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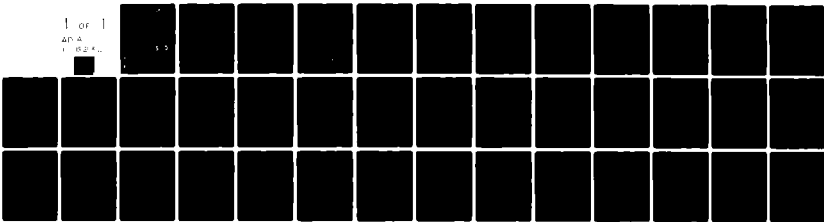
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Reductions in Aprotic Media, II. Influence of Catalytic Hydrogen
Reduction on the Course of Hydrocarbon Reduction.

by

B. Stanley Pons and S.B. Khoo

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Edmonton, Alberta

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REDUCTIONS IN APROTIC MEDIA. II. INFLUENCE OF CATALYTIC
HYDROGEN REDUCTION ON THE COURSE OF HYDROCARBON REDUCTION

Stanley Pons* and S.B. Khoo, Department of Chemistry, University
of Alberta, Edmonton, Alberta, Canada T6G 2G2

Key Words: Cathodic Reduction, Modulated Specular Reflectance,
Hydride, 9,10 Diphenylanthracene

Proofs are to be sent to: Stanley Pons
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada
T6G 2G2

ABSTRACT

The reduction of polycyclic aromatic hydrocarbons at platinum electrodes in aprotic solvents does not normally occur before surface hydrogen is reduced. The reduced hydrogen reacts with the hydrocarbon before the anion radical can be formed. The intermediate species formed after electron transfer are easily observed at very low concentrations by using modulated specular reflectance spectroscopy (MSRS).

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INTRODUCTION

The technique of modulated specular reflectance spectroscopy (MSRS) is a powerful spectroelectrochemical technique having advantages of simplicity, high resolution speed (microsecond), sensitivity (presently on the order of 10^{-17} moles-cm⁻²) and full continuous spectral coverage (infrared (EMIRS) to ultraviolet) (1-12). We have used the technique on a millisecond timescale to elucidate certain heterogeneous processes at a platinum electrode that heretofore have been observed but not understood.

The incorporation of hydrogen gas into metal lattices is a process that is well known (13), and will occur to various extents to metals that have been used to evolve hydrogen in an electrochemical cell. The process also occurs in certain metals that are merely exposed to an atmosphere containing hydrogen gas. The diffusion of hydrogen into palladium has been extensively studied (14). Sorption of hydrogen into platinum substrates occurs readily (13) and is of particular interest because of its wide uses in electrochemical kinetic studies and preparative electrolysis work.

Fleischmann et al have recently reported the formation of hydride ion at -2.70 volts vs. S.C.E. in aprotic media (15-17). This process was found to be operative in a variety of cathodic reduction reactions, including those leading to carbanion formation from weakly acidic compounds. We have reported evidence for similar intermediates at the cathodic reduction limit in acetonitrile (18). These results imply competition by

hydrogen for the reduction process in any reaction normally occurring at high cathodic potentials; the hydrogen being present at the interface by virtue of diffusion to that location from the metal lattice.

Electrochemists have noted the generally poor reproducibility and non-reversibility of various electrode kinetic measurements in aprotic media at platinum electrodes at high negative potentials (20-22). The same reactions many times are much more well behaved under identical conditions except at say a vitreous carbon, mercury, or lead cathode; electrodes that have a high hydrogen overpotential (13,19).

In this work, we will look at one typical class of reactions, and show that it is surface hydrogen reduction that is the complicating competitive reaction that is involved in cathode kinetic measurements at a platinum electrode.

Such a mechanism is present in the cathodic reduction of polynuclear aromatic hydrocarbons at a platinum electrode in acetonitrile or N,N-dimethylformamide. Kinetic and mechanistic studies on both short and long timescales have been performed for these systems (23). In anhydrous pure solvent/electrolyte systems (tetraalkylammonium salts), the generally accepted mechanism in the first wave is the one electron reduction to the π anion radical:



The second electron transfer, which occurs some 600 mV more cathodic, is the formation of the dianion



It should be noted that there are differing voltammograms in the literature for this second process (16,24). These differences can be attributed to varying degrees of catalytic hydrogen reduction, and not to experimental errors. An implication of the presence of this reaction is that there may be errors in prior work in the determination of homogeneous rate constants associated with heterogeneous electron transfer systems that have been studied at high negative potentials at platinum electrodes in dry aprotic media.

EXPERIMENTAL

Solvent

Caledon "HPLC" grade acetonitrile (nominally 0,003% water) was refluxed for 2 hours over calcium hydride and Woelm N alumina (Super Grade I), and subsequently distilled from the mixture. The dry solvent was stored over alumina and in a dry argon atmosphere. The process was repeated if the steady state background current at -3.00 volts of a 0.1 M solution of tetrabutylammonium tetrafluoroborate at a carbon electrode exceeded $20 \mu\text{a-cm}^{-2}$.

Electrolyte

Tetra-n-butylammonium tetrafluoroborate was prepared as

described in the literature (25), recrystallized twice from methylene chloride/diethyl ether, and dried in vacuo at 110°C for three days before use.

Instrumentation

The electrochemical instrumentation used was supplied by Hi-Tek Instruments, High Wycomb, England, and consisted of a DT2101 potentiostat, PPR1 waveform generator, AA1 512 bit signal averager, and a gated integrator.

The optical bench consisted of a 200 W Hg-Xe lamp (Hanovia) focussed into a GCA 270 monochromator with a stepper motor wavelength drive. The light was focussed onto the electrode which was housed in a quartz/glass cell (see below). The reflected light was collected and focussed into an EMI 9558 QB photomultiplier. The current from the lamp was preset on a Hi-Tek current sensitive amplifier, and the output of the amplifier was integrated and fed into the external control output of the photomultiplier power supply. In this way, the DC output of the photomultiplier was maintained at a constant value, giving a normalized output at all wavelengths.

The small modulated signal (ca 10^{-6} as large as the amplitude of the optical system) was extracted from the photomultiplier output with a Hi-Tek lock-in amplifier system. For spectral scanning, the signal was further processed through a Kron-Heit active notch filter system (96dB rejection) to further enhance sensitivity. For absorbance-time transients, the signal of the photomultiplier was signal averaged. Each averager was

triggered by the status trigger on the waveform generator which is available at the beginning of each pulse. Typically a maximum of 256 scans was sufficient in this work to obtain a curve of adequate signal to noise ratio in the diphenylanthracene system, the actual number dependent on pulse duration.

