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Catalytic Reduction of Iodoethane and 2-Iodopropane at Carbon Electrodes Coated with Anodically Polymerized Films of Nickel(II) Salen

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In acetonitrile containing tetramethylammonium tetrafluoroborate, nickel(II) salen undergoes anodic polymerization onto a carbon electrode. Nickel(II) in the polymer film exhibits reversible one-electron reduction to form nickel(I), which can catalytically reduce iodoethane or 2-iodopropane to form an ethyl or 2-propyl radical, respectively, and to regenerate nickel(II). Kinetics studies with the aid of hydrodynamic voltammetry indicate that the catalytic reduction of iodoethane belongs to the ER regime of Savéant and co-workers, whereas catalytic reduction of 2-iodopropane is of the S classification. Controlled-potential electrolyses of iodoethane and 2-iodopropane at nickel(II) salen-coated reticulated vitreous carbon cathodes give product distributions in accord with the relative importance of radical coupling and disproportionation. Direct reduction of iodoethane at a bare cathode generates products via a carbanion mechanism. Products obtained from direct reduction of 2-iodopropane depend on the potential employed; at a potential corresponding to the first voltammetric wave, product distributions are nearly identical with those obtained from the catalytic reduction, whereas at a potential after the second voltammetric wave, the products are derived from the 2-propyl carbanion.

A number of studies have dealt with the use of nickel(I) macrocyclic complexes as homogeneous catalysts for the reduction of alkyl halides.¹⁻¹⁵ In one of the earliest investigations, Gosden, Healy, and Pletcher¹ demonstrated that the electrochemically generated nickel(I) analogue of [[2,2'-(1,2-ethanediylbis(nitrilomethylidene)]bis(phenolato))-N,N',O,O']-nickel(II), hereafter called nickel(II) salen, catalytically reduces *n*-, *sec*-, and *tert*-octyl bromides, and product distributions obtained from preparative-scale electrolyses of

these alkyl bromides were consistent with the intermediacy of an alkyl radical. In the mid-1980s, Bakac, Espenson, and co-workers⁶⁻¹¹ used ultraviolet-visible spectroscopy to explore the kinetics and mechanisms of the catalytic reactions between alkyl halides and electrochemically or photochemically generated nickel(I) macrocyclic complexes. Stolzenberg and Stershic¹²⁻¹⁴ have examined the catalytic reduction of several alkyl halides with an electrogenerated nickel(I) tetrapyrrole derivative to form the original nickel(II) tetrapyrrole and an alkane. In recent work¹⁵ in our laboratory, the reductive intramolecular cyclization of 6-iodo- and 6-bromo-1-phenyl-1-hexyne was induced with electrogenerated nickel(I) salen to form benzylidenecyclopentane in yields ranging from 84% to 95%.

In addition to studies of the homogeneous catalytic reduction of alkyl halides with nickel(I) complexes, several reports¹⁶⁻¹⁹ of the incorporation of nickel(II) species into polymer films on electrodes have been published. Horwitz and Murray¹⁶ synthesized 4,4'-di(*N*-methyl-*N*-phenylaminomethyl)nickel(II) salen and oxidatively polymerized this compound onto the surface of a platinum electrode. At about the same time, Goldsby and co-workers^{17,18} oxidatively polymerized nickel(II) salen onto platinum, as well as indium-doped, tin oxide-coated glass electrodes; the resulting polymer films were characterized with the aid of ultraviolet-visible spectroscopy and scanning electron microscopy. A few years later, Bedioui and colleagues¹⁹ studied the oxidative polymerization of nickel(II), cobalt(II), and manganese(III) salen onto glassy carbon electrodes; most notably, the nickel(II)-nickel(I) redox couple exhibited good reversibility within a polymer coating on an electrode.

In the present work, we have investigated the catalytic reduction of iodoethane and 2-iodopropane in acetonitrile containing 0.050 M tetramethylammonium tetrafluoroborate at glassy carbon electrodes coated with anodically polymerized films of nickel(II) salen. Cyclic voltammetric studies have been employed to establish that catalytic reduction of these alkyl iodides occurs at the filmed electrodes. Voltammetry with a polymer-coated rotating disk, in conjunction with theory developed by Savéant and co-workers,^{20,21} has allowed us to

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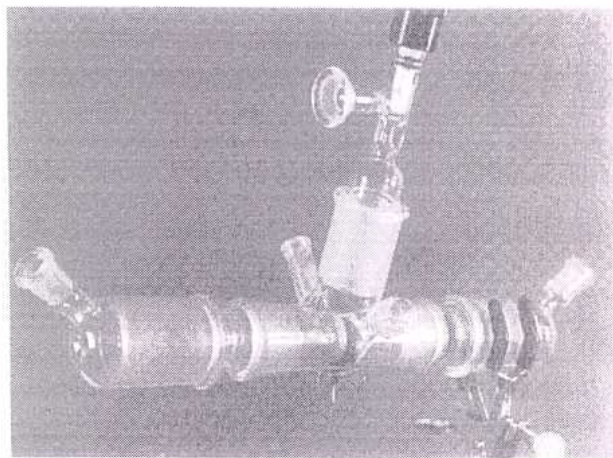


Figure 1. Electrochemical cell used for oxidative polymerization of nickel(II) salen and for controlled-potential electrolyses.

determine the parameters which limit the catalytic processes. Controlled-potential electrolyses have been performed at polymer-coated reticulated vitreous carbon disks, in a specially designed electrolysis cell, to identify and quantitate the products derived from the catalytic reduction of iodoethane and 2-iodopropane. Finally, we have conducted experiments to determine the robustness of nickel(II) salen-coated reticulated vitreous carbon cathodes for preparative-scale electrolyses.

