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UNIV SALT LAKE CITY DEPT OF CHEMISTRY S PONS ET AL.
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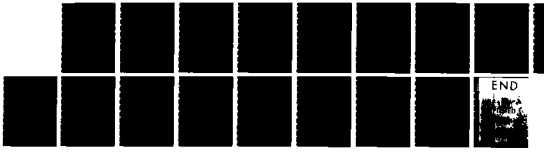

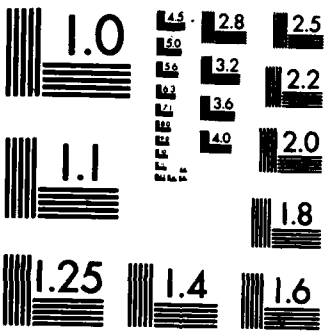

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KEY WORDS (Continue on reverse side if necessary and identify by block number)

Anodic Oxidation; Furans; Spectroelectrochemistry

ABSTRACT (Continue on reverse side if necessary and identify by block number)

The anodic oxidation of furans in the presence of substituted 1,4-napthoquinones leads to coupling of the two. In the absence of the quinones, furan oligomers are formed. Further oxidation of these oligomers leads to the formation of conductive polymer films at the electrode surface.

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TECHNICAL REPORT NO. 26

Anodic Oxidation of Furans in Aprotic Solvents

By

Stanley Pons*
A. Scott Hinman

Prepared for Publication in

Electrochimica Acta

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A-1

Anodic Oxidation of Furans in Aprotic Solvents

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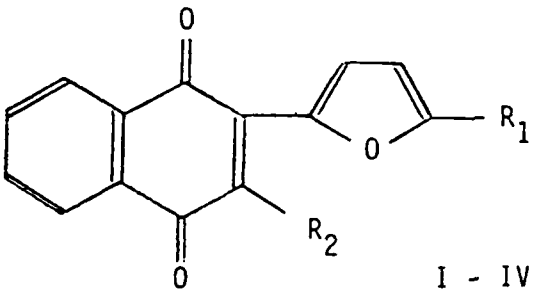
Abstract

The anodic oxidation of furans in the presence of substituted 1,4-napthoquinones leads to coupling of the two. In the absence of the quinones, furan oligomers are formed. Further oxidation of these oligomers leads to the formation of conductive polymer films at the electrode surface.

Introduction

We have recently been interested in the properties of electro-oxidized furan conductive polymers, and have encountered passivating film formation at the electrode when trying to prepare such films. The coupling of substituted furans and 1,4-napthoquinones (1) has been shown to provide intermediates that are of potential use in the synthesis of anthracyclinone antitumor agents (2). The use of the 1,4-napthoquinone nucleophile as a possible mediator for the polymer formation was thus considered. The resulting coupling reaction is almost quantitative, and thus a highly efficient synthesis of substituted furylnapthoquinones is afforded. Thus anodic oxidation of the indicated substituted furans in the presence of substituted 1,4-napthoquinones leads to the compounds I-V in high isolated yields.



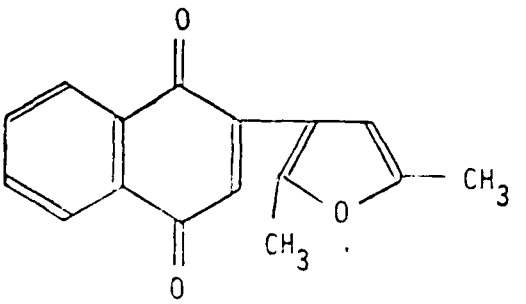
I - IV

I. $R_1 = R_2 = H$

II. $R_1 = CH_3$; $R_2 = H$

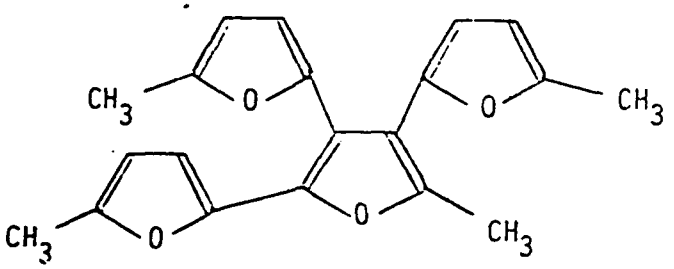
III. $R_1 = H$; $R_2 = CH_3$

IV. $R_1 = CH_3$; $R_2 = CH_3$

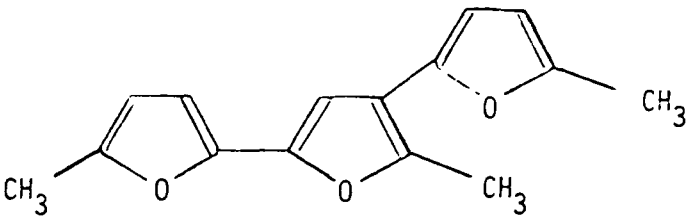


V

The isolation and characterization of soluble furan oligomers (VI and VII) from some of the reaction mixtures provide information on the structure of the passivating polymer. These oligomers are different from those precursors that are known to form conducting polymers (3).