The potentials were applied to the electrode from the waveform generator as a square wave train. Potential levels were from a region where no faradaic process was occurring, to a region where the cyclic voltammetry indicated uncomplicated diffusion controlled kinetics. For diphenylanthracene, this was +0.50 volts to -2.50 volts vs silver/silver ion (0.01 M in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile) reference.

Cell

The optical cell was fabricated to hold a platinum mirror disc electrode mounted in the end of a 9 mm Kel-F rod. A Luggin capillary reference probe was inserted through a ground glass joint in the top of the cell and the tip was adjusted to give the best response/location characteristics near the platinum mirror electrode. A platinum disc 4 cm in front of, and parallel to the working electrode face served as the secondary electrode. The light beam entered the cell through a quartz window (1 cm diameter) mounted in a glass tube whose axis was oriented at a 45° angle to the platinum mirror electrode. An identical light exit window was mounted on the opposite side of the electrode so that the light beam entrance-exit angle was 90°. The light beam was focussed so that the entire surface of the electrode was

covered by the beam. The entire cell was mounted on a laboratory jack and placed in a light-tight wooden box. The exit slit of the monochromator and the photomultiplier entrance face were located on adjacent walls inside of the box.

RESULTS AND DISCUSSION

An MSRS spectra of diphenylanthracene (1.0 mM) in acetonitrile at a pyrolytic graphite electrode is shown in Figure 1b. The modulation was from 0.0 V to -2.50 V vs silver/silver ion (ref.), and the frequency of modulation was 40 Hz. The spectrum is essentially the same as that obtained by conventional transmission techniques (26) for the anion radical. If a polished platinum electrode is used in the same solution, the spectrum in Figure 1a is obtained. The portions of the two spectra pertaining to the anion radical are virtually identical. Considering the two spectra, there is obviously another absorbance under the platinum electrode spectrum tending to raise the baseline in the 550.0 to 400.0 nm range. Coupling of overlapping spectra of several possible intermediates following an initial electron transfer is entirely probable, and deconvolution of these complicated spectra is quite straight forward (4). If one monitors the absorbance-time relationship at a variety of wavelengths across the spectrum of the reduction at the graphite electrode, the profile of the transients over various timescales serve to identify the species responsible for the absorption at each of those wavelengths, as well as the

associated kinetic parameters of formation and decay. Application of this procedure to the graphite electrode/diphenylanthracene/acetonitrile system produces the same general shape at all wavelengths, except for the intensity. The intensity at identical time points on each profile vary exactly as the extinction coefficient across the entire set of profiles. This result may be coupled with the equation for theoretical absorbance-time profile for the product of a simple electron transfer:

$$\Delta R/R = \frac{4\epsilon C^0 (Dt)^{1/2}}{\cos \theta}$$

to show that the entire spectrum is due solely to that of the anion radical. ($\Delta R/R$ is the normalized absorbance, C^0 is the bulk concentration of diphenylanthracene, ϵ is the extinction coefficient, D is the linear diffusion coefficient of the diphenylanthracene, t is the time, and θ is the reflectance angle.) These results are entirely in accord with the generally accepted mechanism for this reduction in the first wave (24).

The same procedure applied now to a platinum electrode in the same solution leads to results that are opposed to a simple electron transfer mechanism initially leading to the anion radical. Figure (2a) shows the transient obtained at 612.5 nm. There is a delay of some 3 ms before the rising portion of the transient. Neglecting this initial delay, the remainder of the transient generally follows the response expected for the anion radical. Pretreatment of the electrode at +1.00 V prior to

recording the transient results in a marked reduction in the delay time in the transient (Figure 2b).

Conventional electrochemical experiments have not indicated an adsorption, desorption, or other heterogeneous surface reaction on the timescale of the "dead" zone observed spectrophotometrically. This is in agreement with results obtained by Bard (27) for the same system in dimethylformamide. In fact, a diffusion controlled process of a solution free species is indicated by the electrochemistry.

The 40 Hz spectrum means that the electrode is at the reduction potential for 12.5 ms. The anion radical is apparently being formed for the largest portion of this pulse, and dominates the spectrum. The 40 Hz spectrum is thus based on too long a timescale to observe without anion interference the species responsible for causing the delay of formation of the anion radical. Reducing the pulse to 0.5 ms symmetrically (modulation frequency of 1000 Hz) should eliminate any anion radical absorption (since it will not have time to be formed), and should instead enhance the spectrum of the species formed during the delay (if it absorbs in the spectral region under consideration). Figure 3a shows the MSRS spectrum of the platinum electrode/diphenylanthracene/acetonitrile system taken under these conditions. The spectrum of the new species has a maximum at about 440.0 nm. Control experiments under the same experimental conditions on the solvent/electrolyte only does not exhibit this spectrum, inferring that the electron transfer reaction involves diphenylanthracene, but that the product is not

the simple anion radical.

Further evidence that diphenylanthracene is being depleted at this higher modulation frequency is also present in Figure 3d. The negative $\Delta R/R$ values in the spectrum are due to the fact that the spectra are differential in nature. Beginning at 400.0 nm, diphenylanthracene itself begins absorbing. Thus as the pulse goes into the reduction region producing the anion radical (positive spectrum), the substrate is being consumed and results in negative absorbance values beginning at the sharp descent at 400.0 nm. We note that even though no anion radical spectrum is produced at high frequency (only the new species at 445.0 nm), diphenylanthracene is still depleted.

Pulsing from 0.0 to -2.50 volts at lower frequencies (250 Hz) results in an intermediate spectrum enhanced with more of the "delay" species (Figure 3b) than the 40 Hz spectrum. Holding the potential some 20 minutes at +0.85 volts, and subsequent modulation from +0.85 volts to -2.50 volts at 250 Hz results in a spectrum rich in the anion radical (Figure 3a). This pretreatment reduces the amount of "delay" species formed. The 1000 Hz spectrum from +0.85 volts to -2.50 volts is shown in Figure 3c, showing a decrease in intensity from the 0.0/-2.50 1000 Hz spectrum. Considering these spectra we chose to investigate the kinetic nature of the new species by observing the absorbance-time transient at 440.0 nm. The result is shown in Figure 4. The diffusion controlled reaction is now evident at short timescales.

The results are consistent with the very rapid formation of

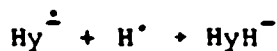
hydride at the surface due to reduction of adsorbed hydrogen gas on the platinum electrode (15-18) as the electrode is pulsed to high negative potentials



and either the subsequent reaction of the hydrocarbon with hydride



or the reaction of hydrocarbon anion radical (as soon as it is formed) with hydrogen atoms:



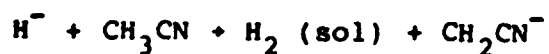
Reactions of this type are well known from studies of sodium naphthalide-hydrogen gas mixtures (28-30). If indeed naphthalene is substituted for diphenylanthracene, the high frequency MSRS spectrum shows a single peak at 437.0 nm, precisely at the same wavelength of the dihydronaphthalene anion as reported by other workers (31).