EXPERIMENTAL SECTION

Reagents. Acetonitrile (Burdick and Jackson high-purity "UV" grade), which was continuously refluxed over calcium hydride, and dimethylformamide (Burdick and Jackson "distilled in glass" reagent) were employed as solvents for all electrochemical experiments. Tetramethylammonium tetrafluoroborate (TMABF₄; Aldrich, 97%) used as supporting electrolyte was stored in a vacuum oven at 65 °C. All deaeration procedures were carried out with Air Products UHP-grade argon.

Each of the following chemicals was used as received: [[2,2'-(1,2-ethanediybis(nitrilomethylidene)]bis[phenolato]]-N,N',O,O']nickel(II) (nickel(II) salen; Aldrich, 98%), iodoethane (Aldrich, 99%), 2-iodopropane (Aldrich, 99%), 2,3-dimethylbutane (Aldrich, 98%), ethane (Air Products, instrument grade), ethylene (Air Products, instrument grade), propane (Air Products, instrument grade), propylene (Air Products, instrument grade), and *n*-butane (Air Products, instrument grade). An authentic sample of diethyl isopropylmalonate was synthesized by means of an established procedure²² from diethyl isopropylidenemalonate (Aldrich, 97%).

Cells, Electrodes, and Instrumentation. Cells for cyclic voltammetry²³ and for voltammetry with a rotating disk electrode²⁴ have been described in earlier papers. Shown in Figure 1 is a cell designed for two purposes: (a) anodic

polymerization of nickel(II) salen onto a reticulated vitreous carbon working electrode and (b) preparative-scale controlled-potential catalytic reduction of an alkyl iodide at the polymer-coated electrode. For this cell the ratio of working-electrode area to solution volume is relatively large, and there are two opposing auxiliary electrodes which promote the formation of a uniform polymer film over the entire surface of the working electrode. In use, the cell was held upright on a Styrofoam platform that was placed on a Tek-Pro Model R4139-5 variable-speed rotator to ensure adequate mixing of the solution in the central compartment.

Controlled-potential electrolyses²⁵ and hydrodynamic voltammetry²⁴ were performed as previously described. For both cyclic and hydrodynamic voltammetry, we used the same disk-shaped planar glassy carbon electrode (Model AFDD20GC, Pine Instrument Co.) with an area of 0.459 cm². For controlled-potential electrolyses, reticulated vitreous carbon disks (Energy Research and Generation), 1 cm in thickness and 2.4 cm in diameter, were used; the procedure employed to fabricate and clean the electrodes before an electrolysis has been published elsewhere.²⁶ All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus the aqueous saturated calomel electrode at 25 °C.^{27,28}

Preparation and Handling of Polymer-Coated Electrodes.

We employed the same procedure to coat both the large reticulated vitreous carbon and the small carbon disk electrodes with films of anodically polymerized nickel(II) salen. A 2 mM solution of nickel(II) salen in acetonitrile containing 0.050 M TMABF₄ was placed into the cell and was deaerated with argon for 20–30 min. After the deaeration period, the solution was allowed to become quiescent while the flow of argon was continued over the surface of the solution. Then the potential of the carbon electrode was scanned cyclically between 0 and +2.26 V at a chosen rate. Both the scan rate and the number of potential cycles can be adjusted to vary the thickness of a film; in this paper, we use the term *anodic polymerization scan* to refer to one complete potential sweep from 0 to +2.26 to 0 V. Next, the electrode was rinsed thoroughly with acetonitrile to remove all solution-soluble monomeric nickel(II) salen.

To remove the polymer film from the small carbon disk electrode after voltammetric studies, the electrode was cleaned with 0.05- μ m alumina on a Master-Tex (Beuhler) polishing pad. On the other hand, the large reticulated vitreous carbon disks were soaked in 6 M hydrochloric acid for 1–3 weeks and then cleaned as described before;²⁶ soaking in hydrochloric acid protonates the film, which then becomes soluble in the solvents used in the cleaning process.

Procedure for Controlled-Potential Electrolyses. After a polymer-coated reticulated vitreous carbon electrode was prepared according to the preceding procedure, the electrode was rinsed repeatedly, without being removed from the cell, with pure acetonitrile and with solvent-supporting electrolyte.

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Fresh solvent-supporting electrolyte was added to the cell and deaerated with argon for approximately 15 min. Next, the filmed electrode and solvent-supporting electrolyte were preelectrolyzed at a potential (-1.00 V) where nickel(II) is reduced to nickel(I), during which period the argon flow was continued and the current decayed to a steady-state background level. When the preelectrolysis was finished, the potential of the filmed electrode was reset to 0 V for approximately 10–20 min to ensure complete conversion of nickel(I) back to nickel(II). Argon flow was then stopped, and the Teflon valve at the top of the cell was closed to create a gas-tight configuration. Known quantities of the starting material and an electroinactive internal standard were injected into the cathode compartment of the cell. Immediately, the electrolysis was begun; a typical time required for the current to attain its previous background level was 30–40 min for iodoethane and 15–25 min for 2-iodopropane. Electrolysis products were separated and quantitated according to an established procedure.²⁵ Ethane, ethylene, and *n*-butane derived from the electrolysis of iodoethane, and propane, propylene, and 2,3-dimethylbutane formed from the reduction of 2-iodopropane, were identified by comparison of gas chromatographic retention times for the suspected compounds with those of authentic samples.

