Selectivity Modification in Electroorganic Reactions by Periodic Current Control: Electroreduction of Nitrobenzene

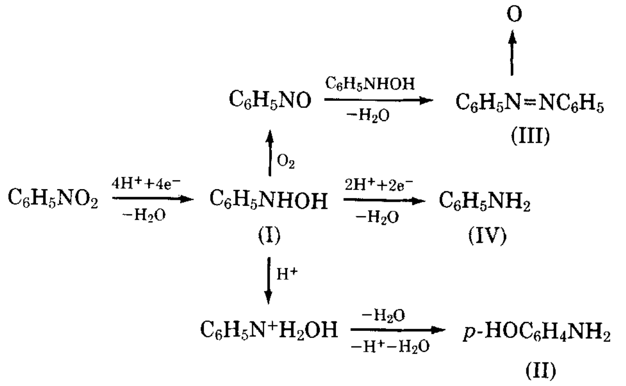
The electroreduction of nitrobenzene in deoxygenated acid solution generates predominantly either *p*-aminophenol or aniline via the common electrochemically generated intermediate, phenylhydroxylamine. Square wave current control increases the reaction selectivity for *p*-aminophenol, which is produced in a chemical pathway from the intermediate over that obtained at the average current of the oscillation. Data collected under electrokinetic-controlled reaction conditions on a planar copper electrode in a water-propanol-sulfuric acid medium show an order of magnitude increase in selectivity at 100 Hz over that measured at the average direct current. The electrode is depolarized under periodic current control which results in lower rates of undesired electrochemical reactions with a consequential increase in chemical product selectivity. Implications and limitations of periodic electrochemical reaction rate control are discussed.

P. S. FEDKIW and J. C. CHAO
Department of Chemical Engineering
North Carolina State University
Raleigh, NC 27695

INTRODUCTION

It has long been recognized that the yield and selectivity of many types of ordinary chemical reactions may be manipulated by imposing a periodic forcing function upon the reactor; for example, reactant concentration or reaction temperature may be periodically controlled to produce yields and selectivities at the stationary state that are unobtainable at the steady state. Unfortunately, it is not practical in an industrial context to impose periodic temperature and reactant concentration variations; furthermore, temperature oscillations are considerably damped by the thermal mass of solvent, reactor wall, and/or catalyst support. However, it is simple to alter the voltage or current in an electrochemical reactor. The double-layer capacitance, the source of "electrical inertia," usually offers negligible attenuation of the imposed waveform. The electroplating industry routinely uses pulse plating in which the current is modulated between a high and low level to improve the morphology of the deposit; nevertheless, it has been unrecognized that the selectivity of electroorganic reactions may be enhanced by periodic electrical control. Since electroorganic reactions typically proceed by a parallel and/or series arrangement of coupled chemical and electrochemical reactions, the rate of the electrochemical steps may be directly manipulated during the reaction by changing either the current or electrode voltage. In addition, the rate of chemical reactions that are dependent on an electrochemically generated reactant, may be indirectly modulated. In this manner, it is possible that the selectivity of the reaction sequence may be tuned by optimal waveform choice. A recent publication (Fedkiw and Scott, 1984) has reviewed the use of periodic control strategies for chemical and electrochemical reactions and presented calculations that illustrate the possible beneficial effect of periodic electrode-voltage manipulation for select reaction sequences under electrokinetic-controlled reaction conditions. In this communication, the experimental results of periodic current control during the electroreduction of nitrobenzene are presented. The data show an increase in selectivity under periodic control in comparison to that obtained at the average steady current.

The electroreduction of nitrobenzene has been well studied (Swann and Alkire, 1980). The six-electron reduction to aniline proceeds by a complex pathway through a number of stable intermediates. In an acidic solution, a simplified version of the reaction sequence is shown below (Pletcher and Marquez, 1980):



The electrochemically generated intermediate I, phenylhydroxylamine, may further react via a chemical rearrangement to II, *p*-aminophenol, or, in the presence of oxygen, may couple to form III, azoxybenzene. In addition, the intermediate may be electrochemically reduced to aniline, IV. If a high production rate of *p*-aminophenol is desired, the intermediate I must concurrently be produced at a large rate. In order to increase the production rate of I, the electrode voltage must be made more cathodic, which increases the rate of undesired electrochemical reactions with a consequent decrease in *p*-aminophenol selectivity. Thus the demand for high production rate of *p*-aminophenol is at the expense of decreased selectivity for this product.

In the work reported here, the current was modulated in a square-wave fashion between a high and low cathodic value. In

---

Correspondence concerning this paper should be addressed to P. S. Fedkiw.
J. C. Chao is currently at Packard Electric, Warren, OH.

