27. S. Menezes, L. F. Schneemeyr, and H. J. Lewerenz, *Appl. Phys. Lett.*, **38**, 949 (1981).
28. L. Peraldo Bicelli and G. Razzini, *Surf. Technol.*, **22**, 115 (1984).
29. R. Noufi, R. Axton, C. Herrington, and S. K. Deb, *Appl.*
30. L. Fornarini and B. Scorsati, *Electrochim. Acta*, **28**, 667 (1983).
31. O. P. Bahl, E. L. Evans, and Y. M. Thomas, *Surf. Sci.*, **8**, 473 (1967).
*Phys. Lett.*, **45**, 668 (1984).

# High-Pressure Electrochemical Oxidation of Benzene at a Lead Dioxide Electrode in Aqueous Bisulfate Solutions at 25° to 250°C

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## ABSTRACT

The oxidation of benzene at a lead dioxide electrode which produces predominantly benzoquinone, maleic acid, and carbon dioxide, has been investigated in aqueous NaHSO$_4$ solutions as a function of temperature up to 250°C. An increase in the benzene concentration does not increase the concentration of benzoquinone formed at high temperature, which is different from the behavior at 25°C. The formation of biphenyl at high temperature was also discovered. A novel type of single-pass flow reactor for studying high temperature electrochemistry is described.

The oxidation of benzene to benzoquinone at a lead dioxide electrode in aqueous sulfate solutions is limited by the low solubility of benzene in water. Clarke *et al.* have determined a reaction order with respect to benzene of 2 (1). Benzene solubility in water increases significantly with increasing temperature; the two fluids become miscible at 297°C at a pressure of 243 bar (2). This study examines the effect of increasing temperature and increasing benzene concentration on the electrochemical oxidation of benzene on lead dioxide in the temperature range 25°-250°C.

Supercritical water has a combination of low dielectric constant and high dipole moment that make it useful for a number of novel chemical applications. Water has a dipole moment of 1.84 debye, and at ambient conditions it is extensively hydrogen bonded. This gives rise to a high dielectric constant, 78 at 25°C, making water an excellent solvent for ions and a poor one for nonpolar species. High temperature disrupts the hydrogen bonding and correlated orientation of water molecules (3) and decreases the density and thereby lowers the dielectric constant to 5.2 at the critical point (374°C, 221 bar) (4). Because of the low dielectric constant, water in the critical region is an excellent solvent for organic molecules. The water dipoles still orient in the vicinity of an ion, however, and produce a locally high dielectric constant, so strong electrolytes remain dissolved and dissociated in supercritical water. The simultaneous solvation of both polar and nonpolar molecules makes supercritical water a powerful solvent. The MODAR process takes advantage of this superior solvent power in using supercritical water as a reaction medium for the destructive oxidation of organic waste (5). Other workers have investigated the use of supercritical water at milder conditions to clean and liquify coal (6), and to hydrolyze plant material into useful fuels (7).

In a previous paper, we described electroanalytical measurements made in supercritical water at temperatures up to 390°C (8). An electrochemical cell was developed to operate at the extreme temperature and pressure of supercritical water. In addition, the voltammetric behavior of water, KBr, KI, and hydroquinone was studied, and the diffusion coefficients of I$^-$ and hydroquinone were measured. Building on this experimental background, the present work is an expansion into the area of high-temperature electro-organic synthesis, specifically benzene oxidation. In supercritical water, high concentrations of nonpolar materials can be combined with strong electrolytes in a one-phase system, and this presents the possibility of synthetic routes that are not hindered by mass transfer across a phase boundary. Although temperatures above 250°C are not reported here, the apparatus and experimental procedures described could be used up to 375°C with only minor modification.

The electrochemical oxidation of benzene was first studied near the end of the last century (9) and has been discussed frequently in the literature (1, 10-14). Work through 1976 has been summarized by Clarke *et al.* (1). The desired product from the oxidation is benzoquinone, which can then be reduced to hydroquinone. Hydroquinone is used as an anti-oxidant in the manufacture of rubber and other products. Other major products from the oxidation are maleic acid and carbon dioxide.