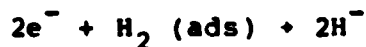
That hydrogen is intimately involved in this process may be further evidenced by the following considerations: (a) Hydrogen is known to be easily and fluently adsorbed into the crystal lattice of platinum metal. If prolonged pulse experiments similar to those described above are carried out for extended

periods of time, the "delay" period is shifted to shorter times presumably due to the depletion of hydrogen at the surface due to its reaction with the hydrocarbon or solvent (15-18) (Figure 2b). (b) If the electrode is electrolyzed for several minutes at hydrogen evolution potentials in aqueous sulfuric acid solutions, the 612.5 nm transient appears as in Figure 5. The excess hydride/hydrogen atom now at the surface is enough to suppress the stable formation of anion radicals for much longer times than "untreated" electrodes. (c) The delay effect is not observed at electrodes that are known not to be catalytic toward hydrogen reduction (i.e. lead, graphite, etc.) (Figure 6).

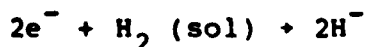
The background cyclic voltammetry (0.1 M tetrabutylammonium tetrafluoroborate) is shown in Figure 7 for a platinum electrode. The electrode was mechanically polished in air, washed in acetonitrile, and dried in air. The acetonitrile/tetrabutylammonium tetrafluoroborate system was not highly protected from atmospheric moisture. Cathodic breakdown occurs at potentials around -2.70 volts (Figure 7a). After 20 seconds of anodic pretreatment at +1.00 volt, the breakdown potential has moved to more cathodic potentials, and the evidence of catalytic reaction (foldover in Figure 7b) at +1.00 volt results in only marginal improvement over that in Figure 7c. If the electrode is allowed to stand for 10 minutes in the solution, the resulting voltammogram is virtually identical to Figure 7a). We propose that additional interstitial hydrogen has had time to diffuse to the surface, and is responsible for the resulting increase in cathodic current.

The cyclic voltammetry of diphenylanthracene is shown in Figures 8 and 9 for carbon and platinum electrodes respectively. The carbon electrode exhibits the classical twin reduction leading to dianion formation at about -2.80 volts. The oxidation of the protonated dianion (carbanion) is clearly seen at -.35 volts. The same reduction at platinum (mechanically polished and/or flamed to red heat and exposed to air) typically does not exhibit such classical behavior. There is a rising background throughout the cathodic region, and the first reduction is reasonably well behaved. The second reduction begins at -2.70 volts and is due to the rapid initiation of background processes. The peak potential of the second anthracene wave is in the -2.90 volt region now, and is well placed into background reduction. If one now purges the surface of the electrode of hydrogen, as well as the diffusion supplied "sink" of hydrogen within the electrode, by holding the electrode at anodic potentials greater than about 0.50 volts, the subsequent voltammogram (run from +0.6 volts about 30 seconds after anodic "hold") changes markedly (Figure 9b). The uncomplicated reduction of the cation radical is now evident. There is no supply of hydrogen to form hydride, and no catalytic hydrogen abstraction of the solvent to dominate the double layer chemistry (15-18):





and/or



where $H_2 (\text{sol})$ is dissolved hydrogen, and $H_2 (\text{ads})$ is adsorbed hydrogen.

CONCLUSIONS AND COMMENTS

The reduction of hydrogen must be considered when investigating electron transfer kinetics at a platinum cathode at high potentials. The prevention of this reaction seems to be "pseudo" controllable if pretreatment at positive potentials is utilized. The existence of hydride (and its prevention) in less reactive forms (16) may be of consequence in practical applications, such as its influence on undesirable side reactions in lithium/sulfur dioxide cells. Work is continuing in this area.

The transients obtained from the versatile MSRS technique are providing information that should lead to a clearer insight into the mechanisms of electron transfer at interfaces, including subsequent reactions in the reaction layer. Also under consideration are UV/VIS/IR spectra of adsorption and double layer structure. The infrared spectra of interfaces under the

influence of these processes are now attainable (1,2,5-7,9), and are being investigated both in these laboratories and in those at Southampton.

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LEGEND OF FIGURES

- (1) MSRS spectra of 1 mM 9,10-diphenylanthracene at 40 Hz modulation from 0.0 V to -2.50 V at (a) a carbon electrode, and (b) an untreated platinum mirror electrode.
- (2) Signal averaged (256 scans) transient at 612.5 nm. (a) Untreated platinum electrode, (b) electrode held at +1.00 V for 2 m before averaging transients. Note decrease in delay upon preanodigation. (1 mM 9,10-diphenylanthracene in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile.)
- (4) Signal averaged (256 scans) transient at 440.0 nm, untreated platinum electrode in 1 mM 9,10-diphenylanthracene in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile.
- (5) Signal averaged (256 scans) transient at 612.5 nm, platinum electrode previously used to evolve hydrogen gas from a 1.0 M H_2SO_4 solution in triply distilled water. Transient made in 1 mM solution of 9,10-diphenylanthracene in 0.1 M tetrabutylammonium tetrafluoroborate.
- (6) Signal averaged (256 scans) transient at 612.5 nm, carbon electrode in 1 mM 9,10-diphenylanthracene in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile.
- (7) Cyclic voltammetry of 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile at $100 \text{ mV}\cdot\text{s}^{-1}$. Platinum mirror electrode (a) freshly polished and dried in air, (b) same system after 20 s preanodization at +1.00 V, (c) same system after an additional 20 s preanodization.
- (8) Cyclic voltammetry of 1 mM 9,10-diphenylanthracene in 0.1 M