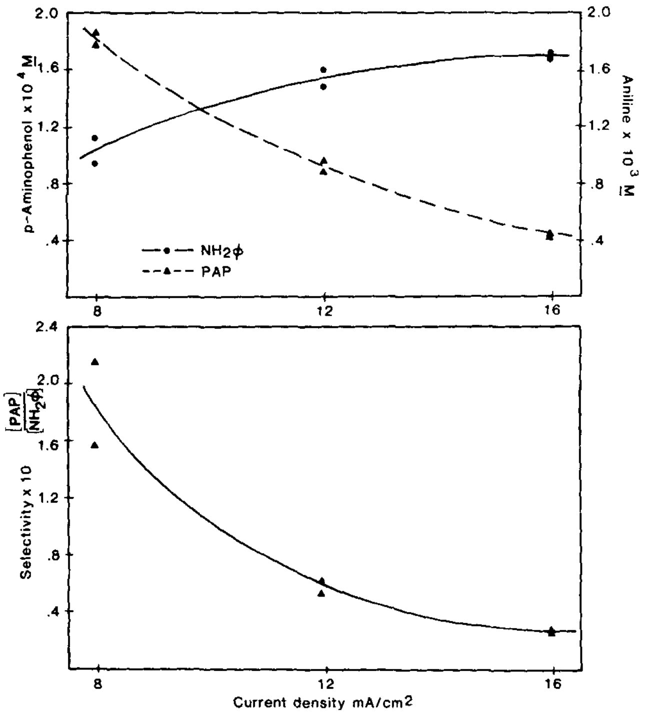


Figure 1. Product concentration and selectivity for electroreduction of nitrobenzene when 172.9 coulombs have been passed under DC control.

this manner, it was postulated that the intermediate, which is produced at a greater value during the high portion of the current, would react in the chemical pathway during the low current portion of the cycle. The net effect of this control strategy would increase the production of *p*-aminophenol at a higher selectivity.

EXPERIMENT

The working electrode was a 1 cm^2 copper foil placed in a glass H-cell with a Nafion separator between the two compartments. The electrolyte was a 50/50 (vol. %) water-propanol mixture with 1 M H_2SO_4 as the electrolyte. The initial nitrobenzene concentration was 0.05 M and the temperature was maintained at 22°C. The working electrode compartment was well agitated to reduce mass transfer limitations. Two types of experiments were performed: steady current control (DC) and square wave current control (AC). In all experiments the conversion of nitrobenzene was maintained below 5%, and the reaction products were quantitatively analyzed by HPLC. Further experimental details are available (Chao, 1984).

RESULTS AND DISCUSSION

In both DC and AC experiments, the charge passed was maintained at 172.9 coulombs. Under this protocol, the amount of electron "reagent" added was common to all experiments; consequently, at the higher currents a shorter period of time was required. No attempt was made to find waveforms or reaction conditions to maximize the selectivity and production of *p*-aminophenol; rather, the intent of the experiments was to demonstrate the inherent enhancement on reaction outcome that can be obtained under an imposed periodic current over DC control.

Reaction Rates with Steady Current

Figure 1 shows the concentration of aniline and *p*-aminophenol measured after passage of 172.9 coulombs. As anticipated, the concentration of *p*-aminophenol decreased with an increase in the current while the concentration of aniline increased; consequently, the selectivity for *p*-aminophenol decreased. During the time frame of the experiment at 8 mA, no change in the electrode polarization—measured with a saturated calomel reference electrode—was observed. However, a 300 mV cathodic polarization increase occurred during the course of the run when 16 mA was used.

Reaction Rates with Square Wave Current

The cathodic current was modulated in a square wave fashion from a high of 16 mA to a low of 8 mA at a 50% duty cycle (equal time at high and low current) for an average current of 12 mA.

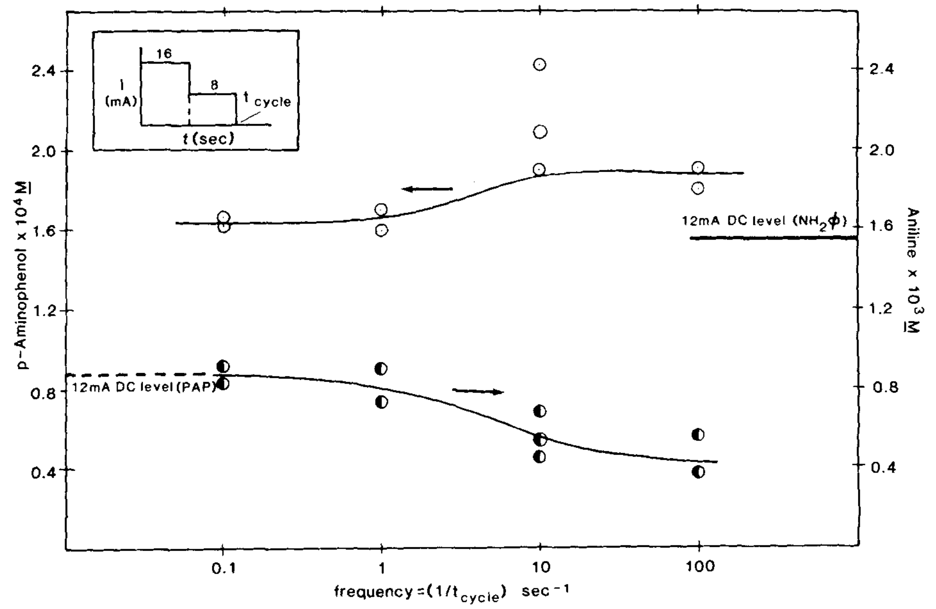


Figure 2. Product concentration for electroreduction of nitrobenzene under square wave current modulation as a function of the cycle time when 172.9 coulombs have been passed. Average current of modulation is 12 mA; product concentrations at this current under DC control are also indicated.

