THE ELECTROCHEMICAL REDUCTION OF SUCCINIMIDE

REACTIVITY OF QUATERNARY AMMONIUM IONS UNDER ELECTROLYSIS CONDITIONS

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Abstract—A solution of succinimide in ether acetonitrile or N, N-dimethylformamide containing tetra-n-butylammonium fluoborate shows a single, irreversible reduction wave at a platimum cathode by cyclic voltammetry. Coulometry demonstrates that a single electron is transferred. The reaction is accompanied by the evolution of hydrogen at a rate such that the passage of one Faraday of charge results in the generation of almost exactly 0.5 mole of hydrogen. The product of these reactions is the succinimide anion which is stable in the electrolysis solution, but reacts with tetra-n-butylammonium ion during vpc analysis or in refluxing N, N-dimethylformamide to form N-n-butylsuccinimide.

Although studies of the electroreduction of phthalimide and N-substituted phthalimides have appeared, ^{1,2} succinimide electrochemistry has received little attention. Tafel *et al.*³ reduced succinimide in 50% sulfuric acid to mixtures of 2-pyrrolidone and pyrrolidine; the relative yields of these products depended upon the experimental conditions employed. However, all previous electrochemical studies involving succinimide predate the advent of modern electroanalytical techniques and none was carried out in aprotic solvents.

This study investigates the electrochemical reduction of succinimide to its anion in aprotic media. When the electrolysis mixtures, without work-up, were analyzed by vpc, N-alkylsuccinimides were produced by reaction of quaternary ammonium ions with the succinimide anion. These reactions, which occurred in the vpc apparatus, were studied in detail.

RESULTS AND DESCUSSION

Electroanalytical studies. Succinimide, in either acetonitrile (AN) or N,N-dimethylformamide (DMF) containing tetra-n-butylammonium fluoborate (TBAF). shows a single, irreversible reduction wave upon examination by cyclic voltammetry. Fig. 1 shows cyclic voltammograms for succinimide and the first reduction wave for phthalimide which were obtained with a platinum cathode in DMF containing 0.2 M TBAF. Cyclic voltammograms for succinimide showed no signs of reversibility even at more rapid scan rates (up to 500 V/s) and at lower temperatures (-20°).

Figure 2 shows a cyclic voltammogram obtained for succinimide under conditions which encompass the entire, accessible potential range. In order to increase the probability of observing voltammetric peaks for the succinimide reduction products, the initial electrode potential was maintained at -2.0 V vs SCE for several minutes before obtaining the cyclic voltammogram. In addition to the cathodic reduction peak for succinimide near -1.5 V, other noteworthy features are the presence of anodic peaks centered at -0.65 and at +1.6 V. The larger anodic peak (at -0.65 V) is probably due to the oxidation of H atoms, which are adsorbed on the pla-



Fig. 1. Cyclic voltammograms obtained for 5.9 mM succinimide (A) and 4.4 mM phthalimide (B) in DMF containing 0.2 M TBAF. Platinum disc electrode area was 0.053 cm² and the potential scan rate was 0.05 V/s.

tinum electrode surface during the succinimide reduction process, and the smaller peak (at +1.6 V) results from the anodic oxidation of the succinimide anion, the main reduction product derived from succinimide under our conditions.

A voltammogram obtained for phthalimide at a platinum cathode in DMF consisted of three separate reduction waves and was similar to voltammetric data reported for phthalimide at a mercury electrode.¹ The first reduction wave for phthalimide involves formation of the phthalimide anion^{1,A,S} and is irreversible at room temperature.

The number of electrons transferred during succinimide reduction was determined by controlled-potential coulometry at -1.9 V vs SCE. A voltammogram



Fig. 2. Cyclic voltammogram obtained for 10 mM succinimide in AN containing 0.2 M TBAF. Platinum disk electrode area was 0.053 cm², the initial potential was -2.0 V, and the potential scan rate was 0.50 V/s.

performed after the electrolysis resembled a blank voltammogram and did not show the characteristic succinimide reduction wave. Integration of the current-time curve yielded n = 0.97, where n is the number of Faradays of charge passed per mole.