VI



VII

Experimental

Preparation of Furyl Substituted Napthoquinones

The furan and napthoquinone (see below) were dissolved in 70 mL acetonitrile (0.003% water, K.F. titration) containing 0.1 M tetra-n-butyl ammonium tetrafluoroborate (TBAF). The solution was exhaustively electrolyzed (95% theoretical coulombic ($2e^-$) charge delivered based on the quantity of furan present) at the voltammetric oxidation peak potential of the furan in a two compartment H-cell. The potential was controlled by a Hi Tek PPR1 waveform generator driving at Hi Tek DT 2101 potentiostat. Destruction of an initially formed insulating polymer layer (see Results) was accomplished by pulsing the electrode voltage positive of the electrolyzing potential for a short period of time (1-5 minutes, depending on the furan used). Potentials were controlled vs. a standard silver/silver ion (0.01 M $AgNO_3$ in 0.1 M TBAF/acetonitrile) reference electrode. Charge consumed was continuously monitored with a Hi Tek digital gated integrator.

After electrolysis, the solution was decanted from the anode compartment, and the solvent evaporated on a rotary evaporator at 25°C (water bath temperature). The residue was extracted with 3 x 20 mL portions of diethylether, and the combined extracts washed with 3 x 25 mL portions of saturated NaCl solution to remove any residual supporting electrolyte. The ether residue was dried over sodium sulfate (10 g). The mixture was separated by column chromatography (XAD crosslinked polystyrene, 99:1 to 1:99 methanol/diethylether) after concentrating the residue to a viscous oil on the rotary evaporator under the aforementioned conditions. The fractions were traced by a UV lamp, and after collection were stripped of solvent by evaporation and analyzed.

2-(2-furyl)-1,4-napthoquinone (I). 2.0 mmol (316 mg) of 1,4-napthoquinone and 2 mmol (136 mg) of furan were electrolyzed as described to yield (I) (403 mg, 90%): M^+ m/e 224; found (calculated) C: 75.50 (75.02%); H: 3.53 (3.57%); O: 20.97 (21.41%); ^1H NMR (100 MHz, $CDCl_3$) δ 8.08 (m, 2H); 7.70 (m, 2H); 7.50 (m, 2H); 7.25 (s, 1H); 7.20 (d, 1H); 6.20 (m, 1H).

2-(2-(5-methylfuryl))-1,4-napthoquinone (II). 2.3 mmol (316 mg) of 1,4-napthoquinone and 2.3 mmol (189 mg) of 2-methylfuran were electrolyzed as described to yield (II) (469 mg, 81%): M^+ m/e 238; found (calculated) C: 75.59 (75.65%); H: 4.22 (4.20%); O: 20.13 (20.15%); ^1H NMR (100 MHz, $CDCl_3$): δ 8.10 (m, 2H); 7.72 (m, 2H); 7.55 (d, 1H); 7.24 (d, 1H); 6.23 (m, 1H); 2.40 (s, 3H); IR ($CHCl_3$ cast): 1671s, 1642s, 1594s, 1554s, 1379m, 1371m, 1336s, 1317s, 1292s, 1257s, 1185s, 1110m, 1076m, 1012s, 978m, 959m, 932m, 895m, 882m.

2-(2-furyl)-3-methyl-1,4-napthoquinone (III). 2.3 mmol (396 mg) of 2-methyl-1,4-napthoquinone and 2.3 mmol (156 mg) of furan were electrolyzed by the procedure described to yield (III) (465 mg, 85%): M^+ m/e 238; found

(calculated) C: 75.54 (75.65 %); H: 4.16 (4.20%); O: 20.30 (20.15%); ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.14 (m, 2H); 7.70 (m, 2H); 7.56 (d, 1H); 7.20 (d, 1H), 6.29 (m, 1H), 2.35 (s, 3H).

2-(2-(5-methylfuryl))-3-methyl-1,4-napthoquinone (IV). 2.3 mmol (396 mg) of 2-methyl-1,4-napthoquinone and 2.3 mmol (189 mg) of 2-methylfuran were electrolyzed as described to yield (IV) (458 mg, 79%): M^+ m/e 252; found (calculated) C: 76.08 (76.21%); H: 4.79 (4.76%); O: 19.13 (19.03%); ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.19 (m, 2H); 7.77 (m, 2H); 7.59 (d, 1H); 6.29 (m, 1H); 2.42 (s, 3H); 2.33 (s, 3H).

2-(3-(2,5-dimethylfuryl)-1,4-napthoquinone (V). 2.1 mmol (332 mg) of 1,4-napthoquinone and 2.1 mmol (202 mg) of 2,5 dimethylfuran were electrolyzed as described to yield (V) (371 mg, 70%): M^+ m/e 252; found (calculated) C: 76.00 (76.21%); H: 4.96 (4.76%); O: 19.04 (19.03%); ^{1}H NMR (100 MHz, $CDCl_3$): δ 8.25 (m, 2H); 7.52 (m, 3H); 7.23 (s, 1H), 3.60 (m, 3H), 2.20 (m, 3H).

