NMR assistance and helpful discussions and Lynn Jacob for her many contributions.

Supplementary Material Available: Spectral characterization of **1f-1g** and a description of HLE assay (1 page). Ordering of information is given on any current masthead page.

Electrochemistry in Near-Critical and Supercritical Fluids. 1. Ammonia

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We report electrochemical studies in near-critical and supercritical ammonia and the behavior of solvated electrons and *m*-chloronitrobenzene in this medium. Thermodynamic and solubility studies of supercritical solutions have been an active area of research.[1] We are interested in applying electrochemical techniques to near-critical and supercritical fluids to obtain a better understanding of the thermodynamics and kinetics of reactions, particularly homogeneous and heterogeneous electron-transfer reactions, that occur in these media and perhaps to utilize these solutions for electrosynthetic purposes. The high temperatures and pressures necessarily associated with electrochemically useful supercritical solutions necessitate the use of highly specialized cells and electrodes. In addition, the increased reactivity of species and the highly corrosive environment of supercritical ammonia limits the types of useful electrolytes and redox couples that easily can be studied as test systems.

As the critical temperature of a liquid is approached, the gaseous and liquid phases merge into a single, space-filling phase called a supercritical fluid. For ammonia, the critical point occurs at 133 °C and 112.5 atm; addition of low concentrations of electrolyte do not change these values appreciably. The characteristics that typify these fluids include decreased viscosities, densities, and dielectric constants, unusual changes in inter- and intramolecular forces, and altered solvation characteristics. A primary question of interest is whether electrochemical studies can be carried out in a supercritical fluid containing an electrolyte. We show here that electrochemical techniques, such as cyclic voltammetry and chronocoulometry, with near-critical and supercritical ammonia can be used to probe changes in redox potentials, electrogenerated product stability, and diffusion coefficients. Of the limited number of electrochemical studies that have been carried out on supercritical solutions, most have dealt with the corrosion of metals in contact with water.[2] To our knowledge, the only previous attempt at obtaining quantitative electrochemical information from supercritical NH_3 involved a two-electrode, constant-current, electrodeposition of silver.[3]

There are two primary experimental difficulties associated with these types of experiments: containment of a high-pressure, space-filling, corrosive fluid and design of electrode feed throughs that can withstand the supercritical environment and remain insulated from the walls of the cell. The base of the electrochemical cell we have fabricated is of 316 stainless steel; the interior is cylindrical and has an internal volume of 75 mL. A detachable lid of the same material is bolted to the base by means of a flange arrangement incorporating a diamond-shaped copper gasket. Three electrodes, supported by standard Swagelok fittings, pass through the lid. Provisions are also made for evacuation, filling, sample addition, and a rupture disk. All electrode feed throughs consist of tungsten wire passed through a commercially available graded glass to Kovar seal. Construction of the feed through is completed by sealing the glass to the wire. The working electrode is a disk-shaped cross section of a tungsten wire, and the counter and quasi-reference (QRE) electrodes consist respectively of platinum and silver wires soldered onto the tungsten. These electrodes have withstood pressures of 340 atm at 160 °C.

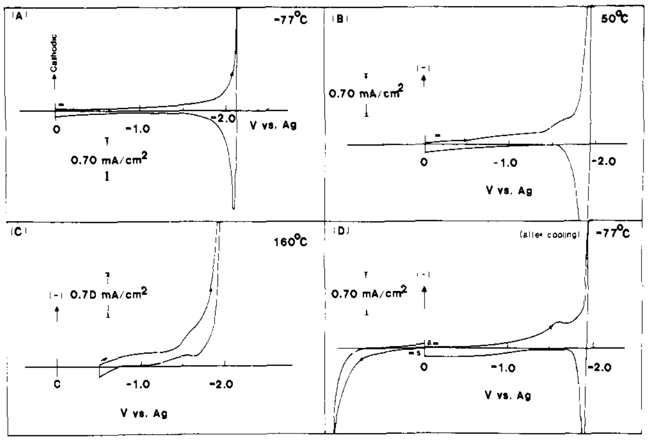

Figure 1. Cyclic voltammograms for generation and oxidation of solvated electrons in NH_3. (A) -77 °C, 0.2 M KI; (B) 50 °C, 20 atm, 0.2 M KI; (C) 160 °C, 252 atm, 0.1 M KI (supercritical); (D) -77 °C (after cooling from 160° C), 0.2 M KI. Scan rate, 200 mV s^{-1}.

