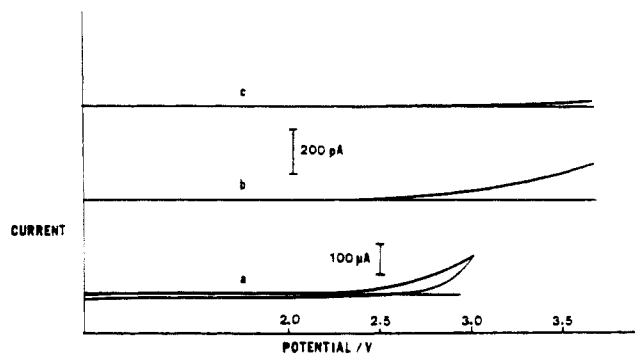
It is clear that because of the high resistance of most pure solvents that added supporting electrolyte is necessary to carry the charge passed at a large electrode through the bulk solution. The extremely small currents present in the ultramicroelectrode systems described herein may be carried in the bulk by ions present from autoprotolysis of the solvent, or by the presence of impurities at low levels. The quantitative treatment of the problem has been discussed.<sup>10,11</sup> The use of ultramicroelectrodes in solutions containing little or no deliberately added supporting electrolyte has been demonstrated previously.<sup>12,14,22</sup> It is pointed out that many other interfering processes are also eliminated in electrochemical experiments where supporting electrolytes are absent; these include ion-pair association reactions of the reactant and its electrogenerated intermediates and intermediates with the supporting 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 Section

Full details of the preparation of platinum microdisk and gold microring electrodes have been described previously.<sup>22</sup> The platinum disk electrodes used in this work had diameters from 0.6 to 25 μm. These were mounted in soda glass tubes. The

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**Figure 1.** Voltammetry of 0.1 M TBAF in acetonitrile, scan rate 10 mV/s: (a) macro platinum wire electrode, 0.5 mm  $\times$  1 cm; (b) 10- $\mu$ m platinum disk ultramicroelectrode; (c) 1- $\mu$ m platinum disk ultramicroelectrode.

exposed cross sectional disks were polished immediately before use. 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  $\text{Ag}^+$  solution separated from the working solution by a fine glass frit and a modified short Luggin capillary arrangement. In each case the secondary electrode system was placed about 1 mm from the working electrode.

The cell consisted of a small four-necked pear-shaped flask with a bulb in the bottom to accommodate about 5 mL of 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 very 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 (steam generated from triple distilled water), and dried at 100  $^{\circ}\text{C}$  in a vacuum oven.

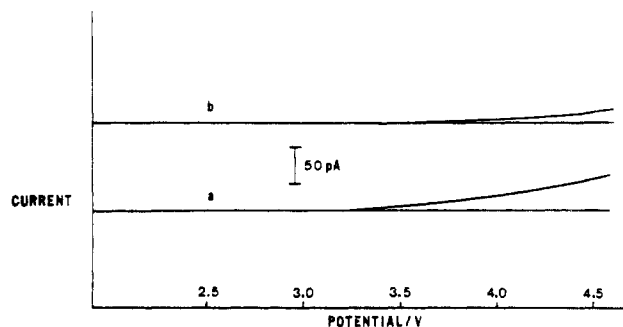
The solvent was acetonitrile (Burdick and Jackson, Distilled-in-Glass, nominal water content 0.003%) and was used after further drying over activated alumina.

Tetra-*n*-butylammonium tetrafluoroborate (TBAF) was prepared by the method of Lund and Iversen<sup>15</sup> and was dried at 80  $^{\circ}\text{C}$  in a vacuum oven 8 h before use. The hydrocarbon substrates were obtained from Matheson (gases) or Aldrich and were used as received.