RESULTS AND DISCUSSION

Cyclic Voltammetric Studies of Anodically Polymerized Nickel(II) Salen. Figure 2A depicts the first three sequential cyclic voltammograms for the anodic polymerization of nickel(II) salen onto a glassy carbon disk in acetonitrile containing 0.050 M TBAF₄. Our observations are similar to those reported in previous investigations.^{18,19} As the potential is scanned for the first time in the positive direction, two poorly resolved anodic waves are seen, the first corresponding to oxidation of nickel(II) to nickel(III) and the second due to oxidation of the salen ligand itself. On the first negative-going scan, a single wave for reduction of nickel(III) to nickel(II) appears. For the second and all succeeding positive-going scans, the polymer film becomes thicker so that the two anodic processes merge into a single wave. We believe that the anodic current is larger than the cathodic current for each complete cycle because the combined oxidations of nickel(II) and the salen ligand obviously require passage of more electricity than reduction of nickel(III) alone. As repetitive potential scans are made at 100 mV s⁻¹, the anodic and cathodic waves centered at approximately $+1.7$ V grow until scans 12–15, at which point the thickness of the film impedes further electron transfer. In agreement with the findings of Hoferkamp and Goldsby,¹⁸ we have found that the apparent thickness of the polymer film on the electrode surface increases linearly as a function of the first several anodic scans. Anodic polymerization of nickel(II) salen onto a carbon surface probably occurs in a manner similar to that of the oxidative carbon-carbon coupling of phenols, as discussed in the literature,²⁹ and Goldsby, Blaho, and Hoferkamp¹⁷ have concluded that oxidative polymerization of unsubstituted nickel(II) salen takes place via coupling of monomers at the para positions.

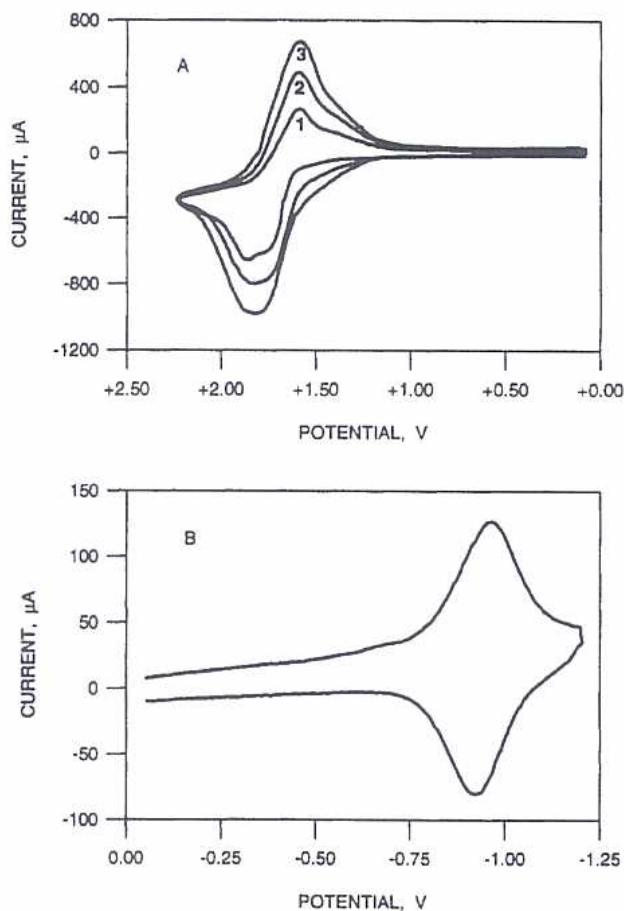


Figure 2. (A) First three cyclic voltammograms for anodic polymerization of 2.0 mM nickel(II) salen onto a glassy carbon electrode (area, 0.459 cm²) in acetonitrile containing 0.050 M TBAF₄ at a scan rate of 100 mV s⁻¹ from 0 to $+2.26$ to 0 V. (B) Cyclic voltammogram for a nickel(II) salen-coated electrode (5×10^{-9} mol cm⁻²) in acetonitrile containing 0.050 M TBAF₄ at a scan rate of 100 mV s⁻¹ from -0.05 to -1.20 to -0.05 V.

Figure 2B displays the cyclic voltammetric behavior in acetonitrile containing 0.050 M TBAF₄ of a nickel(II) salen-coated electrode (5×10^{-9} mol cm⁻²) which was formed through one anodic polymerization scan at 300 mV s⁻¹. As repetitive scans are made with this modified electrode, the current for reduction of nickel(II) to nickel(I) slowly decreases. However, if the electrode is held at 0 V for 1–2 min, the original behavior is restored. Such characteristics have been observed with other polymer films and have been explained through loss of film solvation or through exclusion of electrolyte as the film is cycled through the neutral oxidation state.¹⁶

An in situ ultraviolet-visible spectrum for a nickel(II) salen film polymerized onto an optically transparent, indium-doped, tin oxide-coated quartz electrode shows two prominent maxima at 320 and 410 nm. We have verified that the absorption maxima and spectral features for the polymer-coated electrode are in accord with those obtained in separate experiments with solution-soluble nickel(II) salen and with the free salen ligand in acetonitrile containing 0.050 M TBAF₄. In addition, preliminary spectrochemical measurements have demonstrated that nickel(I) is indeed formed upon reduction of nickel(II) in the polymer film and that the nickel(II)–nickel(I) interconversion can be followed in a cyclic voltammetric experiment.