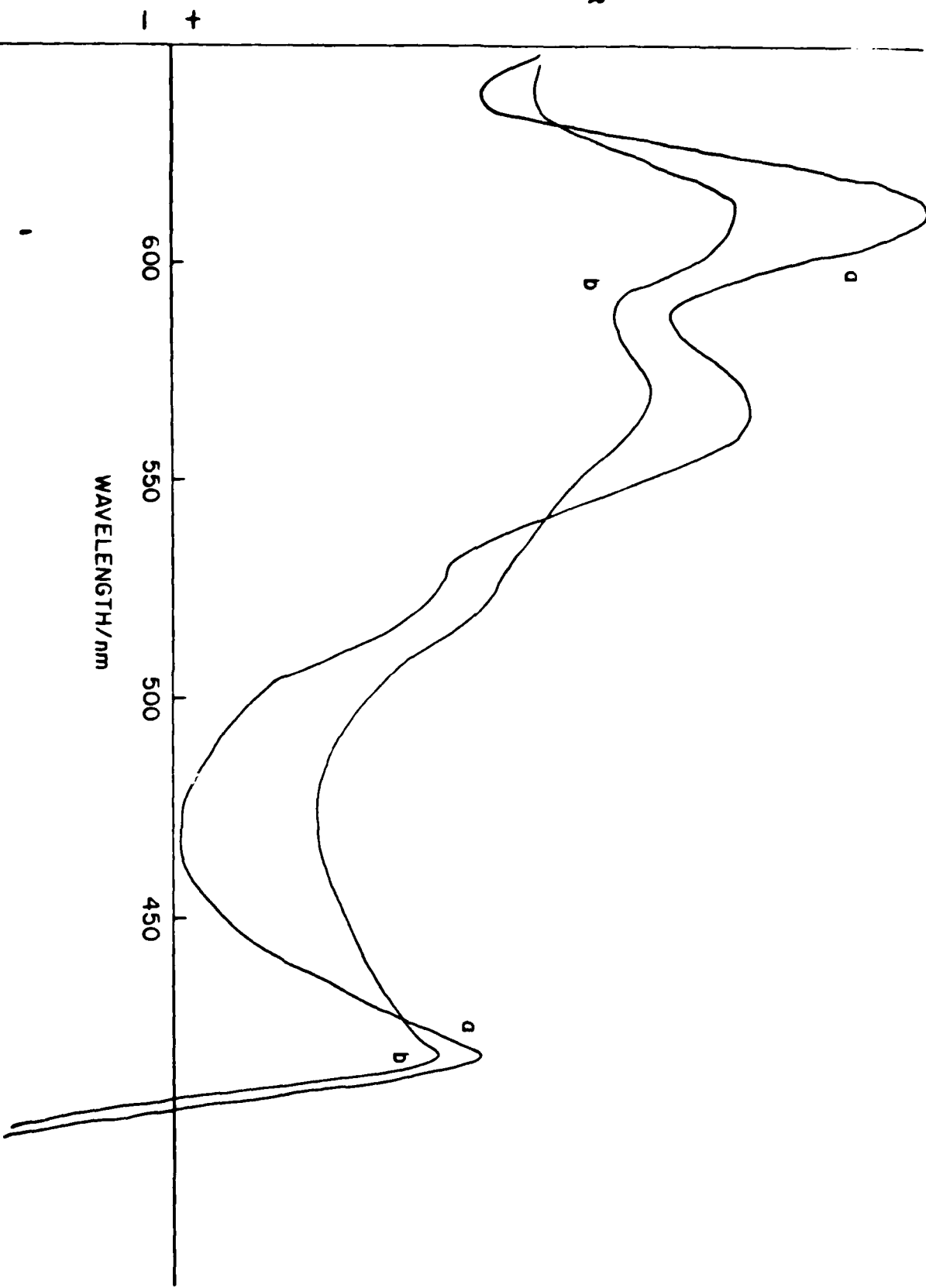
tetrabutylammonium tetrafluoroborate in acetonitrile at 100 $\text{mV}\cdot\text{s}^{-1}$. Carbon electrode.

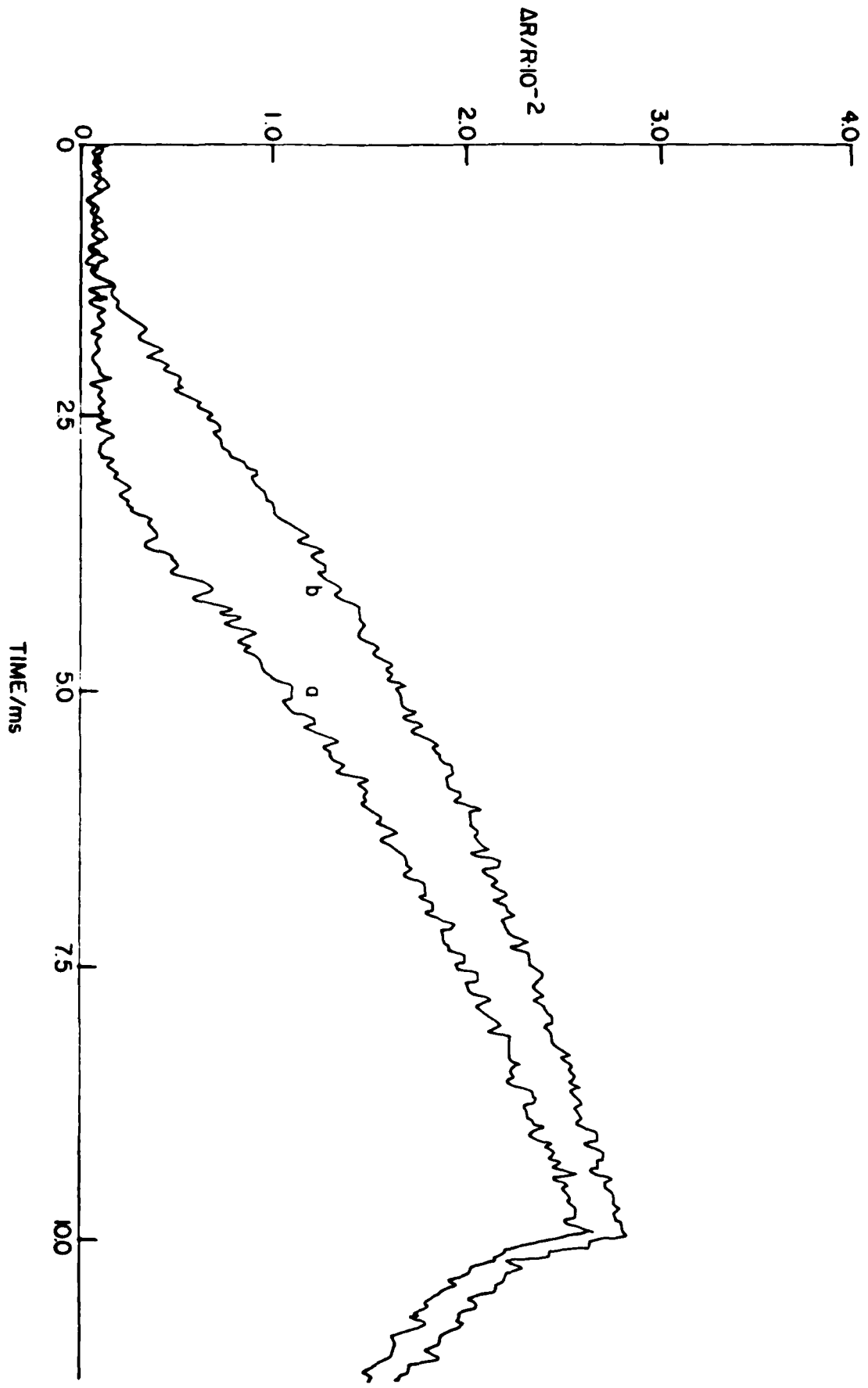
- (9) Cyclic voltammetry of 1 mM 9,10-diphenylanthracene in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile at 100 $\text{mV}\cdot\text{s}^{-1}$. Platinum electrode (a) untreated and (b) preanodized at 1.00 V for 60 s.

