Detection of the Electrohydrodimerization Intermediate Acrylonitrile Radical Anion by Scanning Electrochemical Microscopy

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A long-sought goal in electrochemistry has been the observation of the intermediate, presumably the anion radical, produced in the electrohydrodimerization (EHD) of acrylonitrile (AN). The EHD of activated olefins is an important class of electroorganic reactions, especially because a commercial process for adiponitrile synthesis is based upon the EHD of acrylonitrile.[1-3] A number of studies of the EHD of more sterically hindered olefins, e.g., dialkyl fumarates and fumaronitrile, have appeared.[4,5] On the basis of these, the proposed reaction mechanism involves electrogeneration of the radical anion, R^-, followed by dimerization of R^- and then protonation to yield the hydrodimer:

$$R + e^- \rightleftarrows R^{\bullet -} \tag{1}$$

$$2R^{\bullet -} \xrightarrow{k_2} R_2^{2-} \tag{2}$$

$$R_2^{2-} \xrightarrow{H^+} R_2H^- \xrightarrow{H^+} R_2H_2 \tag{3}$$

The methods for elucidating the reaction mechanism, i.e., cyclic voltammetry (CV), double-potential-step chronoamperometry, rotating ring disk electrode (RRDE) voltammetry, and electron spin resonance, largely depend upon detection and quantification of R^-. However, the lifetime of AN^- is too small to allow such studies with AN, and it has even been suggested[3] that the EHD reaction mechanism for AN might occur via reaction of the dianion with the parent. An additional complication in studies of EHD is the tendency for the formation of oligomers and polymers, e.g., by the reaction

$$R_2^{2-} + R \rightarrow R_3^{2-} \rightarrow \ldots \tag{4}$$

and the protonation of R^- by H_2O or excess acid (HX) leading to the two-electron ECE route, i.e., reaction 1 followed by

$$R^{\bullet -} + HX \rightarrow RH^{\bullet} + X^- \tag{5}$$

$$RH^{\bullet} + e^- \rightarrow RH^- \tag{6}$$

$$RH^- + HX \rightarrow RH_2 + X^- \tag{7}$$

We have previously suggested[6] that the scanning electrochemical microscope (SECM)[7] can be employed to study rapid reactions of electrogenerated intermediates. The principle of this method is illustrated in Figure 1. An ultramicroelectrode tip (UME) (e.g., a gold disk, 5-μm diameter, in a glass sheath) is held in close proximity to a larger substrate electrode, with both immersed in the solution of interest. The tip is held at a potential where the reduction of AN, eq 1, occurs at a diffusion-controlled rate with a tip current, i_T. The substrate electrode is held at a potential where the intermediate, AN^-, is oxidized (or collected) so that the substrate current, i_S, is a measure of the amount of AN^- that reaches this electrode before it reacts. For a stable tip-generated species, $i_S = -i_T$, or the collection efficiency $|i_S/i_T| = 1$. However, for a reactive tip-generated intermediate, i_S/i_T will depend upon the spacing between the tip and substrate, d. As discussed previously,[6] a plot of i_S/i_T against d/a (where a is the UME radius) can be employed to determine the rate constant for reactions of the intermediate. These principles, i.e., generation at one electrode and collection at another, are analogous to those employed in RRDE studies. The SECM approach, however, has the advantage of larger collection efficiencies, larger fluxes between electrodes, and the ability to vary continuously the interelectrode spacing. It is also experimentally more convenient, since construction of an RRDE is difficult, and high rotation rates to effect interelectrode transport are not required in SECM. Rapid reactions can also be studied by fast transient techniques, e.g., cyclic voltammetry at high scan rates (v) at a UME.[8,9] However, we have found that such fast transient methods are often difficult to apply in practice because of large contributions from nonfaradaic double-layer charging and simultaneous electrolysis of adsorbed species on the electrode surface. The current for these latter effects increases linearly with v, while contributions of the electrolysis of the dissolved species increase with $v^{1/2}$.[10] This implies that measurements at very large v can be difficult, especially with small bulk concentrations of the species of interest as required in this investigation. In a previous study of AN reduction at a UME (in aqueous solutions), only steady-state limiting reduction currents were reported.[11]

