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ELECTROGENERATED CHEMILUMINESCENCE

PART II. EMISSION FROM ACETONITRILE SOLUTIONS CONTAINING NO ADDED LUMINESCORS *

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ABSTRACT

Electrochemiluminescence (ECL) was observed from MeCN solutions containing only tetrabutylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte when very negative potentials (< -3.5 V vs. Ag) were applied to a platinum working electrode. The addition of tetrabutylammonium persulfate ((TBA)₂S₂O₈) produced a strong (10 to 100 times) increase in the ECL intensity at the same applied potential. In both cases the ECL spectra extended between 390 and 650 nm, with a peak at about 510 nm. Bulk electrolysis of an MeCN solution containing TBABF₄ and (TBA)₂S₂O₈ at -3.5 V vs. Ag formed a thin yellow film on the electrode surface that fluoresced with peaks at 420 nm and 466 nm, and a yellow product in solution with the same fluorescence spectrum. IR absorption and proton NMR spectra of the yellow product showed the presence of $-\text{C}=\text{N}-$ units and suggested that polyacetonitrile is



the species responsible for the ECL and fluorescence.

INTRODUCTION

We describe here electrochemical experiments with MeCN solutions of tetra-n-butylammonium (TBA⁺) BF₄⁻ in which emission occurs upon reduction at background potentials. Addition of (TBA)₂S₂O₈ results in higher levels of emission. Background emission in MeCN is of interest, because MeCN is a widely used solvent for electrochemical and ECL studies [1]. Moreover, ECL has been proposed as an analytical method for low concentrations of luminescours [2] and the lower limit of detection is largely governed by background emission processes. Moreover, there has been recent interest in inverse photoemission from metal electrodes [3]. This results in very low levels of emission that must be distinguished from back-

* Dedicated to the memory of Don Smith.

ground processes and possible effects of impurities. Finally, studies of ECL can provide information about the electrode reactions and homogeneous reactions of electrogenerated intermediates, especially those producing very reactive, and often short-lived, intermediates [4].

We propose that the observed emission can be attributed to the formation of oligomers or polymers of MeCN. Although MeCN is usually considered to be an inert solvent, it can participate in many kinds of chemical reactions [5]. Moreover, it can be polymerized by glow discharge [6], mechanochemical means [7], or catalytic reaction [8]. Electrochemical formation of thin polyacetonitrile (PAN) films on Pt electrode surfaces in an anodic process has also been described [9]. However, except for a brief mention of PAN formation during reduction of MeCN [10], no reports of cathodic polymerization upon background electrolysis have appeared [1,11].

EXPERIMENTAL SECTION

Materials

HPLC grade acetonitrile (Fisher Scientific Company, Fair Lawn, NJ) was purified and dried by continuous refluxing then distillation from P_2O_5 under nitrogen. The solvent was dried further and degassed by three vacuum distillations over dry P_2O_5 and stored over super I Woelm alumina N. Electrometric grade tetrabutylammonium tetrafluoroborate (TBABF₄) (Southwestern Analytical Chemical Co., Austin, TX) was recrystallized three times from ethyl acetate and then dried in a vacuum oven at 85–100 °C for 36 h. Tetrabutylammonium persulfate ((TBA)₂S₂O₈) was prepared from analytical grade TBAOH (Southwestern Analytical Chemicals) and (NH₄)₂S₂O₈ (recrystallized from MCB reagent grade). The reaction mixture of (NH₄)₂S₂O₈ with TBAOH was extracted three times with CH₂Cl₂ and the organic fraction was treated with activated charcoal and dried over anhydrous MgSO₄. The CH₂Cl₂ was removed with a rotating evaporator. The crystals of (TBA)₂S₂O₈ were dried further in vacuo for 24 h.

Apparatus

Electrochemical and ECL experiments were performed with a Princeton Applied Research (PAR) model 175 universal programmer, model 173 potentiostat/galvanostat and model 179 digital coulometer. The ECL spectra were recorded with a PAR model 1215 OMA2 optical multichannel analyzer equipped with a silicon intensifier target vidicon detector with a vacuum UV scintillator to enhance the UV response. ECL intensity vs. potential curves were measured through the bottom of the electrochemical cell with a Hamamatsu model R928 photomultiplier tube. Both one-compartment and three-compartment electrochemical cells were used in different experiments. A Pt disk (0.03 cm²) or a Pt foil (ca. 1 cm²) working electrode, a Pt wire auxiliary electrode or Pt mesh auxiliary electrode and an Ag wire quasi-reference electrode (AgRE) were used. Solutions were prepared either in a Helium Atmospheres dry box or by transferring solvent under vacuum into the electrochemical cell containing predried TBABF₄ or (TBA)₂S₂O₈.