Oligomer (VI). 2.0 mmol (192 mg) of 2-methylfuran was electrolyzed as described to yield product (VI) (166 mg, 52%): M^+ m/e 332; found (calculated for $C_{20}H_{18}O_4$) C: 74.90 (74.55%); H: 5.45 (5.59%); O: 19.65 (19.86%); ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.40 (m, 3H); 5.90 (m, 3H); 2.25 (m, 12H).

Oligomer (VII). A second fraction followed for oligomer (VI): product (VII) (66 mg, 28%): M^+ m/e 252; found (calculated for $C_{15}H_{14}O_3$) C: 74.38 (74.40%); H: 5.40 (5.78%); O: 20.02 (19.82%); ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.30 (m, 2H); 5.80 (m, 3H); 2.25 (m, 9H).

Chemicals. Acetonitrile (Caledon, HPLC grade) was distilled once from calcium hydride on a two meter glass helix packed column onto Woelm super grade neutral alumina where it was stored until used. The furans and napthoquinones

used were Aldrich reagents, and were used as received. Tetra-n-butylammonium tetrafluoroborate was prepared by standard procedures (4), recrystallized from 1,2-dichloroethylene/diethylether, and vacuum dried at 50°C for 7 days.

Modulated Specular Reflectance Spectroscopy (MSRS)

Adsorbance time transients of the intermediates formed upon application of a positive voltage step into the first voltammetric wave were obtained as described previously (5,6). The transients were recorded by a Hi Tek AA1-512 signal averager-transient recorder.

Results and Discussion

Oxidation of the furan mixtures in the first voltammetric wave leads to an insulating polymer layer at smooth platinum electrodes. Further oxidation of this layer at high positive potentials results in a conductive layer through which bulk electrolysis of the mixture can occur. The potential may then be returned to that of the first voltammetric wave. After 2 electrons per mole of furan had been consumed, tlc indicated 90-100% conversion of the furan and napthoquinone to compounds I-III, and 80-90% for compounds IV-V. Isolated yields were 10-20% less in all cases. Proof of structure was supported by comparing the spectroscopic properties of compounds I and II prepared by the chloranil oxidation of a furan-napthoquinone mixture as described by Bridson et. al. (1) with the compounds obtained electrochemically.

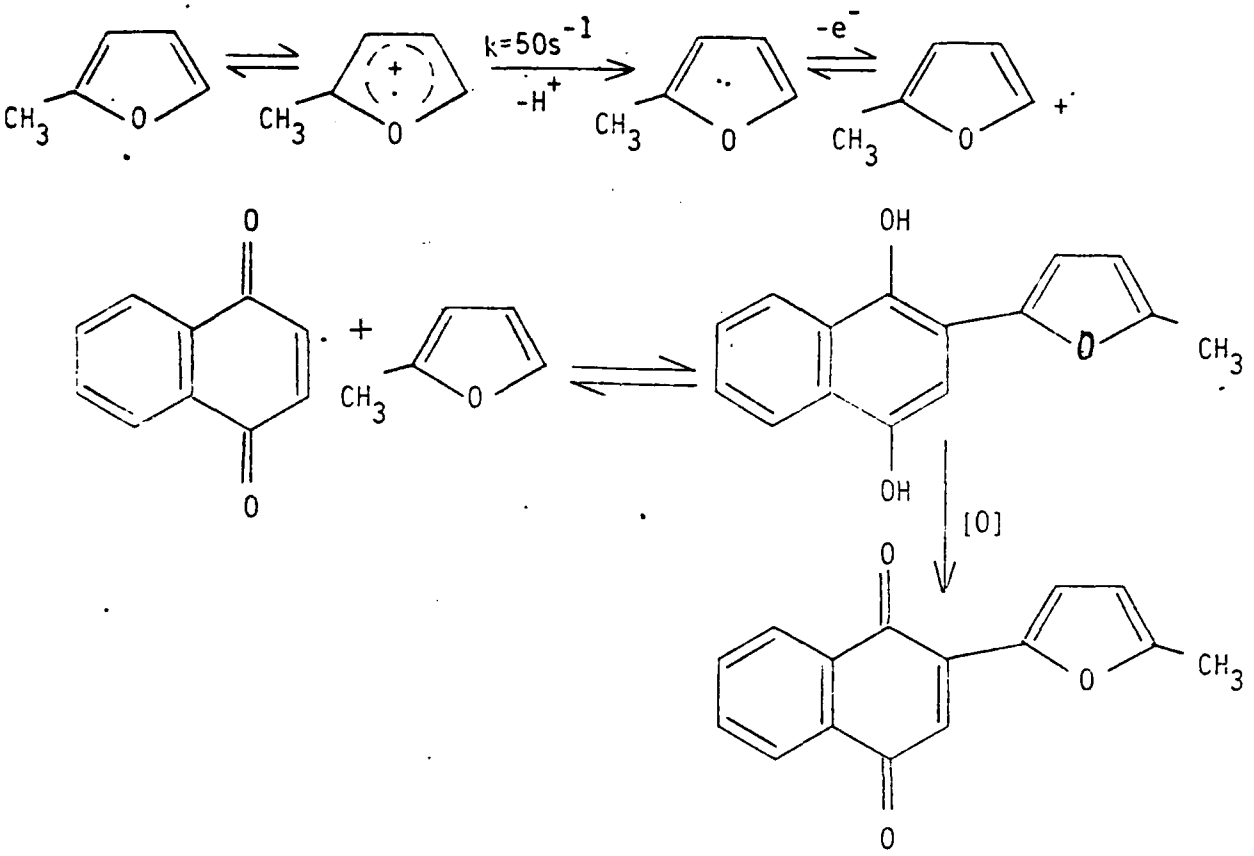
Constant potential electrolysis of an acetonitrile solution containing only the 2-methylfuran results in the formation of insoluble polymer (at the platinum surface), and soluble and insoluble oligomer. Thus VI and VII were isolated from the acetonitrile phase as described in the experimental section. Extraction of the surface polymer for 2 hours in a Soxhlet apparatus