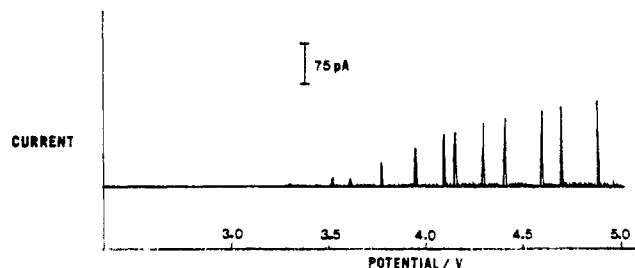
The cell was rigidly mounted in a large  $1/4$ -in. thick solid aluminum Faraday cage. Electrical connections through the cage were made with triaxial bulkhead connectors. Leads from the connectors to the cell and to the potential sources and the picoammeter were triaxial, and were rigidly mounted to prevent the generation of triboelectric noise. Potentials were developed by a Hi-Tek PPR1 waveform generator, added when necessary to a bias obtained from a divider supplied by a large-capacity 12-V battery. Currents were measured through a Keithly Model 616 electrometer (used as a current follower) and the polarization curves were plotted directly on a Hewlett-Packard Model 7015 analog recorder.

## Results and Discussion

**Solvent Reaction.** Typical voltammetric responses for blank acetonitrile solutions containing supporting electrolyte are shown in Figures 1 and 2. In Figure 1a, it is seen that breakdown of the system using a conventional Pt wire electrode begins at about +2.5 V. The curves in the figures all represent first scans at freshly polished 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.<sup>9</sup> Figure 1a represents a platinum wire macroelectrode used in a conventional three-electrode configuration utilizing a high-gain potentiostat setup. (It was observed in other



**Figure 2.** Same parameters as Figure 1 except no deliberately added supporting electrolyte (pure acetonitrile): (a) 10- $\mu$ m platinum disk ultramicroelectrode; (b) 1- $\mu$ m platinum disk ultramicroelectrode.



**Figure 3.** Polarization curve of pure acetonitrile at a 6000- $\text{\AA}$ -diameter platinum disk ultramicroelectrode.

experiments that the use of perchlorate electrolytes gave rise to system breakdown at potentials about 400 mV more cathodic than that in Figure 1a, and the use of hexafluorophosphates allowed the window to be extended to about 2.7 V. These results are in agreement with those reported previously.<sup>1</sup>)

Voltammetry of the same solvent electrolyte system using a 10- $\mu$ m-diameter platinum microdisk electrode is shown in Figure 1b and that at a 1- $\mu$ m-diameter platinum microdisk is shown in Figure 1c. At these microelectrodes, the characteristic relaxation time (time required for limiting currents to be established to a potential step) is less than  $10^{-1}$  and  $10^{-3}$  s, respectively,<sup>13</sup> and the system is at near-steady-state conditions at the potential scan rates used in the experiments (1–10 mV/s). The electrode processes occurring in Figure 1a–c are thus probably the same, oxidation of the supporting electrolyte TBAF at potentials greater than about 2.4 V.

Comparative results for solutions containing no deliberately added supporting electrolyte are shown in Figure 2. It is impossible to use a macroelectrode in a conventional three-electrode setup with a potentiostat under these conditions due to the magnitude of the solution resistance. The use of the 10- and 1- $\mu$ m-diameter microelectrodes in this solution, however, leads to the results in Figure 2, a and b. 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 ionic or oxidizable or reducible impurities in the system will establish conditions of very dilute supporting electrolyte. The theory of the behavior of such systems at microelectrodes has been developed.<sup>10</sup>

The diffusion-controlled limiting current at a microdisk electrode embedded in a large insulator coplanar with the electrode face is given by<sup>13</sup> the expression:

$$i_d = 4nFDcR \quad (1)$$

where  $n$  is the number of electrons transferred,  $F$  is the Faraday constant,  $D$  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 eq 1 (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  $\text{\AA}$ ) electrode is used.

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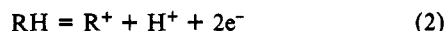
**TABLE I: Ionization Potentials and Half-Wave Potentials for Some Alkanes<sup>a</sup>**

alkane	IP/eV <sup>b</sup>	E/V
methane	12.70	3.87
<i>n</i> -butane	10.63	3.70
<i>n</i> -pentane	10.35	3.61
cyclopropane	10.1	3.41
<i>n</i> -heptane	9.90	3.50

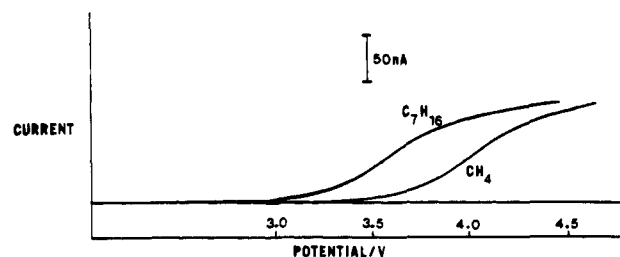
<sup>a</sup> Acetonitrile solution, no added support electrolyte, 10- $\mu$ m platinum microdisk electrode, potential scan rate 10 mV/s. <sup>b</sup> Photoelectron spectroscopy data from ref 18.