The specific overall electrode reactions involved in oxidizing benzene are shown in Fig. 1. The complete conversion of benzene to carbon dioxide requires the removal of 30 electrons and the participation of 12 water molecules. This full oxidation can occur readily at a platinum electrode (15). Lead dioxide is the only reported electrode material that produces large quantities of benzoquinone or maleic acid. A lead dioxide electrode will perform the first stage oxidation to benzoquinone readily in acidic sulfate media; however, the yield and current efficiency vary greatly depending on the specific conditions of electrolysis. As the concentration of benzoquinone builds in the solution, the benzoquinone is usually oxidized further to maleic acid, accompanied by two moles of carbon dioxide. Clarke *et al.* (1) report that at very low over-voltage, the benzoquinone is not oxidized further. The one-step oxidation of benzene to maleic acid was studied extensively by Ito *et al.* (13). This pathway is important under most reaction conditions. Few previous workers analyzed the carbon dioxide generated during oxidation, and no one has discussed the pathway by which it is formed. This study shows that single-step oxidation of benzene to carbon dioxide can occur on lead dioxide, especially at high temperature. (The term single-step is used here to mean that once benzoquinone or maleic acid is formed and desorbed

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*Electrochemical Society Active Member.
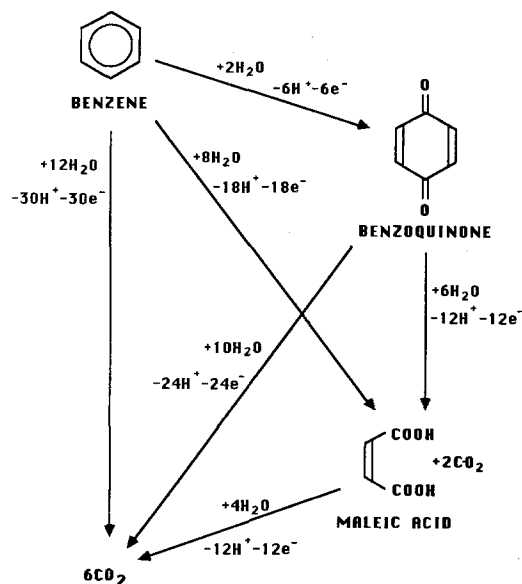**Electrochemical Society Student Member.

Fig. 1. Oxidation reactions of benzene on a lead dioxide electrode. Adapted from Ito *et al.* (13).

from the electrode, they are not further oxidized. No doubt, the oxidation of benzene adsorbed on the electrode involves many elementary steps. This work however, is only concerned with the net result of each encounter between a benzene molecule and the electrode.)

This work differs from previous studies of benzene oxidation in that a single-pass flow reactor is used instead of a stirred tank and the temperature range is much larger (12, 13). The reactant volume used in these previous studies was relatively large, *e.g.*, 90-1500 cm$^3$, so long runs were necessary to build up measurable quantities of product. The products in solution were continually exposed to further oxidation. In the present apparatus, the residence time of the electrolyte in the electrode region is about 2s. The electrode area is large enough so that measurable conversion is achieved in a single pass. Products from the initial oxidation are quickly removed from the electrode with little opportunity to be readsorbed and undergo further oxidation. Thus, analysis of the results is somewhat simplified, since the products are probably formed predominantly by single-step oxidation of benzene; only three of the six reactions shown in Fig. 1 need be considered.

## Experimental

*Apparatus.*—The experiments were performed in a high-temperature and -pressure, two-electrode flow cell (Fig. 2). The cell body is a 0.635 cm (¼ in.)-od by 0.318 cm (⅛ in.)-id, 30 cm (12 in.)-long alumina tube (99.8% Al$_2$O$_3$). Al$_2$O$_3$ was chosen to avoid corrosion and spurious electric fields within the cell. The tube is connected to the endblocks using stainless steel Swagelok fittings with Teflon ferrules. The electrode leads pass through Teflon compression fittings, which have been described previously (8). All metal parts are either 316 stainless steel or Hastelloy Alloy C.

The complete experimental system, including the pump and feed vessels, is shown schematically in Fig. 3. The cell is fed from the saturator, a one-liter Autoclave Engineers'
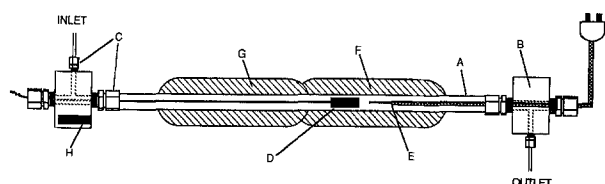


Fig. 2. Diagram of high-temperature cell for electrosynthesis: (A) ¼ in.-od alumina tube; (B) Hastelloy Alloy C endblock; (C) 316 SS Swagelok fittings; (D) Pb working electrode; (E) Pt counterelectrode and type K thermocouple; (F) main cell heater (Nichrome wire coil); (G) preheater (Nichrome wire coil); (H) endblock heater (cartridge heater).
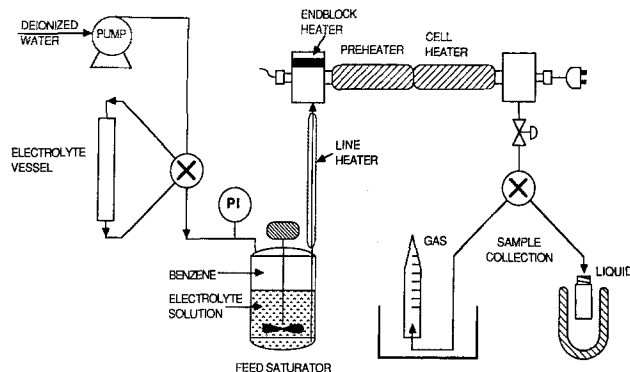