The fluorescence and excitation spectra were taken with a Spex Fluorolog 2 instrument with a 450 W xenon lamp and R508 photomultiplier. The IR absorption spectrum was recorded with a Beckman Acculab Infrared Spectrophotometer. Photoelectron spectra were measured with an X-ray photoelectron spectrometer (VG Scientific Instrument, East Grinstead, Sussex, England). Product separation was done with a Sephadex LH-20 column in cyclohexane/CH₂Cl₂/MeOH (7:4:1) after removal of MeCN from the product.

RESULTS

Background electrochemistry

Figure 1a shows a cyclic voltammogram (CV) at 100 mV/s on the 0.03 cm² Pt disk electrode (polished with 0.05 μm Al₂O₃ and then sonicated in clean water for 20 min before use) in MeCN + 0.1 M TBABF₄. When both the solvent and the supporting electrolyte were purified carefully, the CV did not show any electrochem-

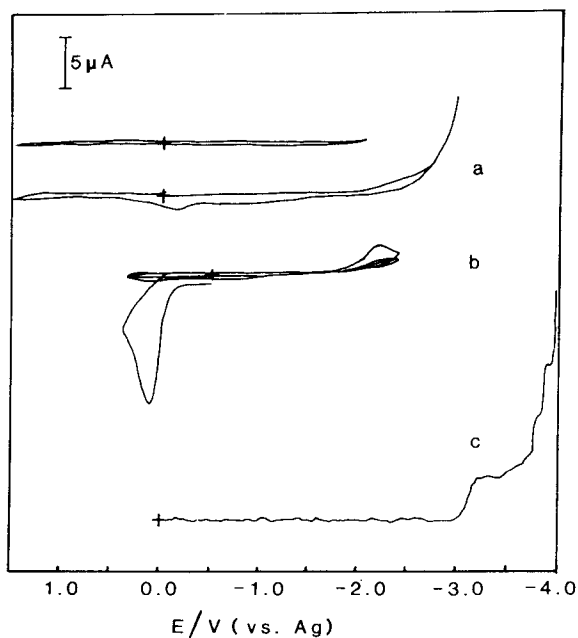


Fig. 1. (a) Cyclic voltammogram of 0.1 M TBABF₄ in MeCN at Pt electrode at a scan rate of 100 mV s⁻¹. (b) Cyclic voltammogram of 0.1 M TBABF₄ in MeCN taken after ECL was seen. Scan rate, 100 mV s⁻¹; initial scan direction, positive. (c) ECL intensity-potential profile of 0.1 M TBABF₄ in MeCN. Scan rate, 100 mV s⁻¹. Arbitrary unit for ECL intensity scale.

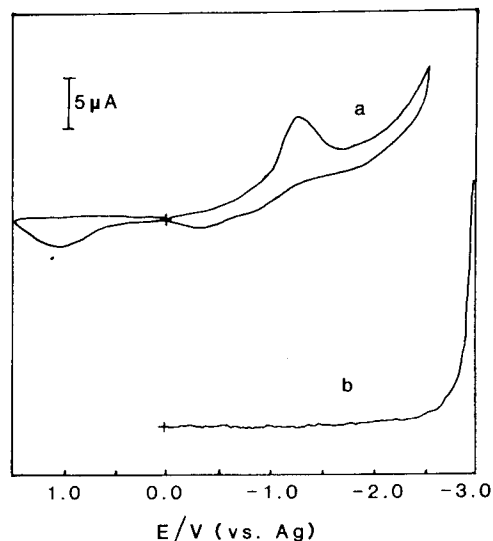


Fig. 2. (a) Cyclic voltammogram of 20 mM $(\text{TBA})_2\text{S}_2\text{O}_8$, 0.1 M TBABF₄ in MeCN at Pt electrode at scan rate of 100 mV s⁻¹. (b) ECL intensity-potential profile of 20 mM $(\text{TBA})_2\text{S}_2\text{O}_8$, 0.1 M TBABF₄ in MeCN. Scan rate, 100 mV s⁻¹. Arbitrary unit for ECL intensity scale.