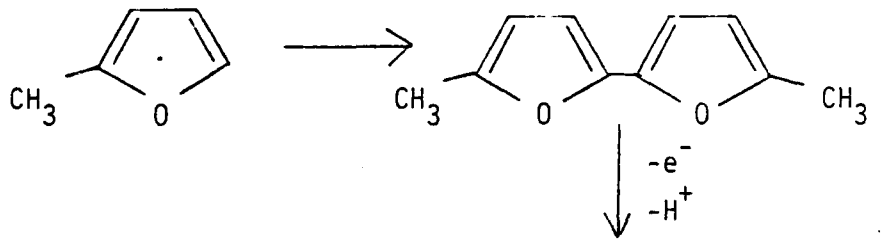
with diethylether resulted in a 13% recovery of VI based on the total polymer weight. The polymer itself is insulating at the platinum surface. Figure 1 shows cyclic voltammetric results for two subsequent scans of the solution of 2-methylfuran which had been degassed with argon. Figure 2 shows the results for a clean electrode in the same solution after presaturation with oxygen. To make the film conductive for the electrolyses, the voltage was pulsed repeatedly between 1.35 and 2.35 V (0.33 Hz square wave) for approximately 1-5 m, after which the current rose rapidly to values expected for normal electrolysis of the bulk solution. Thus the initially formed polymer film is not a conductive medium like that formed from electrooxidation of furan in similar electrolytes (3). Solutions containing oxygen required longer pulsing times to render the polymer film conductive.

The oxidized poly-2-methylfuran is highly conductive (σ_{298K}/Ω-cm = 33; pressed pellet, galvanostatic pulse) and very adherent to the metal surface, and is the subject of further investigation.

Apparently, the anodic oxidation of furan and 2-methylfuran in anhydrous acetonitrile solution proceeds initially with the net loss of 2 electrons and a proton. In the absence of the napthoquinone, the radical intermediate rapidly polymerizes, fouling the electrode surface (Figures 1,2). By using MSRS spectroscopy (5,6) in a potential region where the above reaction takes place and where the film product is reduced, it is possible, at least semi-quantitatively, to obtain some kinetic information. Obtaining a UV-VIS spectrum of the intermediates in the Scheme is very difficult due to the fouling obtained when the MSRS requirements of a reasonably fast (> 10 Hz) and symmetrical modulation potential are used. The subsequent reactions of the intermediates are quite fast, and thus equilibrium concentrations of these species are quite small. Signal averaging at λ = 315 nm, however, produced

SCHEME





to oligomers VI - VII

and polymers

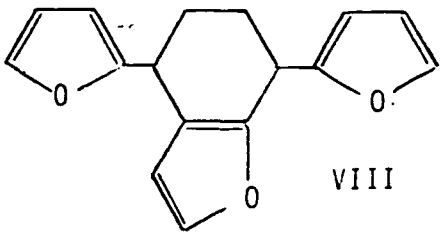
the absorbance-time transient shown in Figure 3. The signal is small, and the wavelength of observation corresponds to a strong line in the Hg-Xe lamp spectrum, which increases the signal-to-noise ratio. Even though the signal may not be at λ_{max} of the adsorbing species, it is clear that the transient is due to formation of the cation radical: the signal begins increasing immediately upon application of the potential step (allowing time for double-layer charging), and the absorbance-$(time)^{1/2}$ plot is linear until a following chemical reaction (proton loss--see below) depletes the cation concentration (Figure 4). The rate constant for proton loss is calculated from this plot (5) to be 50 s^{-1}. If a cyclic voltammogram is recorded on a time scale faster than the proton loss induction period (10 ms), then a one-electron transfer quasi-reversible wave is observed instead of the two electron irreversible wave observed at slower sweep rates. The loss of the proton is evidenced by the appearance (after furan oxidation) of a reduction wave at -0.20 V.

The mechanism of the furan-napthoquinone reaction by homogeneous oxidation by chloranil[1] is thought to proceed by oxidation of the furan-napthohydroquinone adduct (shown in the Scheme) formed in small amounts in solution. The results herein are consistent with such a mechanism if the oxidizing agent is the furan carbonium ion or the electrode. Both would lead to formation of oligomer and the furylnapthoquinone with the observed voltammetric and spectroscopic results. Oxidation of the adduct by the cation radical is precluded because of the insensitivity of the spectroscopic transient on the concentration of napthoquinone.