A typical experiment involved evacuating the cell, to which electrolyte had previously been added, followed by the addition of sufficient dry ammonia under vacuum line conditions to generate the desired pressure and density at a specified temperature. The cell was isolated from the vacuum line by means of a high-pressure valve, and removed to an armored autoclave for heating above the critical temperature (~140 °C) of the electrolytic solution. To probe changes in the available potential range of NH_3 and the stability of solvated electrons (e_s^-) as a function of temperature, cyclic voltammetric scans were employed (Figure 1).[4]

As the temperature increased, the polarizable range of the ammonia solution decreases as evidenced by a positive shift of the solvated electron peak and a negative shift of the anodic background (vs. QRE). A small shoulder preceded the onset of solvated electron production at higher temperatures which persisted when the solution was cooled back to -77 °C (curve D). A similar wave was observed at -77 °C in single-compartment glass cells and thus is probably associated with the reduction of a species generated at the counter electrode. Above the critical temperature (curve C) generation of solvated electrons is still observed, although on the voltammetric time scale little, if any, oxidation is seen upon scan reversal. This can be attributed to a decrease in the stability of the solvated electrons, probably by reaction with NH_3 at the higher temperatures.[5] Upon cooling the solution to -77 °C, the system returns to essentially its initial condition, demonstrating no extensive contamination or irreversible changes in the solution. The apparent shift in potential of the solvated electron peak

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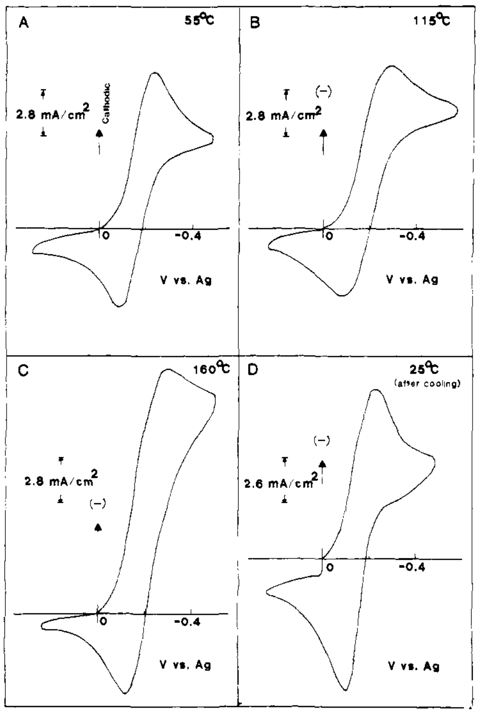

Figure 2. Cyclic voltammograms for reduction of *m*-chloronitrobenzene (MCNB) in NH_3. (A) 55 °C, 10 atm, 8 mM MCNB, 0.2 M KI (ΔE_p = 130 mV); (B) 115 °C, 82 atm, 6 mM MCNB, 0.2 M KI (ΔE_p = 180 mV); (C) 160 °C, 265 atm, 5 mM MCNB, 0.1 M KI (ΔE_p = 160 mV); (D) 25 °C (after cooling from 160 °C), 10 atm, 8 mM MCNB, 0.2 M KI (ΔE_p = 120 mV). Scan rate, 500 mV s^{-1}.

(between curves A and D) is probably caused by a change in potential of the silver wire (QRE).