ically detectable impurities within the potential limits of MeCN. No appreciable cathodic current was observed until the potential was scanned to -2.5 V vs. AgRE. The second cycle and the following cycles reproduced the first cycle with no significant change in the CV behavior, if the potential was not scanned into the background. A CV at a Pt disk electrode in an MeCN solution containing both TBABF₄ and tetrabutylammonium persulfate ($(\text{TBA})_2\text{S}_2\text{O}_8$) (Fig. 2a) shows a reduction wave beginning at -0.3 V vs. AgRE, followed by a broad wave that merges with the background. The potential limit for solvent reduction was not affected by the presence of persulfate. When the potential of the Pt electrode was scanned into the lower background region, light emission (described below) was observed. Cyclic voltammograms taken immediately after the potential was scanned into this region are shown in Fig. 1b. The reverse (positive) scan showed an oxidation wave with a current peak at $+0.1$ V and, on reversal, a small reduction wave with a current peak at about -2.2 V. Both waves were irreversible, with the oxidation peak height on the first scan at $+0.1$ V much larger than the reduction peak at -2.2 V. If the potential was reversed following the negative scan at -2.4 V, the oxidation peak height on the second scan at $+0.1$ V vs. Ag was greatly reduced compared to that obtained on the first scan. For the following scans, this peak became smaller and smaller and finally vanished. The presence of persulfate altered the CV behavior. The reversal oxidation peak was not seen, even when the potential was scanned into the lower background where the ECL was detected.

Electrogenerated chemiluminescence

In MeCN + TBABF₄, ECL was detected when the potential was scanned to about -3.0 V vs. AgRE. In this region, the more negative the applied potential (the larger the cathodic background current), the more intense the emission (Fig. 1c). The threshold potential for ECL was shifted to slightly more positive potentials (-2.5 V), if the electrode remained at the lower background potential for a while. The addition of persulfate shifted the threshold potential for ECL to -2.5 V vs. AgRE for the first scan (Fig. 2b). This threshold potential also shifted to more positive potentials (e.g., to -2.0 V) with the accumulation of electrochemical product. At a given potential, the ECL intensity in the presence of persulfate was one to two orders of magnitude larger than that in the absence of persulfate and could readily be seen with a dark-adapted eye. For example, at -3.5 V vs. AgRE, the ratio of the intensities at 510 nm in the presence and absence of persulfate was 25. Both in the absence and presence of persulfate, when the potential was held in the lower background region, the ECL intensity became stronger with time, suggesting accumulation of a reaction product that was responsible for the ECL emission.

Typical ECL spectra are shown in Figs. 3 and 4. In MeCN + TBABF₄, the emission occurred from about 400 to 600 nm, with a peak near 500 nm (Fig. 3). Because this emission was very weak, the exact peak position could not be determined. In a solution containing (TBA)₂S₂O₈, a broad spectrum was obtained also (Fig. 4). To the dark-adapted eye, the emission looked blue-green superimposed on a white background. The emission had a peak at about 510 nm, and was generally similar to the spectrum from the MeCN + TBABF₄ solutions, suggesting

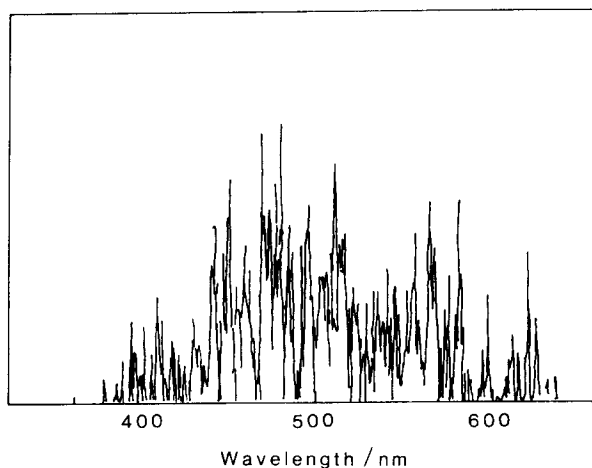


Fig. 3. ECL spectrum taken from an MeCN solution containing only TBABF₄ at a potential of -4.0 V vs. AgRE.