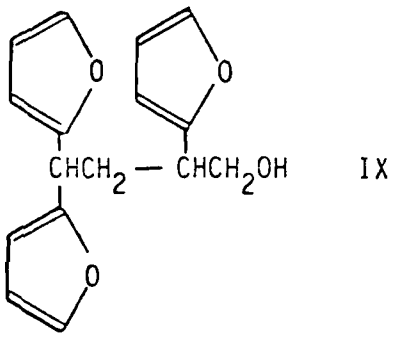
Under the above mentioned conditions for constant potential electrolysis, the electrode becomes fouled quickly due to rapid polymer formation, and is passified with respect to continued anodic current. As mentioned above, the oligomers and polymers formed may be further oxidized by pulsing for a few

minutes to high positive potentials, after which the film becomes conductive, and the electrolysis current rises rapidly. Formation of furan oligomer in solution is not as fast as the reaction of the oxidized intermediate(s) with the napthoquinone as is evidenced by the high yields of the products I-V compared to the yield of the oligomers VI and VII (concurrent yields 1-5%). In the absence of the napthoquinone the oligomers are formed in ca 80% yield.

Trimeric and tetrameric furan and 2-methylfuran have been isolated and characterized from acid catalyzed oligomerization reactions (7,8). Thus oligomers VIII and IX have been isolated in the oxidation reaction of furan in concentrated HCl (10), and X has been isolated from the reaction in phosphoric acid (7). The stable trimers XI and XII (9) and XIII (7) have been



VIII



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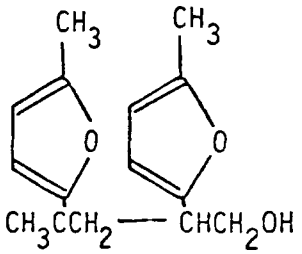
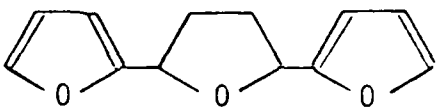
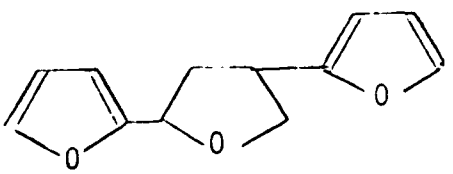


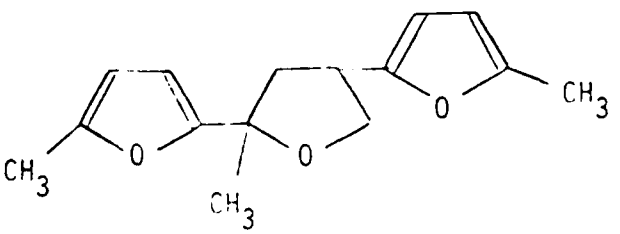
X



XI



XII



XIII

Comparisons of the spectroscopic data of these compounds were used as support for the proposed structures of the oligomers recovered in this work.

It is observed that the presence of O_2 alters the voltammetric behavior (c.f. Figures 1 and 2). The presence of oxyge. has no ultimate effect on the apparent conductivity of the films, but it is interesting to note that these results are in agreement with the work of Srogl et. al. (11) who observed reaction of O_2 with oxidizied furan intermediates, most likely the cation radical (12).