Fig. 3. Schematic of apparatus for high-temperature, high-pressure electrosynthesis.

stirred tank reactor. The saturator can be heated to 200°C in order to increase the concentration of benzene in the feed. The flow is controlled by a Milton Roy Minipump (Model 2396), which provides fresh electrolyte to the saturator.

*Electrodes.*—The working electrode was constructed by welding a 1 cm piece of platinum onto a tantalum wire. The platinum was welded to and wrapped with 0.05 cm thick lead foil (99.9995% Pb from AESAR division of Johnson Matthey), so that the platinum was completely covered. The lead was sealed and trimmed with a soldering iron. The resulting electrode was 1.8 cm long, 0.3 cm wide, and 0.15 cm thick. Before use the electrode was rinsed in 5N nitric acid.

In the cell, the current path is along the axis of the cell, and because of solution resistance, only a portion of the working electrode participates in the oxidation. When the working electrode is oxidized in the cell, lead dioxide forms from the tip to a location about 0.5 cm further away from the counterelectrode. Therefore, this is the area which is active during electrolysis, while the remaining portion passes very little current.

The counterelectrode consisted of a platinum wire welded to the Inconel 600 sheath of an ungrounded thermocouple. Placement of the thermocouple in the flowing stream was necessary to achieve accurate and stable temperature control. Since the counterelectrode was the reducing electrode in these experiments, there was minimum corrosion of the thermocouple sheath during the project.

For cyclic voltammetry, a lead electrode (0.15 cm diam) sealed in glass was used. A silver wire electrode was inserted into the heated portion of the cell as a reference electrode, and a counterelectrode was added downstream. Details of this procedure have been discussed previously (8).

*Procedure.*—The electrolyte vessel was filled with 290 ml of 0.2M NaHSO$_4$ solution saturated with benzene at room temperature. During long experiments, a second electrolyte vessel could be filled and exchanged with the first one with only a brief interruption of the electrolysis. The saturator was filled with 300 ml of benzene and 700 ml of 0.2M NaHSO$_4$ solution. The NaHSO$_4$ was reagent grade and the benzene was spectroscopic grade. Both chemicals were used as received. All water was purified with a Millipore, Milli-Q reagent water system.

In preparation for experiments with the feed benzene concentration higher than the 25°C saturation value, the saturator was heated to the desired temperature, and the contents mixed to saturate the aqueous phase. The phases were then allowed to separate before filling the cell. The flow of electrolyte into the saturator was small compared to the saturator volume, so benzene in the feed was not diluted during an experimental run.

The feed pump was set to the desired flow rate, and the outlet valve was adjusted to give the desired back pressure. Because of the low flow rate, 1.3-1.4 ml/min, the outlet valve had to be operated very near shutoff where its performance was not consistent. The system pressure had

to be continually monitored, and the outlet valve adjusted. Any system pressure that was at least 7 bar above the solution saturation pressure and relatively stable was considered acceptable. After the cell had been flushed with a few volumes of solution, the effluent was analyzed to insure that the feed contained no impurities that would interfere with the measurement of benzoquinone or maleic acid.

All experiments were done at constant current. This made calculation of current efficiency possible without the use of a coulometer. The narrow current path between the two electrodes gives rise to a large cell resistance, so that constant voltage experiments would have little meaning. The cell potential was monitored during the electrolysis and was relatively constant at any particular set of conditions. A value of 7.5V was typical at 25°C while it dropped to about 6V at 250°C due to lower solution resistance.

The temperature of the solution at the working electrode was maintained with an Autoclave Engineers (Erie, PA) proportional-integral temperature controller (Model 520). The temperatures at the preheater, endblock heater, and transfer line heater, were monitored with thermocouples and controlled with Powerstat variable transformers. In experiments conducted with the saturator at room temperature, the preheater was adjusted to between 10° and 25°C below the desired electrolysis temperature and the endblock heater approximately 25°C below the preheater. This minimized the heat load in the reaction zone, and helped stabilize the temperature at the working electrode. In experiments conducted with the saturator heated, the heaters between the saturator and the reaction zone were adjusted to temperatures between that of the saturator and the cell.