To study changes in reversibility and diffusion coefficient (*D*) with *T* and *P*, the reduction of *m*-chloronitrobenzene[6] (MCNB) was investigated; typical voltammograms are shown in Figure 2. The behavior remains essentially Nernstian as *T* is raised; for example, at 160 °C a ΔE_p value[7] of 90 mV was found with a fresh solution (compared to the Nernstian value of 85 mV). However, replicate experiments at 160 °C sometimes showed ΔE_p values up to 160 mV, perhaps because of some, yet undefined, electrode surface effect. As the critical temperature is approached, the voltammograms show convective features such as an unusually shallow drop off of current past the cathodic peak current. The onset of natural convection is promoted by the low viscosity of the solution (0.024 cp at 160 °C). These convective effects probably also account for the i_{pa}/i_{pc} ratio being 0.7 (rather than 1). However, normal and nearly reversible behavior is restored upon decrease in *T* and condensation of the solvent. Chronocoulometric experiments[8] involving potential steps and acquisition of data at short times (50 to 250 ms) to avoid convective problems were used to determine *D* as a function of *T* and *P*. The value found at 160 °C and 272 atm (density, 0.40 g cm^{-3}) was 3×10^{-4} $cm^2\ s^{-1}$. This value can be compared with that calculated from the *D* value at -40 °C (2.8×10^{-5} $cm^2\ s^{-1}$) and the change in viscosity via the Stokes-Einstein equation (6×10^{-4} $cm^2\ s^{-1}$) and appears to be consistent with values of aromatic hydrocarbons in CO_2 at similar viscosities.[9] The results demonstrate the stability of the MCNB radical anion and the enhanced mass transport under supercritical conditions. Further investigations of electrochemistry of NH_3, water, and other fluids at near-critical and supercritical conditions are in progress.[10]

Registry No. MCNB, 121-73-3; MCNB radical anion, 34467-54-4; NH_3, 7664-41-7; KI, 7681-11-0; W, 7440-33-7.

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Exciplex Isomerization in Photosensitized Cycloreversion Reactions of Cage Compounds[1]

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Most photochemical reactions occur diabatically because the electronically excited reactant tends to be converted to the ground state of product via potential energy surface crossing or touching. Some photoreactions that have a small activation energy on the excited surface, usually accompanied by a minor structural change during transformation of reactant to product, e.g., proton transfer and complex formation, are known to occassionally occur adiabatically.[2] Recently, an adiabatic exciplex isomerization of hexamethyl(Dewar benzene) to hexamethylbenzene has been demonstrated by Taylor,[3] and a method to identify the observed exciplex as that from the isomerized product was established by Jones.[4] The efficiency of this adiabatic exciplex isomerization varied with the structure of the photosensitizer (an electron acceptor) with a quantum yield which reached ca. 0.50.[4]

In connection with our recent studies on the photosensitized isomerization of cage compounds **1** to dienes **2** in polar solvents which occurs by a highly efficient radical ion chain mechanism,[5] we turned our attention to the rearrangement that can also be observed in nonpolar solvents. Herein we report an adiabatic exciplex isomerization of **1** to **2** having a quantum efficiency near unity.

Irradiation (λ > 350 nm) of a benzene solution of **1a** containing 3,9-dicyanophenanthrene (DCP)[6] or 9,10-dicyanoanthracene (DCA) resulted in isomerization to **2a**. The quantum yield extrapolated to an infinite concentration of **1a** was near 1.0 in both sensitizations. Interestingly enough, **1a** and **2a** both clearly quenched the fluorescence of DCP in benzene giving a weak,

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(6) In the case of DCP-sensitized reaction, although prolonged irradiation contaminated the reaction, any clear product other than diene **2a**, recovered cage compound **1a**, and DCP could not be isolated. Recovery of DCP was more than 95% at 55% conversion of **1a** to **2a** ([**1a**] = 3.5×10^{-2} M, [DCP] = 2.0×10^{-3} M).

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