Acknowledgement

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

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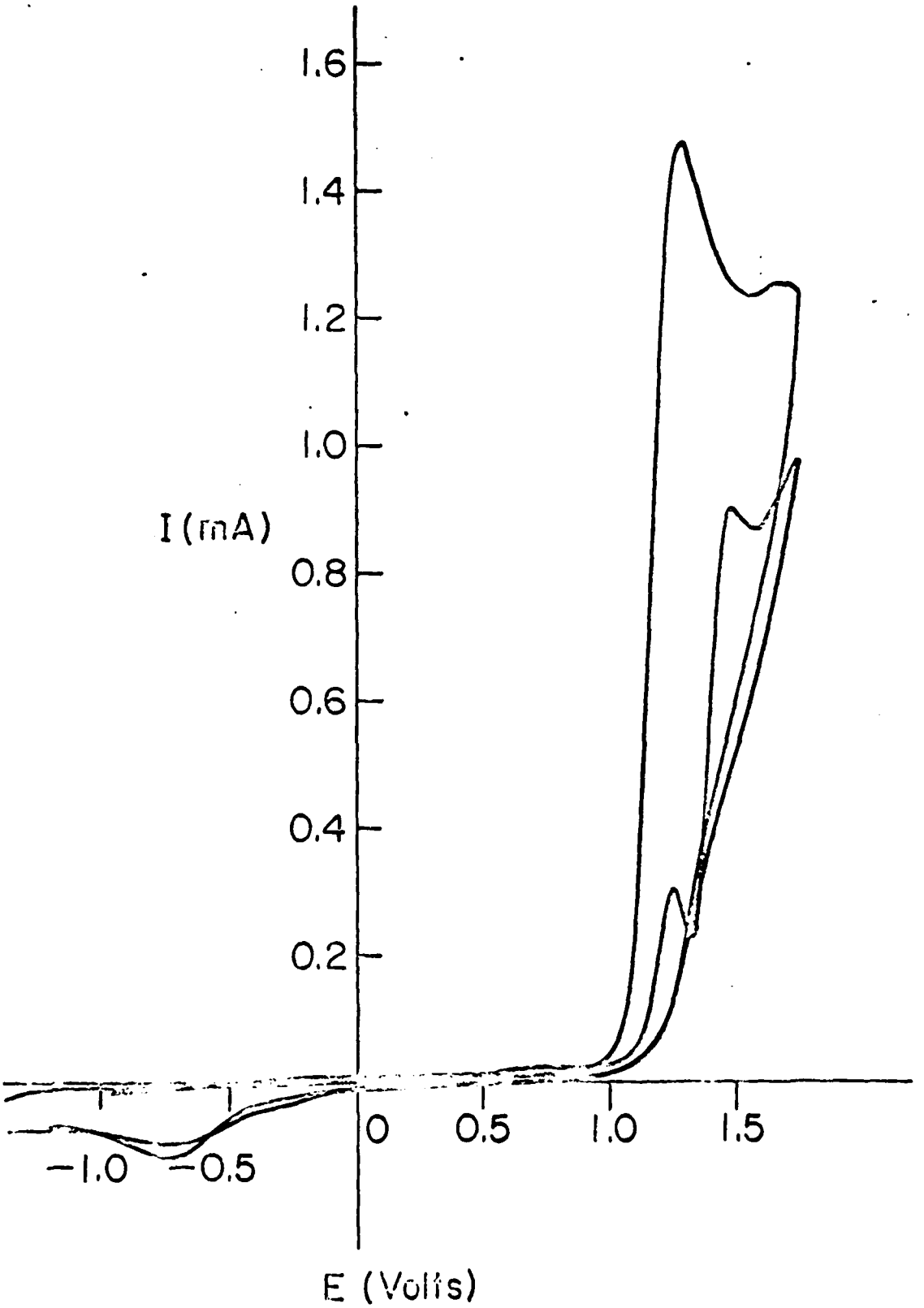
Legends for Figures

1. Cyclic voltammetry of a 10.9 mM solution of 2-methylfuran in acetonitrile (0.1 M tetra-n-butylammonium tetrafluoroborate electrolyte, 0.01 M Ag^+/Ag reference electrode, ν = 100 $mV\text{-}s^{-1}$, degassed with argon, Pt wire working electrode). a) 1st sweep. b) 2nd sweep after a 10 second pause.

2. Same as Figure 1, purged with O_2.
top to bottom: four subsequent sweeps.

3. $\Delta R/R$ vs t data at 315 nm, potential pulse from 0.0 V to 1.55 V.

4. $\Delta R/R$ vs $t^{1/2}$ plot of data in Figure 3.


1.6
1.4
1.2
1.0
I (mA)
0.8
0.6
0.4
0.2
0
0.5
1.0
1.5
−1.0
−0.5
E (Volts)