The electrochemical behavior (e.g., CV) during the reduction of AN in a solvent like *N,N*-dimethylformamide (DMF) depends upon the moisture content. In dry DMF the reduction of AN occurs at −2.0 V vs a Ag wire quasireference electrode (AgQRE) followed by a second smaller wave at −2.65 V vs AgQRE. Upon addition of H_2O (0.5–1.3%), the height of the first wave increases because of the increasing importance of the ECE route, eqs 5–7. Similar results have been found in the CV of AN in MeCN.[5a] However, in dry solvent, the electrode tends to foul after reduction of AN, presumably because of formation of polymer on the surface via eq 4.

Further evidence for the different AN reduction paths under different solution conditions was obtained from measurements of the transient current, $i(t)$, with time, t, at an UME. By normalizing $i(t)$ by the steady-state current at the same UME, i_{SS}, and plotting $i(t)/i_{SS}$ vs $t^{-1/2}$, the magnitude of the diffusion coefficient, D, could be obtained independent of the apparent

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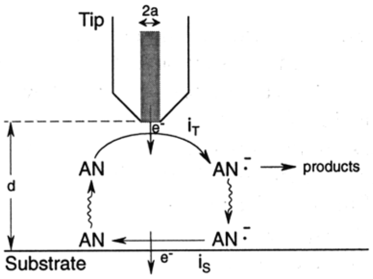

Figure 1. Schematic representation of SECM experiment.

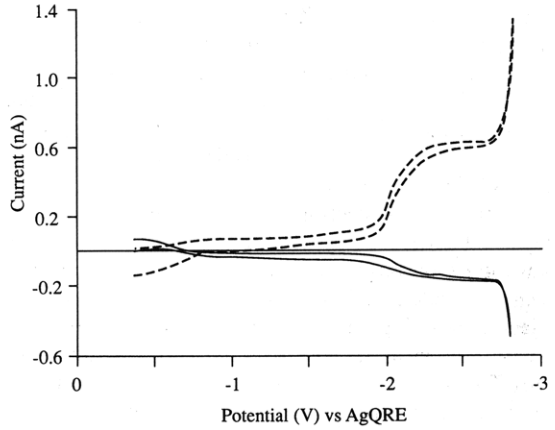

Figure 2. SECM TG/SC voltammograms for the reduction of a 1.50 mM AN solution. The substrate was a 60-μm-diameter gold electrode held at a potential of -1.75 V vs AgQRE while the tip ($a = 2.5$ μm) potential was scanned from -0.4 to -2.8 V vs AgQRE; interelectrode spacing, *d*, 1.36 μm; scan rate, 100 mV/s; (- - -) tip voltammogram, (—) substrate current. Current at both tip and substrate decreased slightly on the reverse scan (-2.8 to -0.4 V), and both showed a wave attributed to the presence of an intermediate, probably R_2H^-, at -0.6 V on reversal.

number of electrons passed per AN molecule, n_{app}.[12] When this experiment was carried out at a 25-μm-diameter Au disk in DMF containing 12.2 mM AN, 0.1 M TBAPF$_6$, and 0.5% H_2O with a potential step into the limiting current region, a *D* of 1.2×10^{-5} cm^2/s was obtained. At this water concentration, from i_{SS}, $n_{app} = 1.6$, showing that there is an appreciable ECE contribution. However, from this value of *D* and i_{SS} for a 10-μm-diameter UME in a DMF solution without added water and an AN concentration of 11.2 mM, $n_{app} = 0.4$, signaling significant polymerization. This polymerization reaction can be minimized by using low concentrations (~1–2 mM) of AN.