After all of the experimental parameters had been set, the system was given time to reach equilibrium. Three samples were collected to determine the reaction products: (*i*) a small liquid sample for immediate analysis of benzoquinone and maleic acid; (*ii*) a timed liquid sample, frozen in a Dry Ice-isopropyl alcohol bath for determination of benzene concentration and verification of flow rate; and (*iii*) a timed gas sample for determination of $CO_2$.

The operation of the saturator was tested by using it to measure the solubility of benzene in pure water. The results are compared with the measurements of Tsonopoulos and Wilson in Fig. 4 (6). The average deviation between these measurements and the literature values is 20%. This confirmed that the saturator was mixing the aqueous and organic phases well without entrainment of benzene in the feed.

*Analysis.*—The concentrations of the soluble liquid products were measured using a high-pressure liquid

chromatograph (HPLC) with a C-18 stationary phase and a variable wavelength detector. Tertiary butyl ammonium hydroxide was added to the mobile phase to ion pair with the maleic acid.

Benzene concentration in the reactor effluent was also determined by HPLC. A volume of 5.0 ml of methanol was added to the frozen samples before bringing them to room temperature. The use of methanol induces total miscibility and lowers the partial pressure of benzene above the solution, which limits the loss of benzene during handling. The added methanol contained 1.96 m$M$ nitrobenzene, which served as an internal standard. The concentrations of benzene and nitrobenzene in the mixed sample were determined. From these data, the volume and concentration of benzene in the original frozen sample were calculated. Since the samples were timed, the sample volume could be used to calibrate the flow rate of the feed pump.

Analysis of carbon dioxide proved difficult because much of the carbon dioxide was dissolved in the liquid effluent. The chosen procedure is as follows. The samples were collected in inverted, 25 ml, graduated centrifuge tubes. The displaced liquid was 2.12$M$ NaHSO$_4$, which is sufficiently dense so that all liquid and gas from the reactor were collected. The tubes were capped with a rubber septum, inverted and stored. The duration of sample collection was set so that the sample tube contained an equal volume of liquid effluent and the original 2.12$M$ NaHSO$_4$ solution. After mixing, the liquid in the sample tube was a 1.22$M$ solution of NaHSO$_4$. The solubility of carbon dioxide in this liquid is known to be 0.5 ml/ml (17). After allowing the gas and liquid to reach equilibrium, the amount of $CO_2$ in the gas phase was determined by gas chromatography, and the total amount of $CO_2$ in the sample was calculated from Henry's law.

## Results and Discussion

*Feed saturated at room temperature.*—The amounts of benzoquinone, maleic acid, and carbon dioxide generated by oxidation of benzene on a lead electrode at various temperatures are shown in Fig. 5. These are data from a single days run with feed saturated at 25°C. The benzene concentration in the feed was 8.5 m$M$. The data presented in this figure, as well as results from other days, are given in Table I.

There is some variability in the amount of product produced on the different days. These runs were made with different electrodes. Though every effort was made to construct identical electrodes, the amount of benzoquinone and maleic acid produced at 25°C varied between electrodes. In examining the variation in yield of these partial oxidation products with changing temperature, there were definite trends in all sets of data, and it is from these trends that conclusions may be made.

The production of benzoquinone was always highest at 25°C. There was a steady decline up to about 150°C, after which the amount levels off at a minimal value. Clarke *et al.* (1) postulate that the oxidation of benzene to ben-
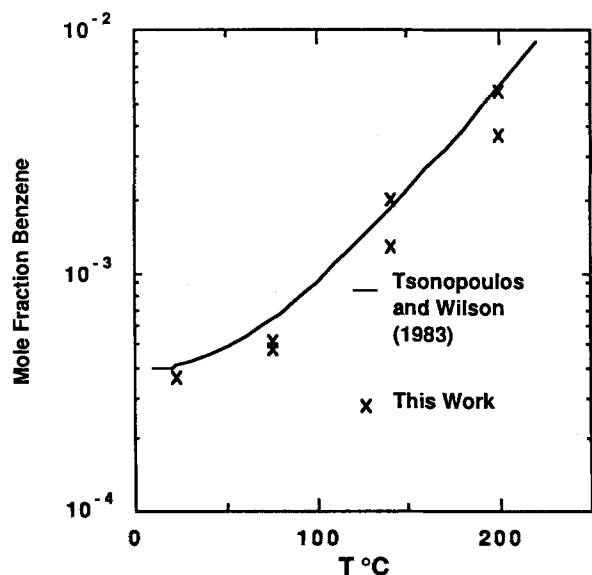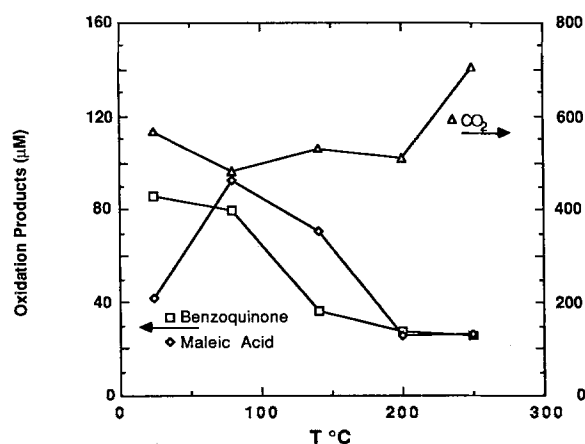