These results suggest passivation of the surface by film formation by a polymeric product. This product is probably formed by chemical reactions following the electron transfer (or chemical reactions of minor amounts of intermediates generated from the solvent) with small trace amounts of impurities in the solvent. The polarization curve at a 6000-Å-diameter microdisk electrode is shown in Figure 3. The steady-state current is seen to remain near zero at extremely high values of applied potential. Periodically the film apparently ruptures either through ionization of parts of the film or mechanical failure and more acetonitrile reactant is able to access the electrode. 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 normal polarization curves at larger electrodes. These transient oxidations terminate by passivation by "plugging" of the film rupture either by electrogenerated polymer in close proximity to the electrode or by oxidation 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, the lower limit seems to be around 1  $\mu$ m for platinum microdisks. Smaller electrodes would lead to higher values of the mass transfer coefficient, and therefore higher local concentrations of the reactive intermediates forming polymers. Precipitation of the polymer is thus more likely at the smaller electrode. Other microelectrode materials or geometries or further purification of the solvent may extend this limit, but it should be pointed out that the ultimate useful limit is the solvent oxidation. The present work demonstrates the effective extension of the useful potential range of electrochemical solvents.

**Alkane Oxidation.** The ionization potentials of straight chain alkanes are, in general, greater than 10.2 eV. From the results of earlier correlation studies,<sup>1</sup> we expect the half-wave potentials in the acetonitrile system to appear at potentials greater than +3.2 V. The results for methane, cyclopropane, butane, pentane, and heptane are summarized in Table I. Typical polarization curves are shown in Figure 4. The anomalously low value for the half-wave potential of cyclopropane is probably due to its oxidation by a totally different mechanism than simple two-electron transfer and loss of proton to the carbenium ion (vide infra).<sup>19</sup> It has been shown that the anodic oxidation of other aliphatic hydrocarbons generally proceeds by the transfer of two electrons and the loss of one proton to give the corresponding carbenium ion:



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 rapid chemical step in which the proton is lost, and then the final rapid electron transfer at the



**Figure 4.** Polarization curves for the oxidation in pure acetonitrile (dry, no supporting electrolyte) for methane and heptane. Concentrations are approximately 5 mM. Scan rate was 10 mV/s. Pt electrode diameter 1.0  $\mu$ m.

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<sup>20</sup>



where 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:



The final products of these reactions depend, therefore, to a large extent on the solvent system and its purity. Alternative reaction paths exist even for the nitrilium ions (reaction 6), 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 reactants 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 redox species without supporting electrolyte leads to distorted polarization curves due to the high resistance of the solution. Since trace amounts of other species are 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 approach the conventional electrochemical three-ion treatment, the theory of which at microelectrodes has been given.<sup>10</sup> At high potentials the currents observed approach the theoretical limiting values. It is concluded that activation of saturated hydrocarbons can be performed in aprotic solvents without supporting electrolytes. 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<sup>21</sup> which use solvents of low dielectric constant in which electrolytes cannot be conveniently dissolved (hexane, benzene, carbon tetrachloride, etc.).<sup>22,23</sup> The development of electrochemical reactors which utilize these unusual conditions for synthetic applications will be described elsewhere.<sup>24</sup>

**Acknowledgment.** We thank the Office of Naval Research, Washington, for support of this work.

**Registry No.** TBAF, 429-42-5; methane, 74-82-8; *n*-butane, 106-97-8; *n*-pentane, 109-66-0; cyclopropane, 75-19-4; *n*-heptane, 142-82-5; acetonitrile, 75-05-8; platinum, 7440-06-4.

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