In a separate experiment the gas evolved from the cathode compartment during succinimide reduction was collected and analyzed. The electrochemical cell was connected to a gas collection apparatus, the design and calibration of which were described previously.⁶ The gas was analyzed by vpc and shown to contain 96% hydrogen. Two independent gas collections yielded an average of 0.48 ± 0.03 moles of hydrogen produced per Faraday of charge. Electrolysis of the solvent-supporting electrolyte system in the absence of the substrate at an applied potential of -2.1 V resulted in essentially no gas evolution at the cathode.

Acetonitrile is a very weak base,⁷ too weak to be protonated by succinimide and too weak to function with succinimide as a Brønsted acid-base pair. A 0.02 M solution of succinimide in AN has a resistivity in excess of $2 \times 10^6 \Omega$ -cm at room temperature, and the cathodic wave observed for succinimide in AN is best attributable to electron transfer to the neutral succinimide molecule.⁸

As will be shown in detail subsequently, the products of the electrochemical reduction of succinimide in AN are the succinimide anion and hydrogen. All of our experimental observations are consistent with a mechanism in which electron transfer to the substrate and H atom transfer to the electrode occur in a single concerted step. Some of the driving force for this reaction may be provided by the adsorption of the H atoms on the electrode surface and their recombination to give hydrogen gas. In this connection it is noteworthy that neither N-methylsuccinimide nor N-n-butylsuccinimide is reducible under our electrochemical conditions. A less probable but not fully eliminated mechanism would be an EC process in which the anion radicals formed in the rate-determining step are unstable and yield the succinimide anions by rapid loss of H atoms (Reactions 1 and 2),



which combine on the platinum surface and evolve as hydrogen gas.⁹

Product studies. Because an efficient extraction method for product isolation was lacking, electrolyzed solutions were initially analyzed by direct injection into vpc. Exhaustive, controlled-potential (-1.9 V vs SCE) reduction of succinimide in AN containing 0.2 M TBAF followed by vpc analysis, without workup, indicated the presence of N-n-butylsuccinimide (63%) and tri-nbutylamine (63%); all yields are absolute, based upon mols of starting material. Similar results were obtained with both AN and DMF as solvent and with TBAF or tetraethylammonium fluoborate (TEAF) as supporting electrolyte. With TEAF as supporting electrolyte in either AN or DMF, direct injection vpc analysis of solutions obtained from exhaustive reduction of succinimide indicated the presence of N-ethylsuccinimide (55%).

The foregoing results suggest the occurrence of electrochemically-induced N-alkylation of succinimide by the quaternary ammonium cation, but there are legitimate grounds for skepticism with respect to the validity of such a conclusion. This laboratory has reported studies of the rates of reaction of benzyldimethylanilinium ion with ethoxide ion in ethanol¹⁰ and with thiocyanate ion in a variety of solvents.¹¹ These reactions are relatively slow even at 50.8° despite the fact that thiocyanate ion is a highly effective nucleophile and displacements on benzyldimethylanilinium ion should be more facile than on either tetra-n-butylammonium ion or tetraethylammonium ion.

In fact, it can be demonstrated with certainty that the product of the electrochemical reaction is a stable solution of the succinimide anion and that the apparent alkylation reaction occurs not during the electrolysis but during vpc analysis. This conclusion is based on the following evidence:

1. Anodic voltammetry, performed after exhaustive reduction of succinimide indicated the presence of a product with $E_p \approx +1.6$ V vs SCE. A nearly identical oxidation potential was obtained for a chemically prepared solution of tetraethylammonium succinimide in AN containing TBAF.

2. When a portion of the electrolyzed solution was acidified with excess fluoboric acid before vpc analysis, the sole product found was succinimide.

3. When excess n-butyl bromide was added to another aliquot of the electrolyzed solution and permitted to react for 1 hr, vpc analysis indicated the presence of N-n-butylsuccinimide but *no* tri-n-butylsumine. This result was verified with a controlled-potential (-1.8 V vsSCE) reduction of succinimide in AN containing 0.2 M TEAF and a 3-fold excess of n-butyl bromide. Directinjection vpc analysis indicated that N-n-butylsuccinimide was formed in 90% yield, and acidification of the solution with fluoboric acid before vpc analysis did not alter this result.

4. When an aliquot of the electrolysis solution was diluted with water and titrated with 0.0500 N HCl, the single end point in the titration curve indicated the presence in the solution of a base, the succinimide anion, in a quantity equivalent to the amount of succinimide found in the same electrolysis solution by vpc after acidification with fluoboric acid.