Fig. 4. Solubility of benzene in water vs. temperature. Data obtained with this apparatus are compared to the empirical relation derived by Tsonopoulos and Wilson (16).



Fig. 5. Products from the oxidation of benzene at various temperatures on lead dioxide. Feed: 0.2M NaHSO$_4$ saturated with benzene at 25°C (8.5 mM benzene). Flow rate = 1.3 ml/min. Current = 10 mA.

Table I. Products from the oxidation of benzene at various temperatures. Concentrations are based on feed volume. Feed: $0.2M$ $NaHSO_4$, flow rate = 1.3 ml/min, current = 10 mA

| | | | Oxidation products ($\mu M$ relative to liquid feed) | | | Current efficiency | | |
|---|---|---|---|---|---|---|---|---|
| | | $T°C$ | Benzoquinone | Maleic acid | $CO_2$ | Benzoquinone (%) | Maleic acid (%) | All products (%) |
| Benzene concentration = 9.2 mM | Rising temperature | 25 | 43 ± 4 | 85 ± 9 | 210 ± 40 | 6 | 34 | 44 |
| | | 100 | 25 ± 2 | 111 ± 11 | 420 ± 80 | 3 | 44 | 69 |
| | | 150 | 7 ± 1 | 59 ± 6 | 590 ± 120 | 1 | 23 | 76 |
| | | 200 | 7 ± 1 | 47 ± 5 | 650 ± 130 | 1 | 19 | 81 |
| | | 250 | 6 ± 1 | 43 ± 4 | 470 ± 140 | 1 | 17 | 60 |
| | Falling temperature | 150 | 7 ± 1 | 56 ± 6 | 720 ± 140 | 1 | 22 | 90 |
| | | 100 | 30 ± 3 | 102 ± 10 | 640 ± 130 | 4 | 40 | 92 |
| | | 25 | 28 ± 3 | 62 ± 6 | 250 ± 50 | 4 | 25 | 42 |
| Benzene concentration = 8.5 mM | Rising temperature | 25 | 86 ± 9 | 42 ± 4 | 570 ± 230 | 11 | 16 | 77 |
| | | 80 | 80 ± 8 | 93 ± 9 | 480 ± 100 | 10 | 35 | 76 |
| | | 140 | 36 ± 4 | 71 ± 7 | 530 ± 110 | 5 | 27 | 72 |
| | | 200 | 28 ± 3 | 26 ± 3 | 510 ± 140 | 3 | 10 | 61 |
| | | 250 | 26 ± 3 | 26 ± 3 | 700 ± 140 | 3 | 10 | 81 |

zoquinone proceeds through a chemical reaction between benzene and lead dioxide. In addition, Clarke *et al.* propose that the other oxidation products are produced when benzene is attacked by some type of oxygen radical on the electrode. Wabner and Grambow have found that relatively high concentrations of hydroxyl radicals (OH·) are formed during oxygen evolution at a lead dioxide electrode (18), so OH· is probably the reactive species called for in the Clarke model. Since lead dioxide is known to decompose in air when heated above 300°C (19), this model may explain the decrease in benzoquinone formation with increasing temperature.

A series of cyclic voltammograms was made to study lead dioxide formation in solution as a function of temperature. There are two electrochemical reactions that take place as the potential is scanned positive. The surface of the electrode is converted to lead dioxide

$$PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$$
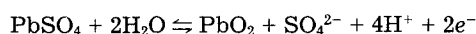
and water is oxidized to oxygen

$$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$$
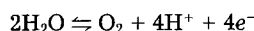
As can be seen in Fig. 6, at 25°C, the surface oxidation forms a distinct wave at about 2.0V where the rate of oxygen evolution is small. Therefore, benzene oxidized at this temperature will encounter $PbO_2$ on the electrode surface. At 100° and 200°C, the surface oxidation wave moves very far positive and merges into the oxygen evolution current. This is a result of $PbO_2$ decomposition through the following reaction