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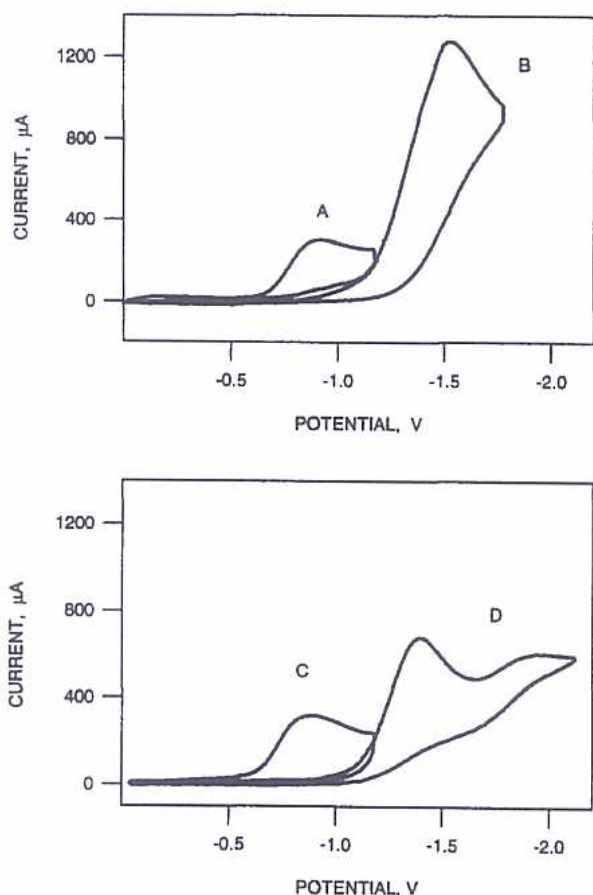


Figure 3. Cyclic voltammograms at a scan rate of 100 mV s^{-1} for reduction of 5.0 mM solutions of alkyl iodides in acetonitrile containing 0.050 M TMABF_4 : (A) iodoethane and (C) 2-iodopropane at a nickel(II) salen-coated electrode ($5 \times 10^{-9} \text{ mol cm}^{-2}$) and (B) iodoethane and (D) 2-iodopropane at a bare glassy carbon electrode.

Cyclic Voltammetric Studies of the Catalytic Reduction of Iodoethane. Figure 3A exhibits a cyclic voltammogram recorded after a 5 mM concentration of iodoethane was introduced into solvent-supporting electrolyte containing a modified electrode. As the potential is swept negatively, an increase in cathodic current (in comparison with Figure 2B) is seen for the catalytic reduction of iodoethane, whereas the anodic current disappears. When a second successive scan is performed, the catalytic current for reduction of iodoethane is lower. However, the full catalytic activity of the modified electrode is reestablished if its potential is held at 0 V for $5\text{--}10 \text{ min}$. One factor which could account for the decrease in catalytic current as repetitive scans are made is that the rate of diffusion of the alkyl halide into the polymer film is slow with respect to the time scale of a cyclic voltammetric experiment.

A cyclic voltammogram for reduction of a 5 mM solution of iodoethane at a bare carbon electrode in acetonitrile containing 0.050 M TMABF_4 is shown in Figure 3B. A single irreversible wave with a peak potential of -1.50 V is observed, which is 500 mV more negative than the potential for the catalyzed reduction at a filmed electrode (Figure 3A). Because the peak current for reduction of 1-iodobutane, which is known

to be reduced to a carbanion in a two-electron process,^{30–33} is similar under identical experimental conditions to the peak current for iodoethane in Figure 3B, we conclude that iodoethane undergoes a two-electron reduction at a bare carbon electrode.

Cyclic Voltammetric Studies of the Catalytic Reduction of 2-Iodopropane. Figure 3C is a cyclic voltammogram for the catalytic reduction of a 5 mM solution of 2-iodopropane at a carbon electrode coated with polymeric nickel(II) salen ($5 \times 10^{-9} \text{ mol cm}^{-2}$). We chose to compare the catalytic reductions of 2-iodopropane and iodoethane because Bakac and Espenson⁶ reported that the former compound reacts 7.5 times faster than the latter alkyl iodide with nickel(I) macrocyclic species. We hoped to discover a significant difference between the catalytic reductions of iodoethane and 2-iodopropane at a filmed electrode. For the second sequential cyclic voltammogram for reduction of 2-iodopropane at the modified electrode, the catalytic current was once again smaller than that for the first cathodic potential sweep.