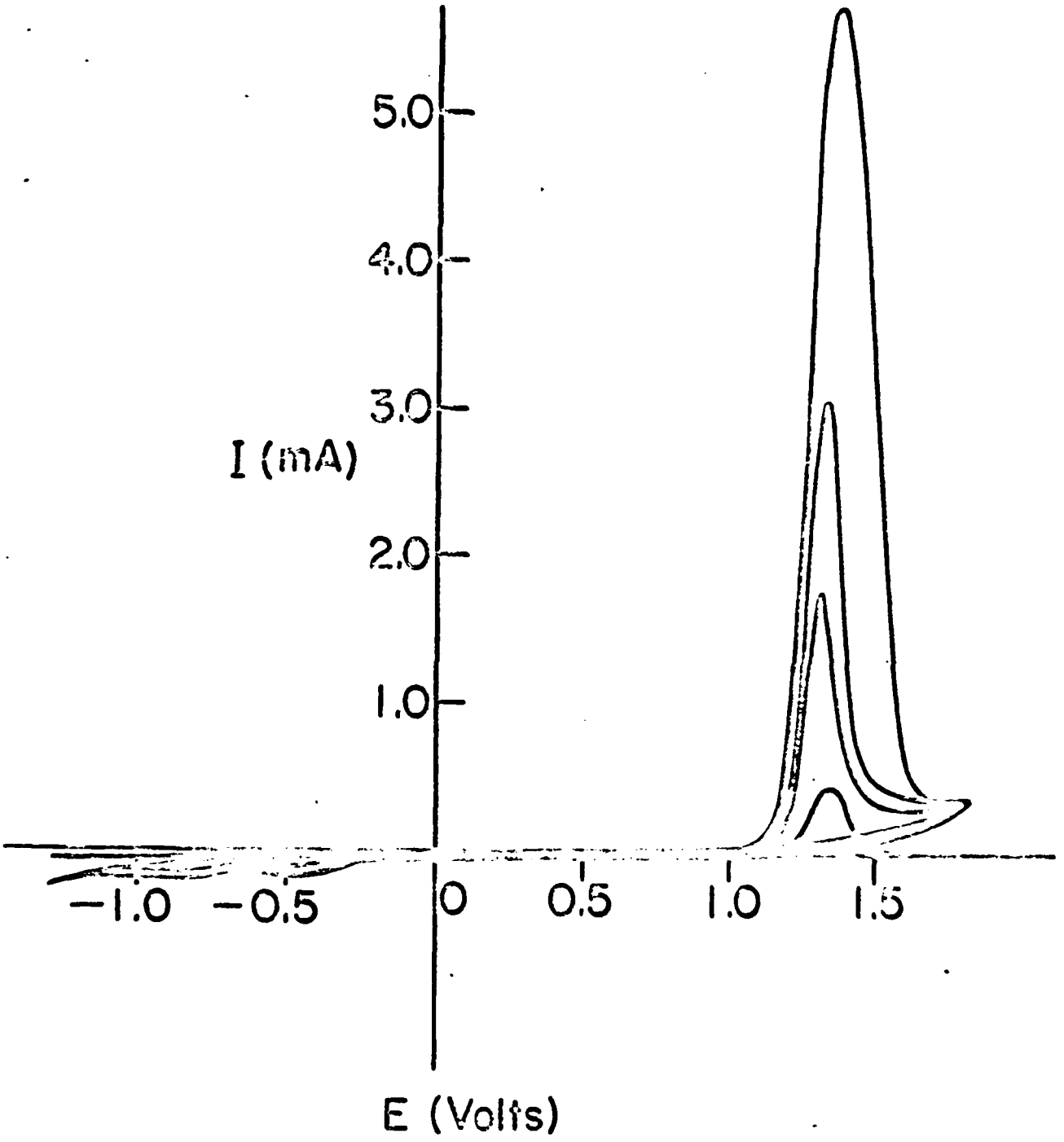

5.0
4.0
3.0
I (mA)
2.0
1.0
−1.0
−0.5
0
0.5
1.0
1.5
E (Volts)