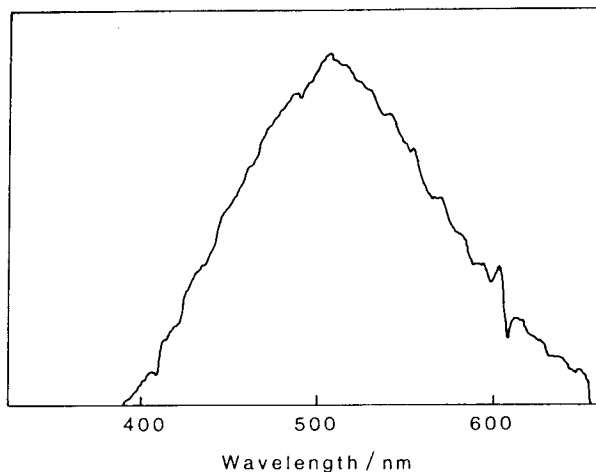


Fig. 4. ECL spectrum with MeCN solution containing 20 mM $(TBA)_2S_2O_8$ and 0.1 M TBABF₄ at potential of -3.5 V vs. AgRE.

that the same compound was involved in both ECL processes. No light emission was observed with MeCN + LiClO₄ solutions. When dimethylsulfoxide (DMSO) was used as solvent, no light emission was detected during the reduction process with TBABF₄ as supporting electrolyte in either the absence or the presence of $(TBA)_2S_2O_8$. Thus, both acetonitrile and TBABF₄ or persulfate were necessary to observe the ECL.

Analysis of electrolysis products

Bulk electrolysis of MeCN solutions containing TBABF₄ and $(TBA)_2S_2O_8$ were conducted beyond the background limit at -3.5 V vs. AgRE. A yellow product accumulated in the solution during the electrolysis, and a yellow film appeared on the Pt disk electrode. Characterization of the products was undertaken in an attempt to understand the reactions that produce ECL. The fluorescence of the electrode film upon photoexcitation at 330 nm shown in Fig. 5 was characterized by two emission peaks at about 420 and 465 nm. X-ray photoelectron spectroscopy (XPS) of the thin film on the electrode surface showed peaks at 285.3, 287.2, 399.5 and 402.8 eV (Fig. 6). The two peaks at 285.3 and 287.2 eV were attributed to two different types of carbon and the two peaks at 399.5 and 402.8 eV were due to two different types of nitrogen. Previous calculations [12] of the partial electric charge localized on the carbon atoms in methyl groups and in carbon–nitrogen double bonds have yielded binding energies of 285 and 287.4 (± 0.5) eV, respectively, for C_{1s}. This suggests that a carbon–nitrogen double bond exists in the compound producing the thin film on the electrode. The peak at 399.5 eV corresponds to the

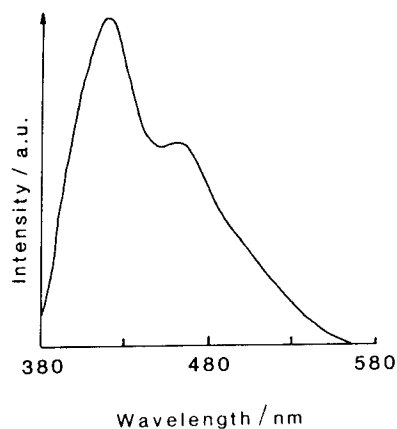


Fig. 5. Fluorescence spectrum from thin film formed on the Pt electrode (after electrolysis for 10 min at -3.5 V vs. AgRE). Excitation wavelength, 330 nm.

nitrogen $1s$ signal. Previous calculations [13] yielded a theoretical value of 398.8 (± 0.5) eV for a nitrogen atom in a carbon–nitrogen double bond, in agreement with experimental values. The XPS spectrum thus suggests a possible structure involving $\{(\text{CH}_3)\text{C}=\text{N}\}_n$, i.e., the polyacetonitrile form. The stronger intensity at 285.3 eV compared to that at 287.2 eV and the appearance of the peak at 402.8 eV might be due to the involvement of some tetra-*n*-butylammonium cation incorpo-