A cyclic voltammogram for the direct reduction of 2-iodopropane at a bare carbon electrode in acetonitrile containing 0.050 M TMABF_4 is shown in Figure 3D. It is interesting that, whereas iodoethane is reduced in a one-step, two-electron process, 2-iodopropane undergoes a pair of stepwise one-electron transfers with peak potentials of -1.30 and -1.80 V , yielding the alkyl radical and then the alkyl carbanion. A similar mechanism has been observed in a previous study of the electrochemistry of 2-iodooctane.²⁶

Voltammetric Reduction of Iodoethane at a Rotating Polymer-Coated Disk. To explore the kinetics of the catalytic reduction of iodoethane and 2-iodopropane in the polymer film, the analysis developed by Savéant and co-workers^{20,21} was employed. Two factors which contribute to the limiting current (i_L) on the plateau of a voltammogram obtained with a polymer-coated rotating disk electrode are the Levich current (i_A) and the current (i_F) arising from kinetics processes occurring inside the film, where i_F can depend on three rate-limiting events: (a) the rate of electron diffusion in the film, (b) the rate of diffusion of substrate within the film, and (c) the rate of the catalytic reaction taking place inside the film. To determine which of the three rate-limiting events, or which combination of these three events, controls the limiting current (i_L), one must construct a Koutecký–Levich plot and ascertain whether it is linear or nonlinear; in addition, one must determine whether a second wave for direct (noncatalytic) reduction of the substrate through the film appears at more negative potentials.

Voltammograms for the catalytic reduction of iodoethane at a rotating disk electrode coated with a nickel(II) salen film ($5 \times 10^{-9} \text{ mol cm}^{-2}$) revealed, as shown in Figure 4A, a second wave for direct (noncatalytic) reduction of iodoethane at the same potential that is required to reduce iodoethane at a bare electrode (Figure 3B). This observation places the catalytic regime most likely into either the R or ER classification. To

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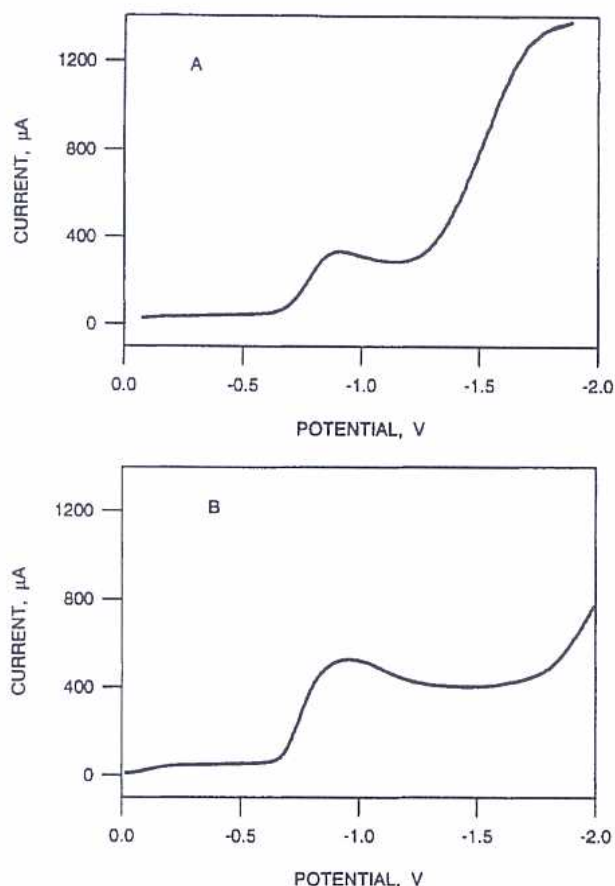


Figure 4. Hydrodynamic voltammograms for the catalytic reduction of a 10 mM solution of (A) iodoethane at a rotation rate of 100 rpm and (B) 2-iodopropane at a rotation rate of 2000 rpm in acetonitrile containing 0.050 M TBAF₄ at a glassy carbon disk coated with polymeric nickel(II) salen (5×10^{-9} mol cm⁻²) at a scan rate of 100 mV s⁻¹.

differentiate between these two scenarios, the linearity of a Koutecký-Levich plot for the first (catalytic) wave is examined; a linear plot signifies the R situation, whereas a nonlinear plot denotes the ER case. Figure 5A demonstrates that Koutecký-Levich plots for three concentrations of iodoethane are nonlinear; every experimental point corresponds to the average of at least nine measurements at each rotation rate. To verify that the catalytic reduction of iodoethane at a nickel(II) salen-coated electrode corresponds to the ER classification, two other parameters can be checked. First, the quotient $i_L(i_2)^{1/2}/(i_2 - i_L)^{-1/2}$ should be constant at all rotation rates for a given concentration, where i_L is the limiting current for the catalytic reduction of iodoethane in the film and i_2 is the current for direct (uncatalyzed) reduction of iodoethane through the polymer film; results displayed in Table 1 establish that this quotient is indeed constant. Second, a Koutecký-Levich plot for the limiting current (i_2) for the second wave should be linear, as is seen in Figure 5B. Therefore, these data confirm that the catalytic reduction of iodoethane at a nickel(II) salen-coated electrode corresponds to the ER situation, for which the limiting current is controlled by a combination of the rate of electron diffusion and the rate of the catalytic reaction. Moreover, the catalytic process is confined to a reaction zone which is small compared with the actual thickness of the polymer film and which is adjacent to the electrode surface, suggesting that iodoethane diffuses well into the polymer film to reach the active catalytic sites.