Each of these experimental results shows that the succinimide anion is formed in good yield $(86 \pm 4\%)$ by electrochemical reduction of succinimide and, further, that this anion is stable in the electrolysis medium.

Saveant and Binh¹² have reported the alkylation of the anion radicals formed in the electrochemical reductions of triphenylphosphine and triphenylphosphine oxide by tetraalkylammonium supporting electrolytes, and Abbot and Bellamy¹³ have noted the ethylation of aliphatic ketones on electroreduction in tetraethylammonium fluoborate-liquid ammonia solutions. Because of these reports it seemed worthwhile to us to attempt experiments aimed at defining the conditions under which displacement reactions by the succinimide anion on tetra-n-alkylammonium ions become possible.

A solution of the succinimide anion as the tetra-nbutylammonium salt in either AN or DMF can be prepared by a non-electrochemical procedure as described in the Experimental. These chemically prepared solutions duplicate the chemistry shown by our electrolytic preparations. Direct injection into vpc indicates the presence of N-n-butylsuccinimide, tri-n-butylamine and a small amount of succinimide; after acidification of the solution with fluoboric acid, vpc analysis gave the expected amount of succinimide and only trace amounts of N-n-butylsuccinimide and tri-n-butylamine; addition of water and titration with 0.0500 N HCl permits the quantitative determination of the succinimide anion.

When a DMF (b.p. 153°) solution of tetra-n-butylammonium succinimide was refluxed 20 hr, acidified with fluoboric acid and analyzed by vpc, more than 80% of the succinimide anion was alkylated by the quaternary ammonium cation to give N-n-butylsuccinimide and trin-butylamine. A similar experiment with AN (b.p. 82°) did not result in the formation of N-n-butylsuccinimide, probably because of the lower boiling point of AN.

Thus, liquid-phase alkylations of anionic nucleophiles by quaternary ammonium ions are possible, but these reactions require conditions that are not common in electrochemical reactions and are not directly comparable to those that obtain in either the injection port or columns of a vpc apparatus. We have suggested that a DMF or AN solution of a quaternary ammonium salt injected into vpc under our analytical conditions (injection port at 225° and polyphenylether column at 150°) should result, to some extent, in reaction (3). To test this possibility a series of 0.1 M solutions

$$\mathbf{R}_4 \mathbf{N}^+ + \mathbf{X}^- \to \mathbf{R} \mathbf{X} + \mathbf{R}_3 \mathbf{N} \tag{3}$$

of tetra-n-butylammonium salts in DMF was analyzed by vpc. The results are shown in Table 1, where the percentage conversion to tri-n-butylamine indicates the extent to which reaction (3) occurs. It should be noted that the reaction occurs only with anions that are significantly nucleophilic and that there is a qualitative parallelism between the % conversions observed and the nucleophilicities of the anions involved.¹⁴

EXPERIMENTAL

Chemicals. The DMF and AN employed were reagent-grade chemicals distilled from calcium hydride. Succinimide was reagent-grade material from Aldrich Chemical Company. It was dried over P_2O_3 in *vacuo* before use. Technical-grade phthalimide from Eastman Kodak was twice recrystallized from water (m.p. 234-237?). TBAF and TEAF were employed as supporting electrolytes for electrochemical studies. These quaternary ammonium salts were prepared by methods which have been previously described.¹⁵ Purified N₂ (Airco, Inc.) was employed to remove dissolved O₂ and to maintain an inert atmosphere during electrochemical experiments. The N₂ was passed through a column of 8-mesh Drierite to remove residual water and was saturated with the appropriate solvent before passage into the electrochemical cell.

Apparatus and instrumentation. Electrochemical experiments were performed with a Princeton Applied Research Corporation (PAR) Model 170 Electrochemistry System. A divided cell, which was fitted with a 2.3 mm diam Pt disc microelectrode for voltammetric monitoring of the reaction progress, was employed for electrolyses at Pt foil electrodes $(2.3 \times 2.3 \text{ cm})$. The Pt elec-

Table 1. Reaction of tetra-n-butylammonium salts, R₄N⁺X⁻, during vpc analysis

x	Nucleophilic constant ^a	% Conversion to R ₃ N
BF4 ⁻		0
CIO4-	<0	Ō
HSO4-	_	1.9
NO ₃ -	1.03	2.2
Br	3.89	76.0
I-	5.04	79.0
(CH ₂ CO) ₂ N [−]	_	95.4

^aData were taken from Ref. [14].

trodes were treated with chromic acid soln, rinsed with water, and dried before use. A saturated calomel electrode (SCE) was the reference electrode. The SCE was placed into a salt bridge tube which contained KCl aq and which was terminated in a porous cracked-glass tip.¹⁷ The salt bridge tube was placed into the reference-electrode compartment, which contained the appropriate solvent-electrolyte soln and which was also terminated in a cracked glass tip. The tip of the reference-electrode compartment was positioned to within 2-3 mm of the working electrode during voltammetric experiments.