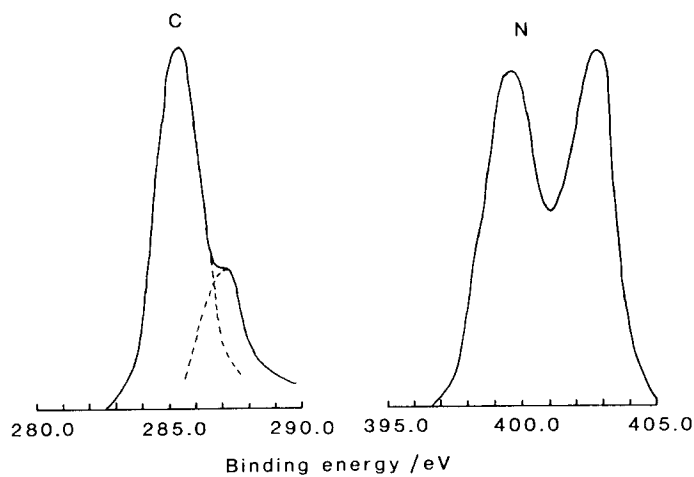


Fig. 6. XPS spectra of thin film formed on the Pt electrode (after electrolysis for 10 min at -3.5 V vs. AgRE).

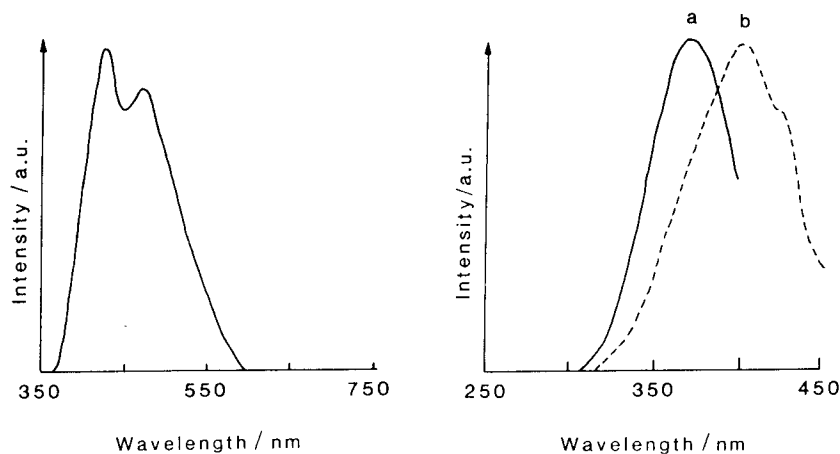


Fig. 7. Fluorescence spectrum of isolated yellow product (produced by electrolysis of MeCN solution containing $(\text{TBA})_2\text{S}_2\text{O}_8$ and TBABF_4 . Excitation wavelength, 360 nm.

Fig. 8. (a) Excitation spectrum of isolated yellow product with emission at 420 nm; (b) excitation spectrum of yellow product with emission at 470 nm.

rated in the film, since Me_4NCl is known to produce a peak at 402.2 eV [14]. To characterize the product formed in the solution phase, the yellow compound was isolated. MeCN was removed from the products and ether was used to precipitate the unreacted TBABF_4 and $(\text{TBA})_2\text{S}_2\text{O}_8$. The yellow compound extracted was then eluted with a $\text{CH}_2\text{Cl}_2 + \text{MeOH}$ mixture through a Sephadex LH-20 column. About 5 mg of a yellow compound was obtained. The fluorescence spectrum of this compound (Fig. 7) was essentially the same as that from the thin film on the electrode surface (Fig. 5). The excitation spectra, taken at emission wavelengths of 420 and 460 nm (Fig. 8), had peaks at 370 and 400 nm. The UV-visible spectra suggested that the product contained a conjugated unsaturated system.

To confirm the polyacetonitrile structure, infrared (IR) absorption and proton nuclear magnetic resonance (NMR) spectroscopic measurements were taken of the isolated yellow compound. The IR spectrum had a number of absorption peaks (at 2930, 2820, 1650, 1470, 1370... cm^{-1}) as shown in Fig. 9. The peak at 1650 cm^{-1} is attributed to the carbon-nitrogen double bond of the conjugated system [15]. Identification of the other peaks is shown in Fig. 9. The NMR spectrum (Fig. 10) showed a strong singlet peak at 2.05 ppm, attributed to the $-\text{CH}_3$ group attached to the carbon atom of the $-\text{C}=\text{N}-$. Both IR and NMR spectra thus provide additional evidence for polyacetonitrile as the reduction product. Other products were also detected after electrolysis at very negative potentials. Gas chromatographic/mass spectroscopic analysis of the solution and gas phase products showed the presence of butane, butene, and tributylamine. The presence of cyanide was inferred by precipitation with Ag^+ .