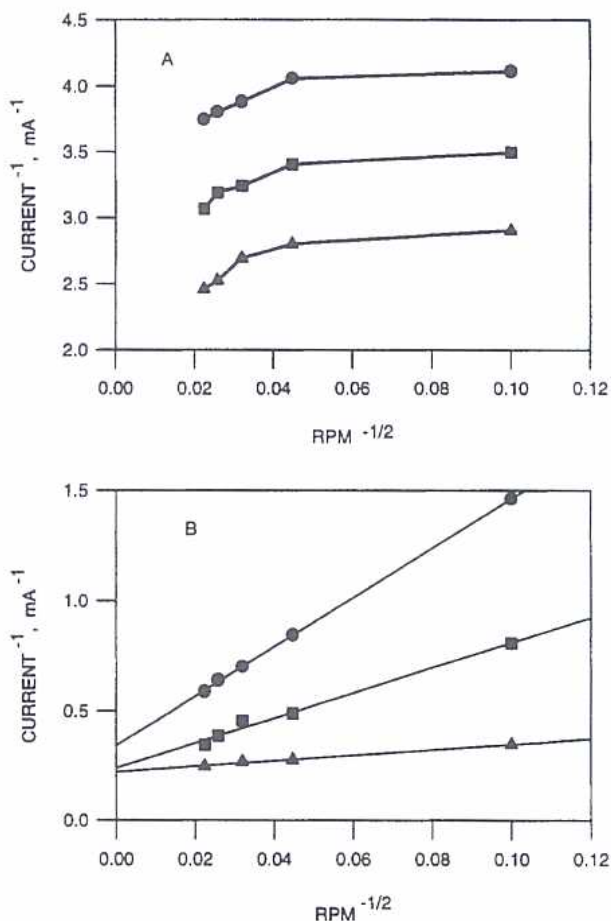


Figure 5. Koutecký-Levich plots for (A) catalytic reduction and (B) direct reduction of (●) 2.5, (■) 5.0, and (▲) 10.0 mM solutions of iodoethane in acetonitrile containing 0.050 M TBAF₄ at a nickel(II) salen-coated electrode (5×10^{-9} mol cm⁻²) at a scan rate of 100 mV s⁻¹.

Table 1. Hydrodynamic Data for Catalytic Reduction of Iodoethane at a Nickel(II) Salen-Filmed Electrode

conc (mM)	$10^9 \Gamma_E^0$ (mol cm ⁻²)	$i_L i_2^{1/2}/(i_2 - i_L)^{-1/2}$ (mA)				
		100 rpm	500 rpm	1000 rpm	1500 rpm	2000 rpm
2.5	5.5	0.30	0.28	0.28	0.29	0.29
5.0	5.5	0.32	0.32	0.33	0.33	0.34
10.0	5.5	0.37	0.38	0.39	0.42	0.43

Voltammetric Reduction of 2-Iodopropane at a Rotating Polymer-Coated Disk. A voltammogram for the catalytic reduction of 2-iodopropane at a rotating electrode coated with polymeric nickel(II) salen (5×10^{-9} mol cm⁻²) is depicted in Figure 4B. Direct reduction of 2-iodopropane at more negative potentials is not observed, which probably classifies this system among the SR, S, E, and S + E regimes. Figure 6A exhibits linear Koutecký-Levich plots for three different concentrations of 2-iodopropane, with slopes and intercepts that are inversely proportional to the concentration of 2-iodopropane. This behavior narrows the preceding four possibilities to just the S and SR cases, which can be distinguished from each other if one performs experiments with different film thicknesses. For the S situation the y-intercept of a Koutecký-Levich plot will be proportional to the film thickness, whereas for the SR regime the y-intercept will be independent of the film thickness. A Koutecký-Levich plot for the catalytic reduction of a 5 mM