The SECM experiments were carried out in the absence of added water and at low AN concentrations to minimize the effects of the reactions in eqs 4–7 and make the predominant route an E_rC_{2i} one[13] (i.e., eqs 1–3). A tip generation/substrate collection (TG/SC) voltammogram obtained with a 5-μm Au tip and 60-μm Au substrate electrode is shown in Figure 2. Ferrocene was used as a mediator at positive potentials so that the conventional SECM feedback response[7] could be used to monitor the tip position when it was in close proximity to the substrate and to determine the spacing, *d*. The substrate was held at -1.75 V vs AgQRE, where any $AN^{\cdot-}$ reaching its surface would be oxidized, and the tip was scanned from -0.4 to -2.8 V vs AgQRE. The substrate current observed in the region of the AN reduction wave thus represents $AN^{\cdot-}$ that traverses the gap. Under these conditions, $|i_S/i_T| = 0.29$, so that an appreciable fraction of the $AN^{\cdot-}$ generated at the tip undergoes dimerization.[14] By determining i_S/i_T as a function of the gap spacing (normalized by the tip radius, *a*), d/a, at three different AN concentrations (0.58, 1.50, and 1.91 mM), the fit to the E_rC_{2i} mechanism could be tested and an estimate of the dimerization rate constant, k_2, obtained. Note that at these AN concentrations, even in the absence of added water, filming of the UME surface was not serious and the steady-state current for ferrocene oxidation dropped only 3–5% after scanning over the AN reduction wave. Any film formed after several scans could be removed by stepping the tip potential to 1.0 V vs AgQRE for a few seconds. Collection efficiency (i_S/i_T vs d/a) plots at the different AN concentrations are shown in Figure 3, along with theoretical curves calculated with the dimensionless parameter $k_2a^2c^*/D$ (where c^* is the bulk AN concentration). Although simulations of the alternative route, involving reaction of $R^{\cdot-}$ with R followed by electron transfer to produce R_2^{2-}, have not yet been carried out, previous reaction order plots of hydrodimerization reactions[4] suggest that this pathway would not fit the observed concentration dependence. The results at the lowest AN concentration fit best, probably because the contribution of the polymerization side reaction is smallest with 0.58 mM AN. However, given the kinetic complications for this reaction, the fit to the dimerization reaction in all cases is quite reasonable and yields $k_2 = (6 \pm 3) \times 10^7$ M^{-1} s^{-1}. This is 2 orders of magnitude larger than that for the dimerization of fumaronitrile.[6]

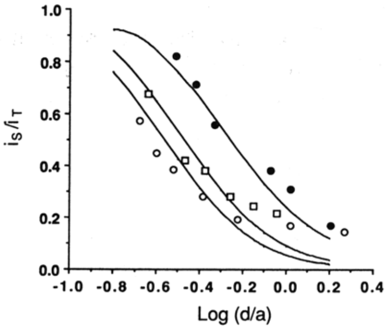

Figure 3. SECM collection efficiencies, i_S/i_T, vs the logarithm of the normalized distance, $\log(d/a)$, for AN concentrations of (●) 0.58, (□) 1.50, and (○) 1.91 mM; $a = 5$ μm. The substrate was a 60-μm-diameter gold electrode. Solid lines are the best theoretical fits for each concentration with values of $k_2a^2c^*/D$ of 100 (0.58 mM), 500 (1.50 mM), and 1000 (1.91 mM).

In conclusion, the SECM has been shown to be a useful technique for observing short-lived electrogenerated intermediates. The acrylonitrile radical anion has been detected for the first time, with the hydrodimerization reaction path for AN following that of other activated olefins and proceeding via coupling of the radical anion. Because SECM measurements can be made under steady-state conditions, short time measurements are not needed and contributions by adsorbed electroactive species are avoided. This technique should thus allow electrode reactions to be investigated that were previously not addressable by other electrochemical techniques.

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[14] The small anodic wave seen at the tip on scan reversal at -0.75 V vs AgQRE is attributed to oxidation of reduced protonated intermediates, e.g., RH^- or R_2H^-, producing a corresponding small cathodic current at the substrate.