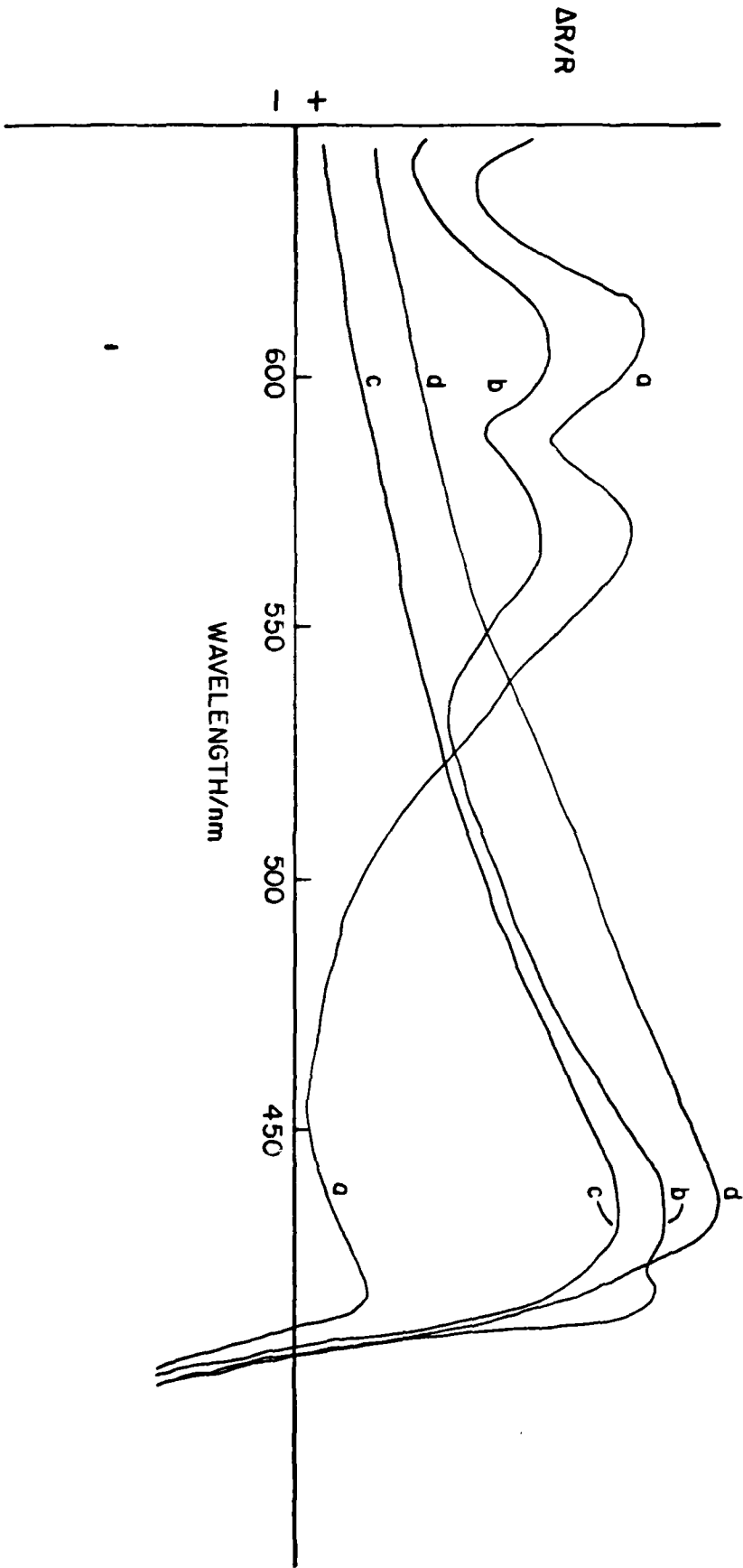
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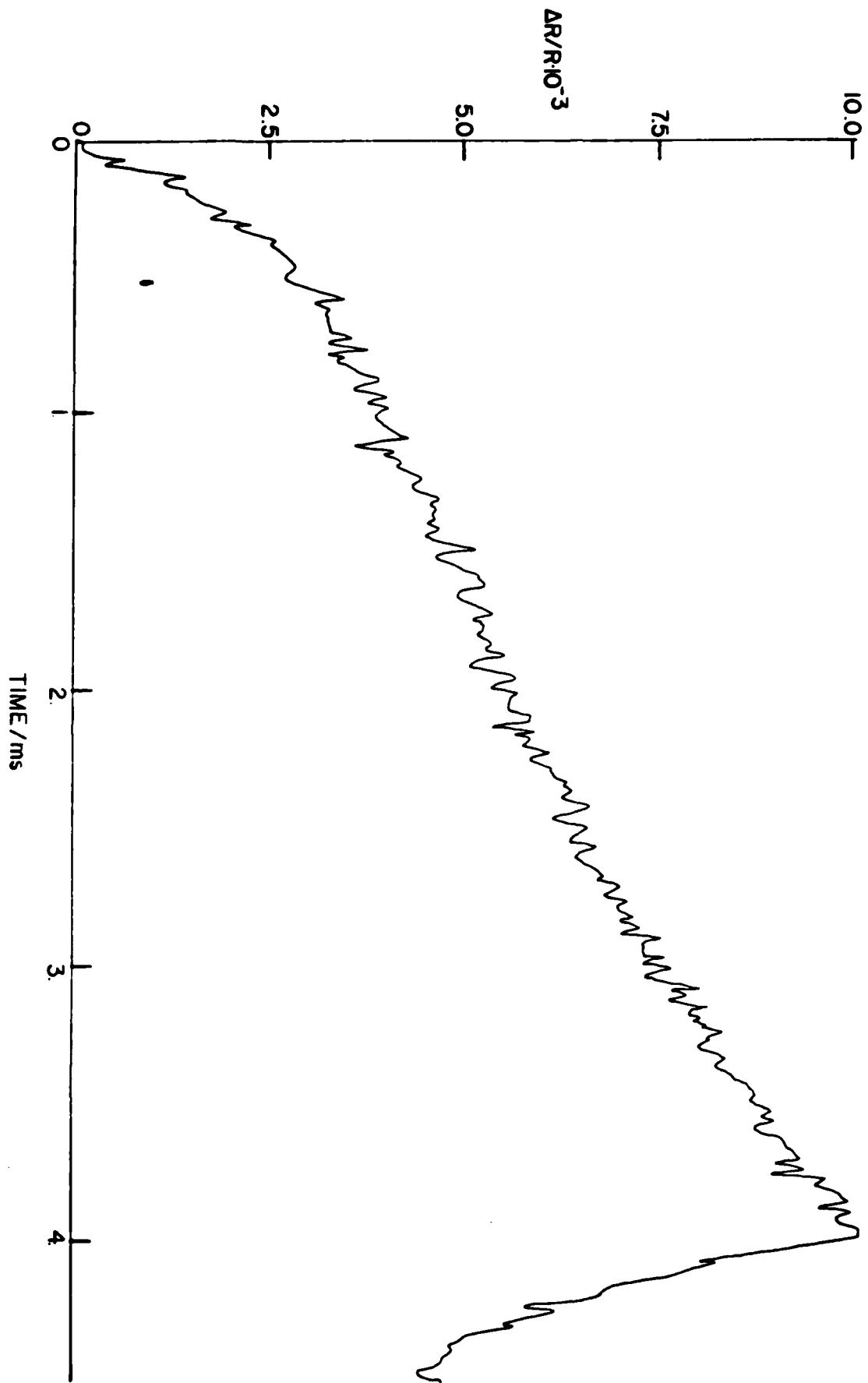
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