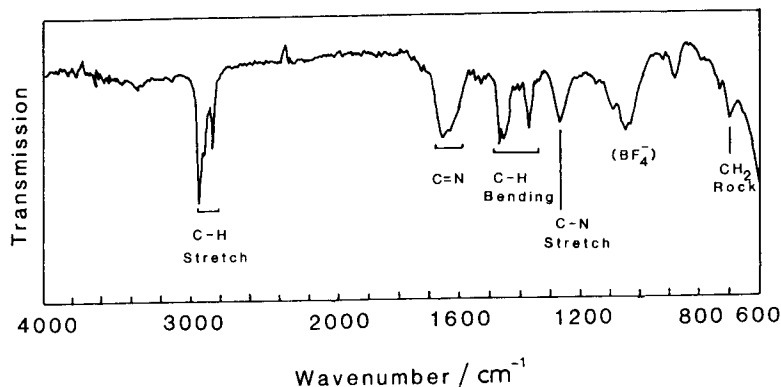


Fig. 9. IR absorption spectrum of the yellow product.

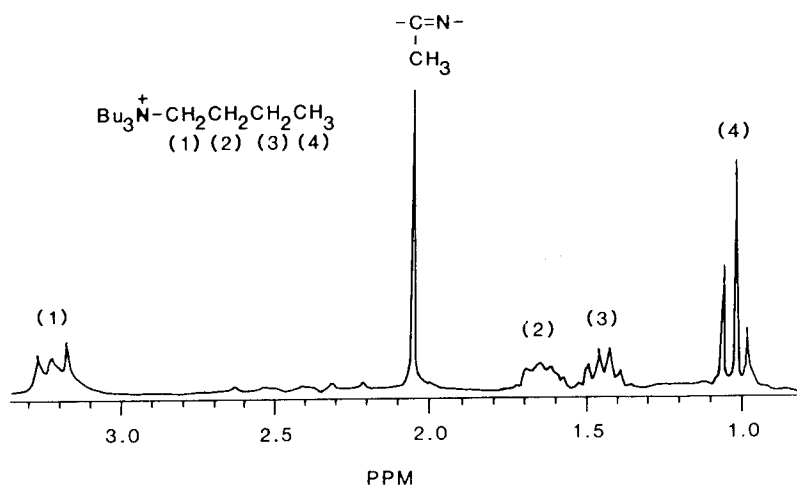
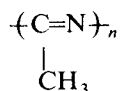


Fig. 10. 200 MHz proton NMR of the yellow product with tetramethylsilane as standard (0.0 PPM) in CDCl_3 solution.

DISCUSSION

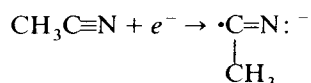
To explain the observed ECL behavior and emission in $\text{MeCN} + \text{TBABF}_4$ and in $\text{MeCN} + \text{TBABF}_4 + (\text{TBA})_2\text{S}_2\text{O}_8$, it is necessary (1) to identify the emitting species and (2) propose a mechanism for producing the excited state of this species. The highly purified solvent and supporting electrolyte showed no fluorescent impurities, nor was there any evidence of electroactive impurities in the background cyclic voltammogram (Fig. 1a). Thus, we believe that the luminescent species is produced at the cathode during reduction of $\text{S}_2\text{O}_8^{2-}$ or by reduction of MeCN itself at very

negative potentials. Following these reductions an unidentified product that is oxidized at about +0.1 V is formed (Fig. 1b). This peak is found only on the first reversal. Based on the product analysis we believe the reduction products are oligomers and polymers of MeCN, i.e., polyacetonitrile:



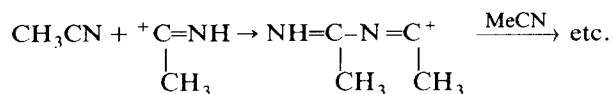
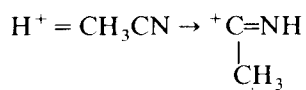
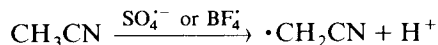
Cathodic polymerization of MeCN has apparently not been reported, although unpublished work is referenced by Rifi and Covitz [10]. Anodic polymerization of MeCN at a Pt electrode has been described [9].