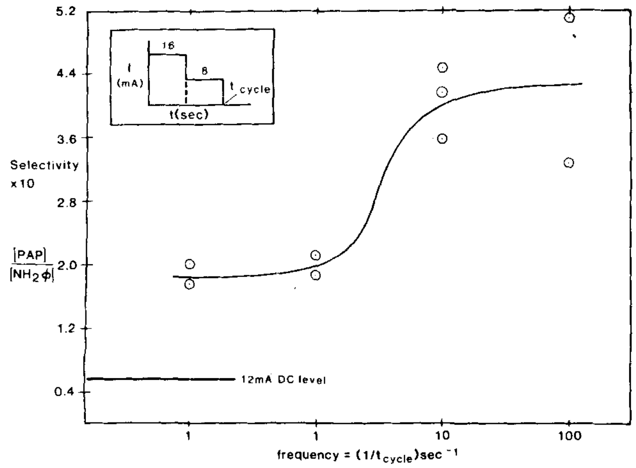


Figure 3. Selectivity of square wave current electroreduction of nitrobenzene as a function of the cycle time when 172.9 coulombs have been passed; selectivity under DC control at the average current of 12 mA is also indicated.

Shown in Figures 2 and 3 are the resulting product concentrations and the *p*-aminophenol selectivity, respectively. The cycle time was varied from 10 s to 10 ms while maintaining the duty cycle at 50%, as shown in the inset on the figures. Also indicated in the figures are the concentrations and selectivity at the average current. Even at the lowest frequency, the selectivity was a factor of 3 above that measured at the average current. At the highest frequency, the selectivity was an order of magnitude above that measured at 12 mA. A significant depolarization of the electrode was measured under periodic current-controlled conditions; for example, at 100 Hz the electrode was depolarized 500 mV from that value at the DC average current. Since the average voltage is lower under the periodic control strategy, the electrochemical follow-up reactions involving the intermediate are maintained at a lower value; hence, the phenylhydroxylamine may more likely react via a chemical pathway to the desired *p*-aminophenol.

SIGNIFICANCE AND CONCLUSIONS

Reaction selectivity in electrochemical reactions that involve coupled chemical and electrochemical reaction pathways may be conveniently modified by modulating the electrical state of the interface during the reaction. Either the electrode voltage or cell current may be manipulated. Since electroorganic reactions typically proceed by series and/or parallel arrangement of chemical and electrochemical reaction steps, they are prime candidates for reaction-selectivity tuning. Optimal waveforms may be calculated a priori if detailed knowledge of the electrode kinetics is available. However, mass transfer limitations and nonuniform potential distributions, which exist in any industrially significant reactor, may diminish the enhancement effect. The increase in reaction selectivity and yield that may be obtained under modulated reaction rate conditions would result in lower capital costs for the reactor and decreased product separation costs; but the decrease in these costs must be balanced with the increased power costs to affect the modulation.

The concept of modifying the selectivity of an electroorganic reaction by modulated current control has been demonstrated for the reduction of nitrobenzene under electrokinetic-controlled reaction conditions. The results demonstrate that a significant increase in the production of *p*-aminophenol is possible, along with a simultaneous decrease in the production of aniline. It is clear that not all electroorganic reaction sequences will be positively affected by periodic reaction control. However, this control strategy, when favorable, may enhance the reaction outcome significantly enough to make an electrochemical processing step competitive with an alternative chemical process.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant No. CPE-8006703.

LITERATURE CITED

Chao, J. C. H., "Selectivity Changes in the Modulated Electroreduction of Nitrobenzene, M.S. Thesis, North Carolina State Univ. (1984).

Fedkiw, P. S., and W. Scott, "Selectivity Changes in Electrochemical Reaction Sequences by Modulated Potential Control," *J. Electrochem. Soc.*, **131**, 1,304 (1984).

Pletcher D., and J. Marquez, "A Study of the Electrochemical Reduction of Nitrobenzene in Acidic Propanol/Water," *J. Appl. Electrochem.*, **10**, 567 (1980).

Swann S., and R. Alkire, Bibliography of Electroorganic Syntheses, Electrochemical Soc., Princeton, NJ (1980).

Manuscript received Mar. 20, 1984; revision received July 24, 1984 and accepted July 20.