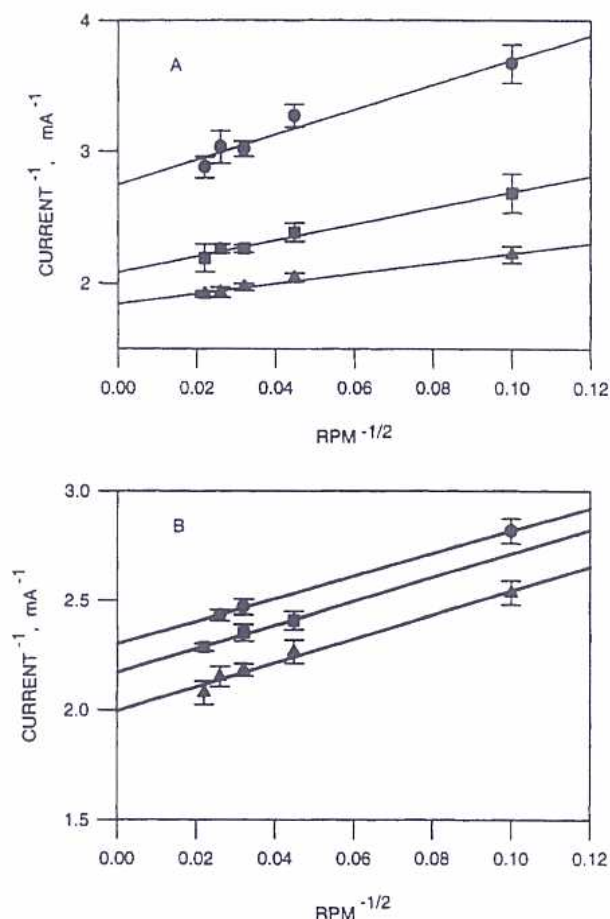


Figure 6. Koutecký-Levich plots for the catalytic reduction of 2-iodopropane at (A) a nickel(II) salen-coated electrode (5×10^{-9} mol cm^{-2}) for concentrations of (●) 2.5 ($R^2 = 0.95$; slope, 9.5; intercept, 2.8), (■) 5.0 ($R^2 = 0.98$; slope, 6.1; intercept, 2.1), and (▲) 10.0 mM ($R^2 = 0.98$; slope, 3.8; intercept, 1.8) and (B) for catalytic reduction of a 5.0 mM solution of 2-iodopropane for different thicknesses of nickel(II)-salen films: (▲) 4.6×10^{-9} ($R^2 = 0.98$; slope, 5.5; intercept, 2.0), (■) 6.6×10^{-9} ($R^2 = 0.99$; slope, 5.4; intercept, 2.2), and (●) 8.6×10^{-9} mol cm^{-2} ($R^2 = 0.99$; slope, 5.2; intercept, 2.3) in acetonitrile containing 0.050 M TBAF₄.

solution of 2-iodopropane at the rotating carbon disk coated with films of different thicknesses is shown in Figure 6B. A y -intercept that is proportional to the thickness of the film is observed; thus, the catalytic reduction of 2-iodopropane at a nickel(II) salen-filmed electrode lies in the S regime, for which the limiting current is controlled by the rate of diffusion of 2-iodopropane within the polymer film.

Controlled-Potential Electrolyses of Iodoethane. Preparative-scale catalytic reductions of iodoethane were performed at reticulated vitreous carbon cathodes coated with polymeric nickel(II) salen in acetonitrile containing 0.050 M TBAF₄ at a potential (−1.00 V) that is 100 mV more negative than the reversible redox potential for the nickel(II)–nickel(I) couple in the film. Coulometric n values and product distributions which are averages of from four to six electrolyses at each of two concentrations are compiled in Table 2. A coulometric n value of 1 was observed for all electrolyses, which is expected if the catalytic reduction proceeds via a radical pathway. We believe that n -butane, the major product, arises via coupling of a pair of ethyl radicals, whereas ethane and ethylene are formed by disproportionation of ethyl radicals. It is interesting that the product distributions in Table 2 are

Table 2. Coulometric Data and Product Distributions for Electrolytic Reduction of Iodoethane in Acetonitrile Containing 0.050 M TBAF₄

E (V)	conc (mM)	n	product distribution (%)			
			n -butane	ethane	ethylene	total
−1.00 ^a	5	1.15	82	19	7	108
−1.00 ^b	10	0.97	72	17	6	95
−1.00 ^c	5	1.40	90	8	3	101
−1.65 ^c	5	1.94	32	55	6	93

^a Polymer-coated electrode (one anodic polymerization scan at 300 mV s^{-1}). ^b With 2.00×10^{-3} M homogeneous-phase nickel(II) salen. ^c Bare electrode.

Table 3. Coulometric Data and Product Distributions for Electrolytic Reduction of 2-Iodopropane in Acetonitrile Containing 0.050 M TBAF₄ or in Dimethylformamide Containing 0.100 M TBAF₄^a

E (V)	conc (mM)	n	product distribution (%)			
			2,3-dimethylbutane	propane	propylene	total
−1.00 ^b	5	1.10	46	33	30	109
−1.00 ^b	10	1.12	40	31	26	97
−1.00 ^c	5	1.37	36	31	28	95
−1.45 ^d	5	1.48	32	33	29	94
−1.90 ^d	5	1.36	12	32	41	85
−1.90 ^{d,e}	5	1.66	20	52	18	101 ^f

^a TBAF₄ is tetra- n -butylammonium tetrafluoroborate (used only for electrolyses at −1.90 V). ^b Polymer-coated electrode (one anodic polymerization scan at 300 mV s^{-1}). ^c With 2.00×10^{-3} M homogeneous-phase nickel(II) salen. ^d Bare electrode. ^e With 80 mM diethyl malonate. ^f Includes 11% diethyl isopropylmalonate.

in accord with experimental measurements in homogeneous media,³⁴ where the rate for ethyl-radical coupling is approximately 6–8 times greater than the rate of disproportionation of ethyl radicals. Table 2 provides a comparison of the catalytic reduction of iodoethane by electrogenerated homogeneous-phase nickel(I) salen with the catalytic reduction of iodoethane at chemically modified electrodes. Product distributions from both kinds of electrolyses are included in Table 2 and show good agreement with each other.

Data from electrolyses of iodoethane at bare reticulated vitreous carbon electrodes in acetonitrile containing 0.050 M TBAF₄ are shown in Table 2. These electrolyses were performed at a potential of −1.65 V, which is 650 mV more negative than the potential required for the catalytic reduction of iodoethane at a nickel(II) salen-modified electrode. When iodoethane is reduced at a bare electrode, the products are ethane, n -butane, and ethylene, in order of decreasing abundance. This distribution of products, along with the observed coulometric n value of 2, signifies that the pathway for direct reduction of iodoethane at a bare carbon surface no longer involves a one-electron radical pathway but a two-electron process to give a carbanion intermediate.