Although we have not attempted to investigate the mechanism of polymerization of MeCN, the cathodic process could clearly proceed in an analogous fashion to that of acetylenes and activated olefins via anionic species [16] (e.g., the anion radical):



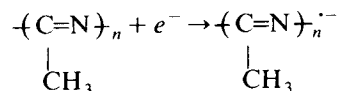
Electron transfer to MeCN can occur either directly from the electrode or via a species formed by reduction of supporting electrolyte. Polymerization would then proceed via reaction of the anion radical with monomer (MeCN) to form a "living polymer" [17].

During the reduction of $\text{S}_2\text{O}_8^{2-}$ an oxidative polymerization may occur. This reduction is known to produce, as an intermediate, the strongly oxidizing $\text{SO}_4^{\cdot-}$ species [18]. This can react directly with MeCN or with BF_4^- (to produce BF_4^{\cdot}) to produce protons and radicals and lead to polymerization in a mechanism analogous to that proposed by Tourillon et al. [9a]:



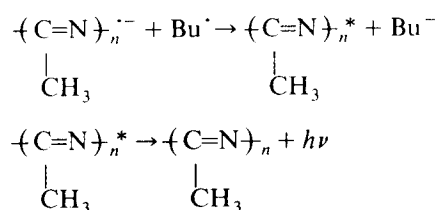
These conjugated oligomers and polymers would be luminescent and lead to the emission observed by photoexcitation after electrolysis and presumably during the ECL process.

To account for the ECL upon reduction by the usual electron transfer route, one has to propose participants in a redox reaction that is sufficiently energetic to produce an excited state. Reduction of the polyacetonitrile species can occur at the negative potentials:

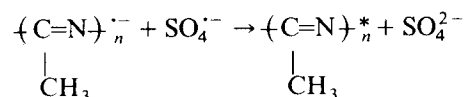


The oxidant must be produced by a bond cleavage reaction of a reduced form (i.e., in a "reductive oxidation"), e.g., as occurs during the reduction of $\text{S}_2\text{O}_8^{2-}$ or H_2O_2 (to produce the oxidants $\text{SO}_4^{\cdot-}$ or OH^\cdot , respectively). We recently studied the ECL that occurs upon reduction of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ and proposed that the oxidant was butyl radical formed during reduction of Bu_4N^+ , i.e., $\text{Bu}_4\text{N}^+ + e^- \rightarrow \text{Bu}_4\text{N}^{\cdot-} \rightarrow \text{Bu}_3\text{N} + \text{Bu}^\cdot$. Reduction of quaternary ammonium compounds (R_4N^+) at a Pt electrode frequently occurs with the net production of the amine, R_3N , and products derivable from the R^\cdot radical [19].

In an analogous way, Bu^\cdot might serve as an oxidant in the scheme proposed here:



While we have some evidence for the production of Bu^\cdot from the analyzed products butane and butene, unfortunately we have no direct evidence for this species nor for the energy of the $\text{Bu}^\cdot/\text{Bu}^-$ couple. In the presence of $\text{S}_2\text{O}_8^{2-}$, clearly $\text{SO}_4^{\cdot-}$ could play the role of the oxidant either directly:



or perhaps by generation of the cation radical of the oligomer.

One problem with the proposed mechanism is the difference in the fluorescence spectra from the reduced solution and the ECL spectra (compare Figs. 3 and 4 with Figs. 5 and 7). At this stage, we can only speculate that the excited PAN species formed in the ECL reaction right at the electrode surface are somewhat different from the stable PAN products detected later as a film or dissolved product in solution. Moreover, the PAN species are not very stable, e.g., in the presence of water, hydrolysis of the $-\text{C}=\text{N}-$ bond occurs, so that some degradation of the isolated product is possible.

CONCLUSIONS

Weak ECL results during the reduction of $\text{MeCN} + \text{TBABF}_4$ with somewhat stronger ECL arising when $\text{S}_2\text{O}_8^{2-}$ is present. This is ascribed to formation of reduced polyacetonitrile species from reduction of MeCN that react with oxidants (e.g., Bu^\cdot or $\text{SO}_4^{\cdot-}$) produced during the reduction.

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