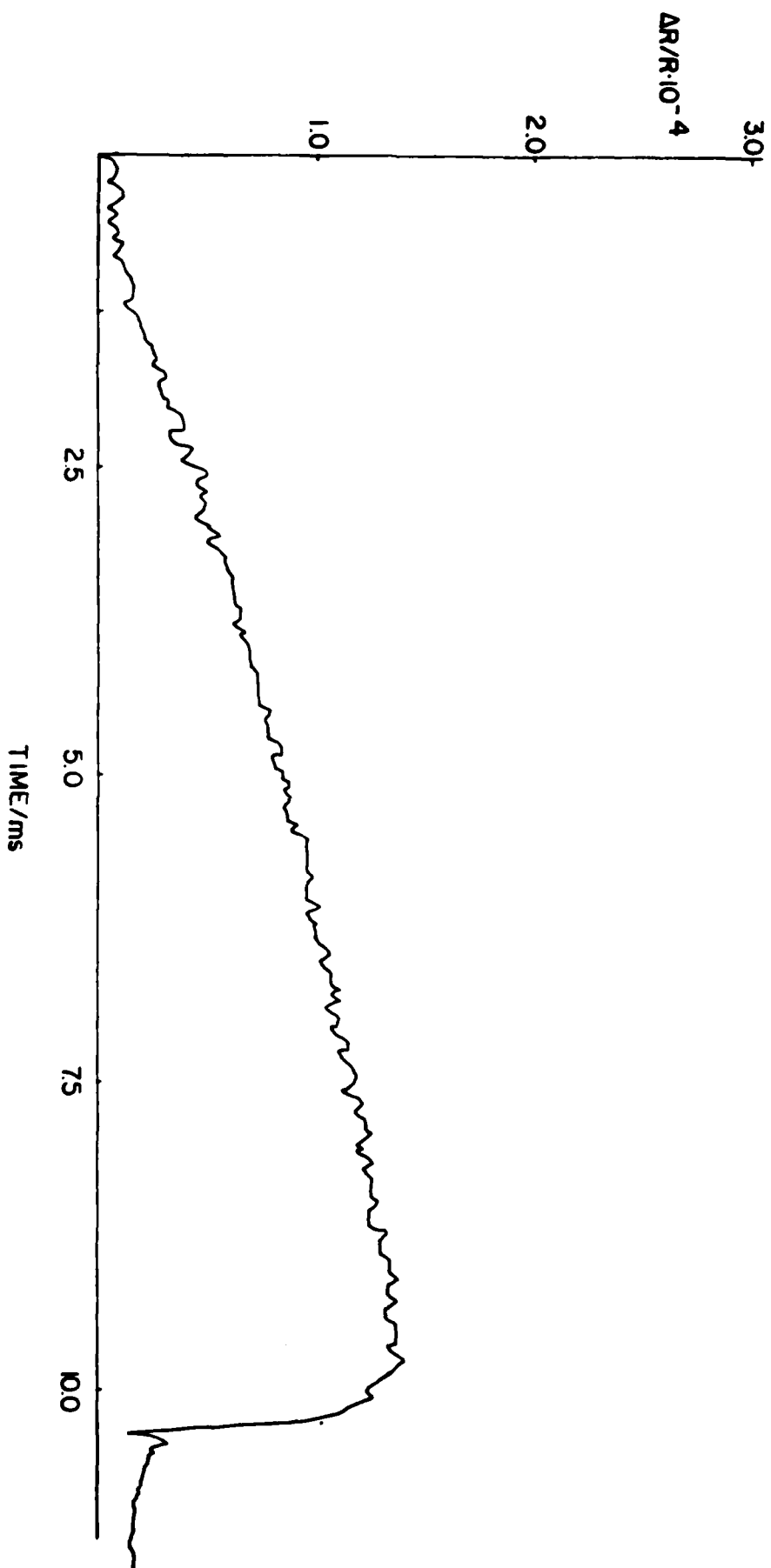
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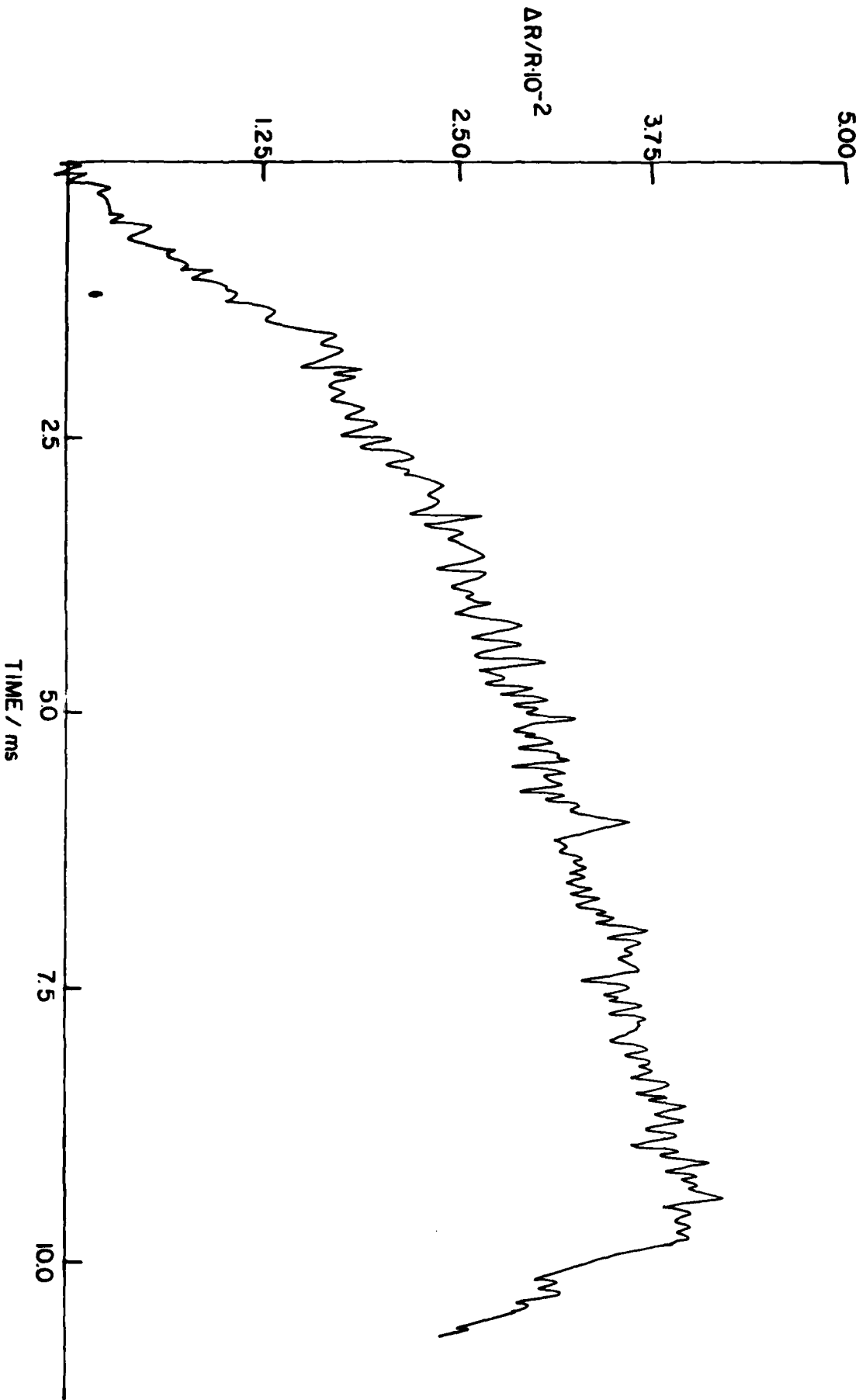