Controlled-Potential Electrolyses of 2-Iodopropane. Electrolyses of 2-iodopropane at large reticulated vitreous carbon electrodes filmed with polymeric nickel(II) salen in acetonitrile containing 0.050 M TBAF₄ were performed at −1.00 V. Table 3 displays coulometric n values and product distributions for electrolysis of 5 and 10 mM solutions of 2-iodopropane. Products derived from the catalytic reduction of 2-iodopropane are 2,3-dimethylbutane, propane, and propylene, and their

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yields are in accord with observed rates of radical disproportionation and coupling, with disproportionation being favored slightly over coupling by a factor of 1.2.³⁴ We compared the product distributions obtained from reduction of 2-iodopropane at a chemically modified electrode with those derived from reductions with nickel(I) salen electrogenerated homogeneously in acetonitrile containing 0.050 M TMABF₄. As the data in Table 3 reveal, the yields of 2,3-dimethylbutane, propane, and propylene formed in the two kinds of electrolyses are nearly indistinguishable.

Electrolyses of 2-iodopropane at bare reticulated vitreous carbon cathodes, in acetonitrile or dimethylformamide containing 0.050 M TMABF₄, were performed at potentials (−1.45 and −1.90 V) corresponding to the first and second voltammetric waves, respectively. We expected that products from electrolyses at −1.45 V would arise via a radical pathway, whereas products from electrolyses at −1.90 V would be generated through an anion route. Product distributions and coulometric *n* values for these experiments are presented in Table 3. At a potential of −1.45 V, the yields of the products (2,3-dimethylbutane, propane, propylene) are similar to those obtained from catalytic reductions at a filmed electrode, and it appears that these species are indeed formed through a one-electron process. In contrast to results obtained at −1.45 V, one finds that, at a potential (−1.90 V) on the second voltammetric wave, the yield of 2,3-dimethylbutane decreases, the quantity of propylene increases, and the amount of propane remains essentially unchanged. It is notable in the fifth entry of Table 3 that the absolute yield of propylene is greater than that of propane. Propylene is probably produced through a base-promoted dehydrohalogenation of starting material; we believe that this process involves deprotonation of adventitious water by a 2-propyl carbanion (or an *n*-butyl carbanion arising from the tetra-*n*-butylammonium cation) which is electrogenerated at −1.90 V and that the resulting hydroxide ion attacks starting material to afford the olefin. Thus, a deliberately added proton donor should react with hydroxide and should hinder the formation of propylene, and as a consequence, more starting material will undergo direct electrolytic reduction. Table 3 shows the results when diethyl malonate was added to a solution of 2-iodopropane electrolyzed at −1.90 V. We found that the yield of propylene decreased from 41% to 18% and that the amount of propane increased from 32% to 52%. These findings provide strong evidence that carbanions are generated in electrolyses of 2-iodopropane at a bare electrode held at −1.90 V.

Robustness of Anodically Polymerized Films of Nickel(II) Salen on Reticulated Vitreous Carbon Electrodes. If a polymer-coated electrode is to be employed successfully for practical preparative-scale electrolyses, two requirements must be met. First, the polymer film must adhere strongly to the electrode surface, and second, the polymer film must permit repetitive catalytic reductions to be performed over an extended period of time.

To investigate how well a film of anodically polymerized nickel(II) salen adheres to the surface of reticulated vitreous

Table 4. Coulometric Data and Product Distributions for Repeated Catalytic Reductions of 5 mM Iodoethane in Acetonitrile Containing 0.050 M TMABF₄ at a Nickel(II) Salen-Coated Electrode^a

elapsed time (h) ^b	<i>n</i>	product distribution (%)			
		<i>n</i> -butane	ethane	ethylene	total
0	1.05	82	19	7	108
24	1.00	58	31	7	96
48	1.40	54	44	7	105

^a See text for details of these experiments. ^b Measured from the time that the reticulated vitreous carbon electrode was first coated with anodically polymerized nickel(II) salen (one anodic polymerization scan at 300 mV s^{−1}).

carbon, cyclic voltammograms were recorded after a polymer-coated electrode was held at −1.0 V for various periods of time. No significant decrease in the cathodic and anodic peak currents was observed after 10, 20, 40, and 60 min, implying that there is no loss of nickel(II) and thus of the polymer film.

To probe the ability of a filmed electrode to be used for repetitive electrolyses, two kinds of experiments were performed. First, several samples of iodoethane were injected sequentially (after catalytic reduction of the preceding sample was complete) into the cell, and the current–time behavior was monitored for each electrolysis. Each electrolysis produced similar current–time behavior, which suggests that the catalytic properties of a film do not diminish after at least several electrolyses. Second, another series of experiments involved removing the electrolyzed solution from the cell after a catalytic reduction, rinsing the electrode with pure acetonitrile and then with solvent-supporting electrolyte, adding fresh solvent-supporting electrolyte, deaerating the cell with argon, and leaving the cell sealed overnight. On the following day, a fresh sample of iodoethane was injected into the cell, another electrolysis was carried out, and the product distribution was determined and compared with that of the preceding day. Table 4 shows coulometric *n* values and product distributions for catalytic reduction of iodoethane at a polymer-coated reticulated vitreous carbon cathode on three consecutive days. Our results indicate that the yield of *n*-butane drops after the first day and remains essentially constant thereafter, that the quantity of ethane rises in absolute terms approximately 12% per day, and that the amount of ethylene does not change. A nickel(II) salen-coated electrode can be used repetitively over several days for catalytic reductions of iodoethane, but we cannot yet explain why the product distribution changes with time.

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