$$PbO_2 + SO_4^{2-} + 2H^+ \rightarrow PbSO_4 + 1/2\ O_2 + H_2O$$
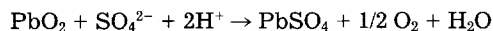
The reaction is very slow at 25°C, but becomes important at higher temperatures. Since the $PbO_2$ is continually breaking down, the surface oxidation reaction must be driven at a faster rate (*i.e.*, more positive potential) to cover most of the surface with $PbO_2$ and produce a "peak" in the voltammogram. The implication of this with regard to benzene oxidation is that at high temperature, the electrode surface is not completely covered by lead dioxide. Therefore there is less $PbO_2$ available for the production of benzoquinone, while the other reactions involving oxygen species adsorbed on the electrode surface continue.

Upon cooling, the electrode regains most of its selectivity toward benzoquinone, as shown in Table I. It is not known why the activity of the electrode is not completely restored at lower temperature, but the formation of a film over part of the electrode is considered likely.

The generation of maleic acid from benzene is enhanced by increasing the temperature above 25°C. The maximum yield of maleic acid occurs around 100°C. A further increase in temperature lowers the yield until a minimum is reached asymptotically at 200°C. The formation of maleic acid involves breaking the aromatic ring which stabilizes benzene. A considerable amount of activation energy must be supplied for oxygen on the electrode to break the ring. This accounts for the region of increasing maleic acid formation with increasing temperature. At higher tempera-

tures, total oxidation to carbon dioxide becomes fast, and the amount of maleic acid produced drops.

There is no discussion in the literature as to why maleic acid should be the major significant product, and others, *e.g.* phenol, are almost absent. The carboxylic acid groups could be oxidized under the conditions necessary to break open the ring. A possible justification for the lack of further oxidation of maleic acid is that this species is less strongly held than benzene, benzoquinone (or other aromatics) on the electrode surface and desorbs. At temperatures above 100°C, the oxidation rate of organic molecules near the surface becomes fast enough to overcome this
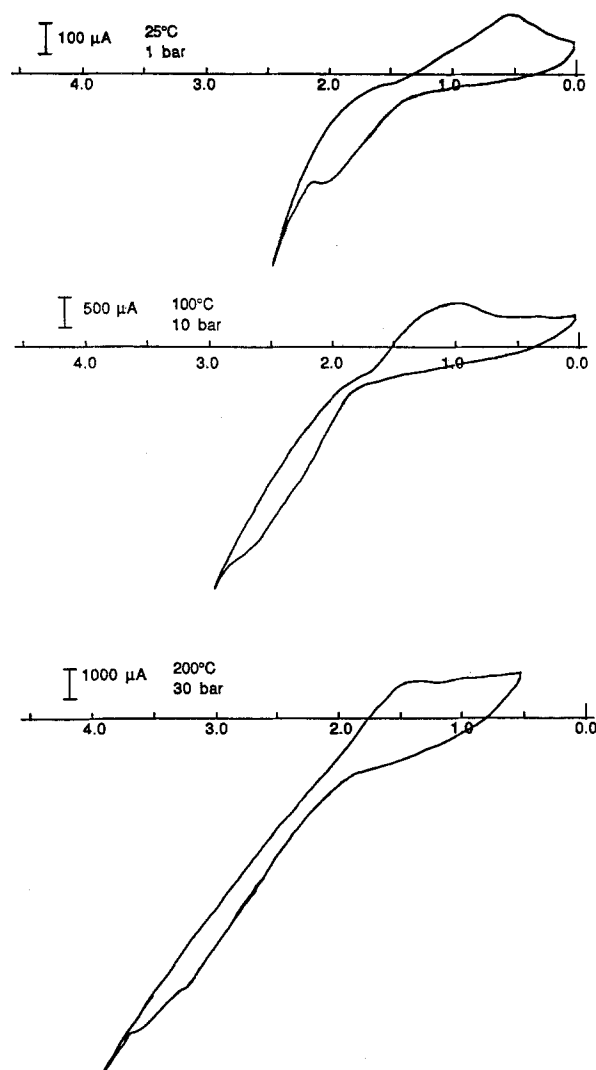


Fig. 6. Cyclic voltammograms of a lead electrode in $0.2M$ $NaHSO_4$. Electrode area = $1.8 \times 10^{-2}$ cm². Scan rate = 1 V/s.

rapid desorption, and the net production of maleic acid drops.