Figure 3

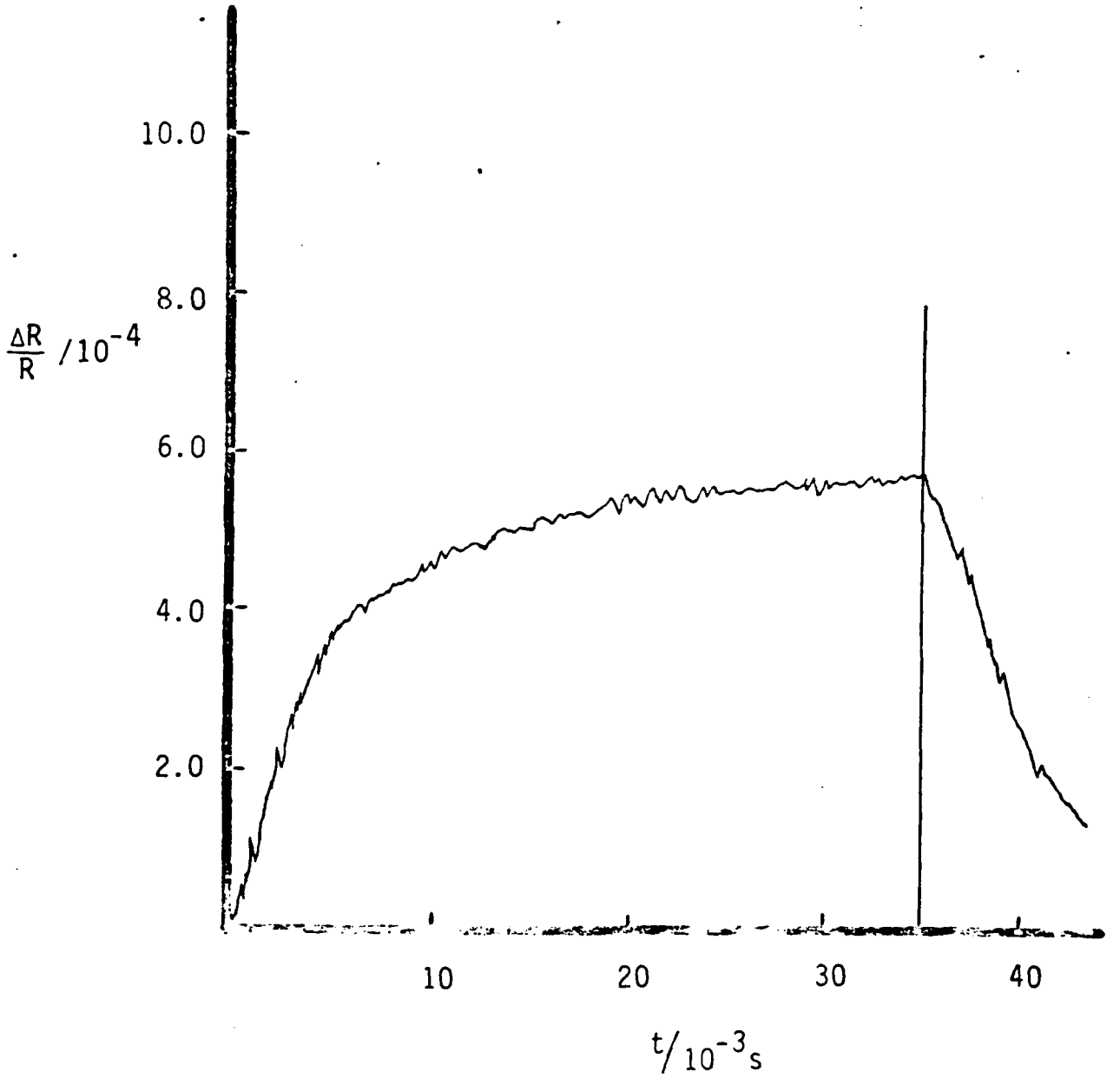
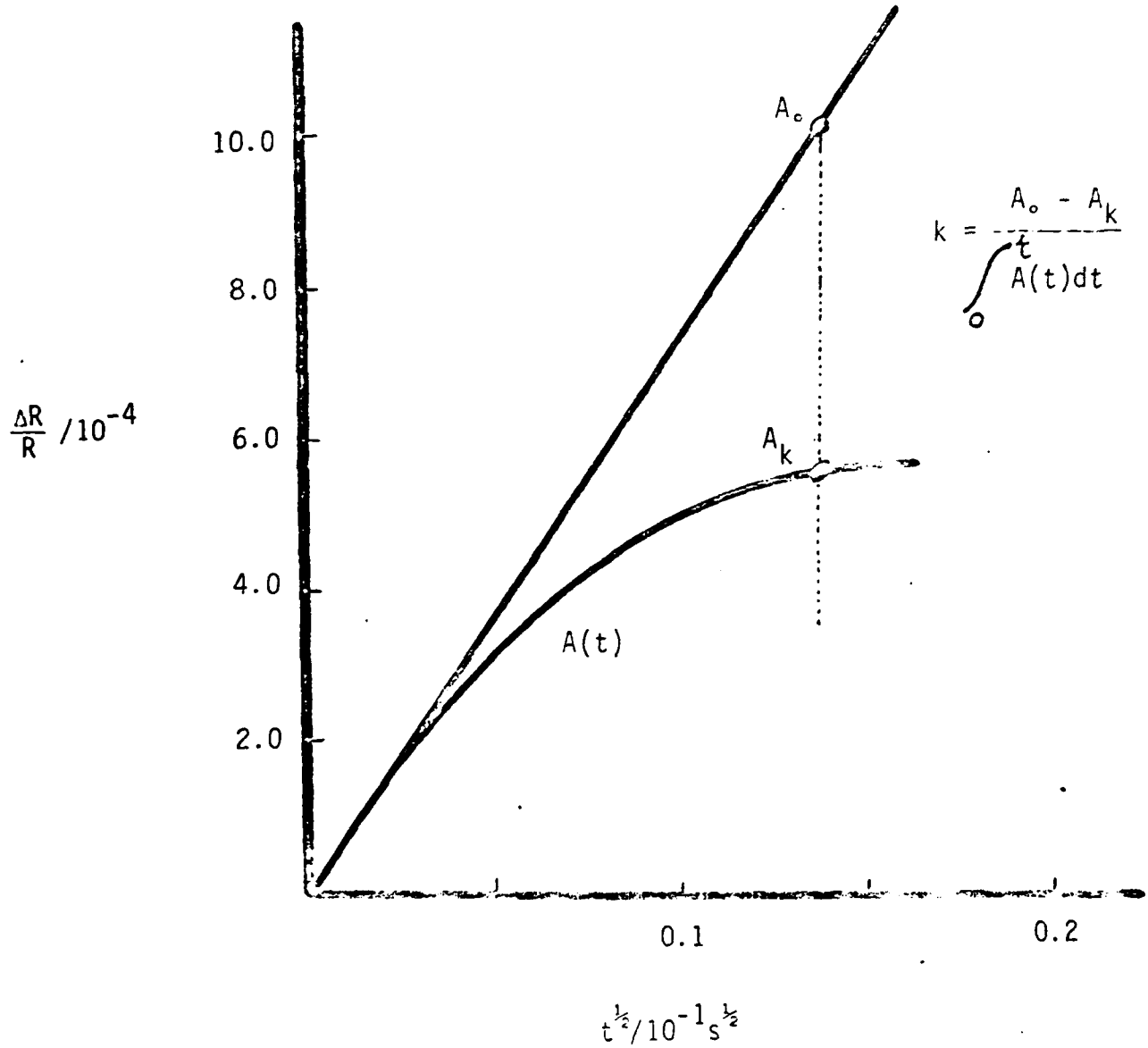


Figure 4


$\frac{\Delta R}{R}$ /10^{-4}
10.0
8.0
6.0
4.0
2.0
A_o
A_k
A(t)
$k = \frac{A_o - A_k}{\int_0^t A(t)dt}$
0.1
0.2
$t^{\frac{1}{2}}/10^{-1}s^{\frac{1}{2}}$

END

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