A Varian Aerograph Model 2720 gas chromatograph was employed for product analysis. The instrument was equipped with a thermal conductivity detector and a $6' \times \frac{1}{4}'$ stainless steel column packed with 10% poly-m-phenylether (six ring) on 80-100 mesh HP chromosorb W. The injection port was maintained at 225°, the detector at 275°, and the column temp was either 180° (for analyses of succinimide and N-alkylsuccinimides) or 150° (for tri-n-butylamine determinations). A Perkin-Elmer 237B Grating IR Spectrophotometer was employed to record IR spectra.

Procedures. Electrolyte soins were freshly prepared. A blank voltammogram was scanned with the Pt disc electrode in order to observe the approximate decomposition potential of the supporting electrolyte. Next, a blank electrolysis was carried out using the Pt sheet cathode and an applied potential which was slightly more negative than that employed for an actual experiment; blank electrolyses were continued until the current decayed essentially to zero. A 0.5-ml aliquot from a concentrated succinimide standard soln (0.10 m) was added to the catholyte to produce a soln suitable for voltammetric investigation. Voltammograms were iR compensated and were performed at potential scan rates ranging from 0.020 to 500 V/s; with scan rates faster than 0.20 V/s, oscillographic recording was employed. An additional aliquot of the succinimide standard was added to the cathode soin, and a final voltammogram was recorded. Based upon inspection of this voltammogram, a potential was selected for large-scale electrolysis which was cathodic with respect to the succinimide peak potential, but safely anodic to the supporting electrolyte decomposition potential. Electrolyses were performed at controlled potential until the current decayed essentially to zero. Magnetic stirring was employed during electrolysis. The quantity of charge passed during an electrolysis experiment was determined by integration of the current-time curve with a compensating planimeter.

Tetra-n-butylammonium succinimide. Tetra-n-butylammonium bromide (6.45 g; 0.02 mole), dissolved in water, was treated portionwise, with magnetic stirring, with excess silver oxide (3.5 g; 0.015 mole). Stirring was continued 1 hr after the addition. At this point a test of the supernatant liquid for bromide ion was negative. The mixture was filtered through Cellite. Succinimide (2.0 g; 0.02 mole) was added to the filtrate, and the filtrate was taken to dryness at the water pump. The crystalline salt, without further purification, was made up to 100 ml with freshly distilled AN or DMF to give a 0.2 M solution of tetra-nbutylammonium succinimide.

Tetraethylammonium succinimide. A soln of this salt was prepared from the available 10% aqueous tetraethylammonium hydroxide (Eastman Kodak). An exactly equivalent amount of succinimide was added to the soln; the soln was taken to dryness at the water pump; the salt was made up to the requisite volume with solvent.

Identification and determination of products. Products were analyzed by vpc, either by direct injection, or after acidification with excess fluoboric acid, or after treatment with n-BuBr. Analyzed components included tri-n-butylamine, succinimide, Nethylsuccinimide and N-n-butylsuccinimide. Individual compontents were obtained pure by the deposition of a thin film of material onto a NaCl plate held near the exit port of the vpc. IR spectra obtained with such samples were compared with authentic reference spectra for positive indentification. N-n-butylsuccinimide was prepared by treating succinic acid with n-butylamine according to the method of Hoey and Lester;¹⁸ b.p. 132-135° at 25 mm. The same method was used to prepare N-methylsuccinimde from succinic acid and 40% aqueous methylamine; m.p. 66-68° from acetone-hexane. N-Ethylsuccinimide was prepared by the reaction of potassium succinimide with EtBr in AN; b.p. 117-118° at 25 mm. Standard solns were prepared from authentic chemicals and used to determine the yields of reaction products by comparison of vpc peak areas.

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