As stated above, the measurement of carbon dioxide was the most difficult of the analyses to perform. The analysis was necessary in order to establish a current efficiency for the consumption of benzene. As can be seen in Table I, this current efficiency was always above 42%, indicating that benzene oxidation was always one of the major electrode reactions in the experiments. Table I also shows individual current efficiencies for the production of benzoquinone and maleic acid and reemphasizes the effect of temperature on their formation.

Though there is significant uncertainty in some of the carbon dioxide measurements, a general trend can be seen in the data of Fig. 5 and Table I. Carbon dioxide production rises with increasing temperature. This fits the hypothesis presented for the behavior of maleic acid with temperature, and the knowledge that high temperature should favor complete oxidation of benzene.

*Feed saturated at high temperature.*—Successful operation of the apparatus with the saturator at high temperature proved to be very difficult. The solution in the saturator becomes much more compressible when heated. This made it much harder to adjust the outlet valve to maintain the system at a stable flow rate, which was necessary for the electrochemical processes to reach steady state. Still sufficient data were obtained to conclude that with the electrode at high temperature, increasing the benzene concentration of the feed did not increasse the production of benzoquinone. Figure 7 compares the results of runs using feed saturated with benzene at 25°C with runs that used feed saturated at higher temperatures. In both cases, with the cell at 140° and at 200°C, the amount of benzoquinone produced drops slightly at the higher benzene concentration, though at 200°C the change is of the order of the accuracy of the measurement. The reason for this drop is not known, but it is clear that increasing the benzene concentration does not increase benzoquinone yield at high temperature.

Apparently, at 140°C and above, the electrode character has changed so that the reaction products are not dependent on benzene concentration. The cyclic voltammetry shows that $PbO_2$ is unstable at these temperatures, so the predominant reaction mechanism would be direct attack of benzene by oxygen radicals on the electrode surface. It was hoped that high benzene concentrations would saturate the electrode surface and limit the degree of oxidation so that more benzoquinone would be produced, but this is not the case.

*Biphenyl.*—A series of preliminary experiments were performed with a two-phase flow of benzene and water. The benzene layer was analyzed by gas chromatography (GC), and a peak with higher molecular weight than ben-

**Table II. Conditions necessary for the formation of biphenyl from benzene in 0.2M NaSO₄ solution. (+) Biphenyl formed at these conditions. (−) Biphenyl not formed. (Blank) No data**

| Experimental conditions | Temperature | | | |
|---|---|---|---|---|
| | 25°C | 140°C | 200°C | 300°C |
| Electrolysis of a two-phase mixture of benzene and 0.2M NaSO₄. | − | | + | + |
| Electrolysis of 0.2M NaSO₄ saturated with benzene. | − | − | + | |
| Two-phase mixture of benzene and 0.2M NaSO₄ saturated with air at 30 bar. Electrodes removed from cell. | − | | | + |
| Single-phase solution of 0.2M NaSO₄ saturated with benzene and air at 1 bar. No current. | − | | − | |

zene was noted. The peak was identified as biphenyl using GC/mass spectrometry. An analytical procedure for determination of biphenyl in aqueous or organic solutions using HPLC was then established.

A series of experiments was performed to determine what conditions were necessary for the formation of biphenyl and a possible mechanism for the reaction. A summary of the results is given in Table II. It is apparent from the data that the reaction does not proceed below 200°C. The other important point is that the reaction is not electrochemical, but involves oxygen in solution. Based on this, the following reaction is proposed

$$2C_6H_6 + 1/2\ O_2 \rightarrow C_{12}H_{10} + H_2O$$
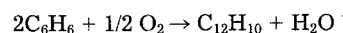
The reaction may take place in solution, or may be catalyzed by the alumina walls of the cell. No products of higher molecular weight, such as terphenyl, were found. Since this project was primarily concerned with electrochemical reactions, there was no further investigation of this reaction.

## Conclusions

As temperature is increased, $PbO_2$ decreases its selectivity toward partial oxidation of benzene. The first stage oxidation product, benzoquinone, is most efficiently produced at 25°C. Current efficiencies from 6 to 10% were found at 25°C, under the conditions described in this study. Higher efficiencies have been reported previously (1), but the electrochemical cells and experimental conditions used were not suitable for high temperature work.

Production of maleic acid, the second major product from the oxidation of benzene, is enhanced by increasing the cell temperature above ambient. In the range 80°-100°C, current efficiency for the production of maleic acid averaged 40%, *vs.* 25% at 25°C. Increasing the cell temperature above 100°C causes a drop in the amount of maleic acid recovered, as the rate of oxidation to $CO_2$ proceeds more quickly.