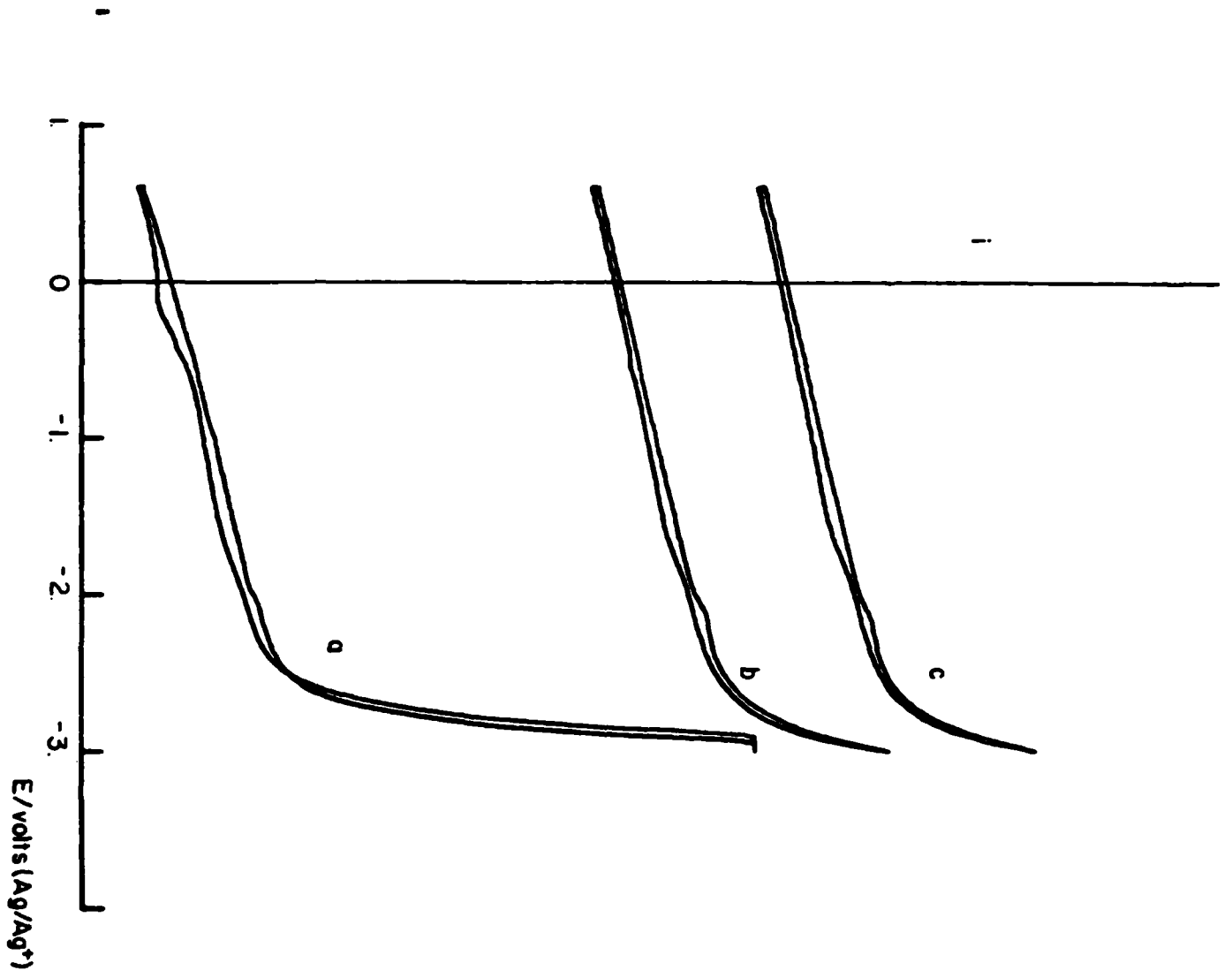


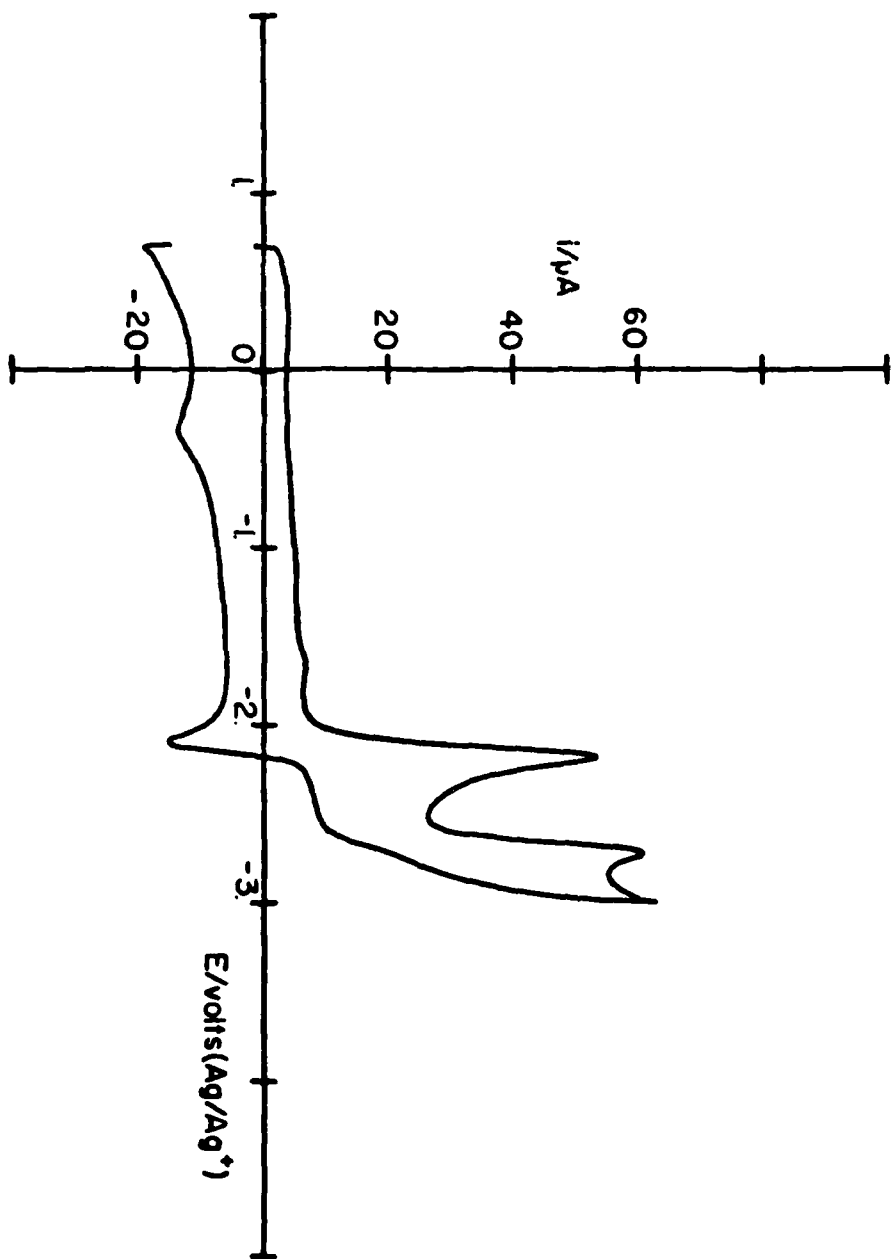


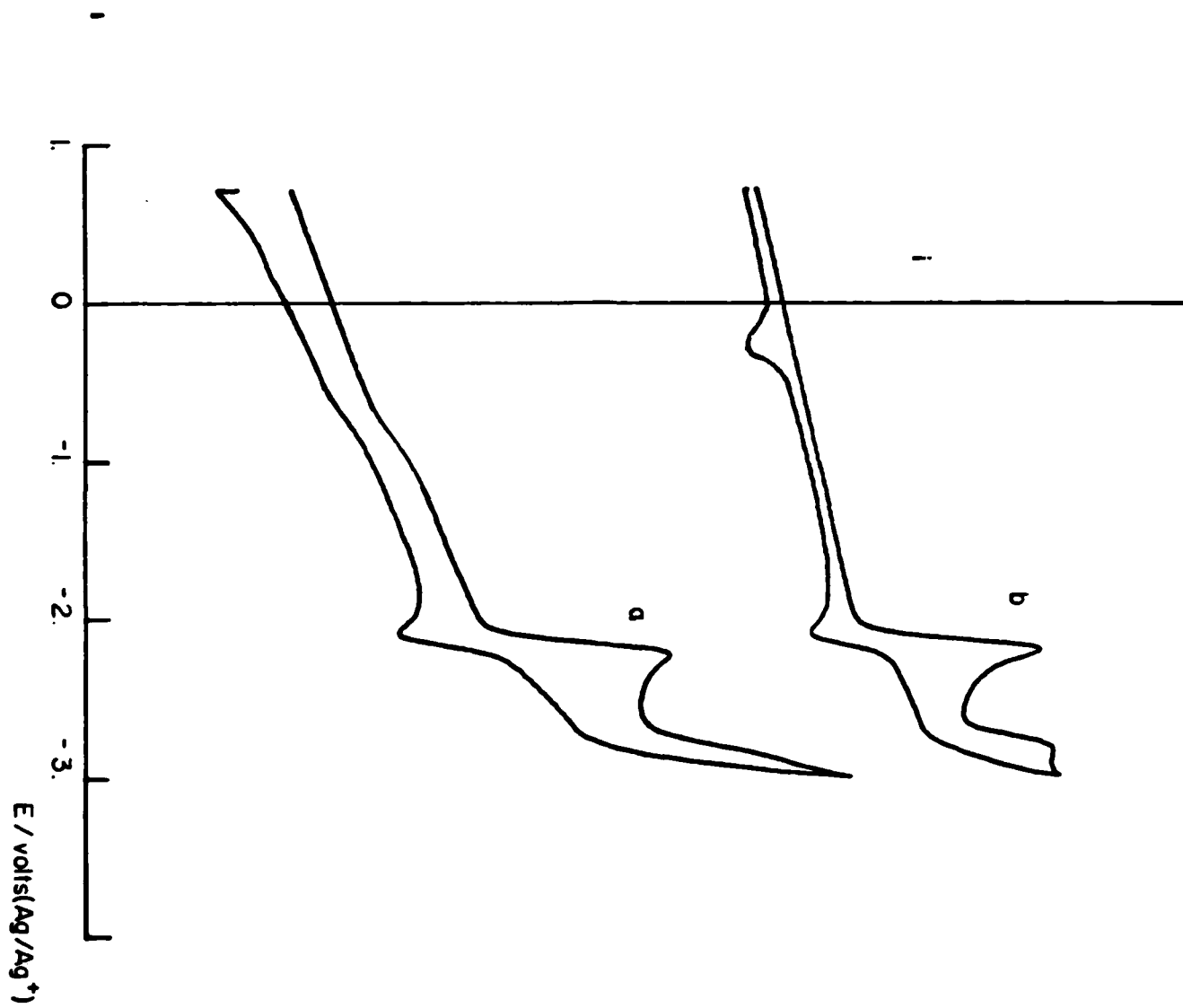












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