At higher temperatures, 140°-250°C, the oxidation of benzene on a lead dioxide electrode proceeds rapidly to $CO_2$. Only small amounts of benzoquinone and maleic acid are recovered in the liquid products. Increasing the concentration of benzene in the feed, by saturating the feed at higher temperatures, did not enhance, and may have been detrimental to, the formation of benzoquinone and maleic acid. At ambient temperature, the oxidation of benzene to benzoquinone is strongly dependent on benzene concentration (1), but at high temperature, the effect of increased benzene concentration is more than offset by the reduction in electrode selectivity.

In addition to the electrochemical reactions studied, a nonelectrochemical reaction was discovered. At 200°C and above, in the presence of oxygen, benzene is coupled to produce biphenyl. The proposed mechanism is a partial oxidation of benzene to produce biphenyl and water. No higher molecular weight products such as terphenyl were identified, but since these are practically insoluble in aqueous solution, it is unknown whether any are formed.
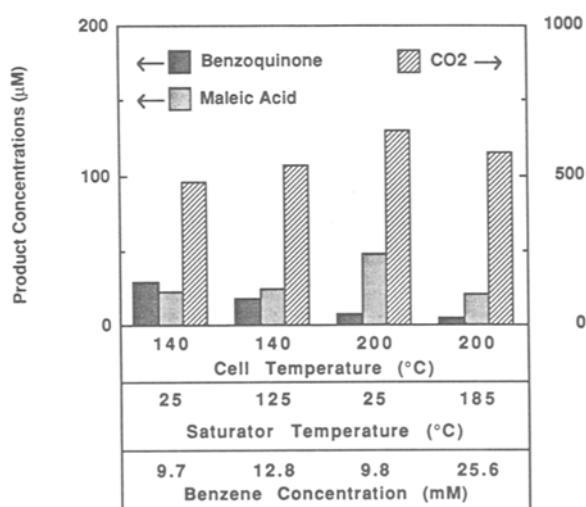


**Fig. 7. Effect of benzene concentration and temperature on product distribution from oxidation on lead dioxide. Feed: 0.2M NaHSO₄. Flow rate = 1.3 ml/min. Current = 10 mA.**

Though operation at high temperature was found to be detrimental to the yield of benzoquinone from benzene oxidation, the electrochemical equipment described here can be used to study a wide range of high temperature aqueous processes, both electrochemically induced or monitored. The potential of chemical syntheses involving high concentrations of nonpolar organics in water has received little attention and holds much promise for future discoveries.

### REFERENCES

1. J. S. Clarke, R. E. Ehigamusoe, and A. T. Kuhn, *J. Electroanal. Chem.*, **70**, 333 (1976).
2. J. P. Connolly, *J. Chem. Eng. Data*, **11**, 13 (1966).
3. E. U. Franck, "Struct. Water Aqueous Solutions, Proc. Int. Symp.," 49-73 (1974).
4. M. Uematsu and E. U. Franck, *J. Phys. Chem. Ref. Data*, **9**, 1291 (1980).
5. M. Modell, U.S. Pat. 4,338,119.
6. S. H. Townsend and M. T. Klein, *Fuel*, **64**, 635 (1985).
7. M. J. Antal, C. P. DeAmeida, W. S. Mok, S. V. Ramayya, and J. C. Roy, Paper presented at the 109th National Meeting of the American Chemical Society, Chicago, September 1985.
8. W. M. Flarsheim, Y. Tsou, I. Trachtenberg, K. P. Johnston, and A. J. Bard, *J. Phys. Chem.*, **90**, 3857 (1986).
9. A. Renard, *Compt. Rend.*, **91**, 175 (1880).
10. F. Fichter and R. Stocker, *Ber.*, **47**, 2003 (1914).
11. A. Seyewetz and G. Miodon, *Bull. Soc. Chim. Fr.*, **33**, 449 (1923).
12. K. S. Udupa, G. S. Subramanian, and H. V. K. Udupa, *Bull. Acad. Pol. Sci.*, **9**, 45 (1961).
13. S. Ito, K. Sasaki, Y. Murakami, and H. Shiba, *Denki Kagaku*, **40**, 733 (1972).
14. B. Fleszar and J. Ploszynska, *Electrochim. Acta*, **30**, 31 (1985).
15. J. O' M. Bockris, H. Wroblow, E. Gileadi, and B. J. Piersma, *Trans. Faraday Soc.*, **61**, 2531 (1965).
16. C. Tsonopoulos and G. M. Wilson, *AIChE J.*, **29**, 990 (1983).
17. M. K. Shchennikova, G. G. Devyatykh, and I. A. Korshunov, *J. Appl. Chem. USSR*, **30**, 1149 (1957).
18. D. Wabner and C. Grambow, *J. Electroanal. Chem.*, **195**, 95 (1985).
19. M. I. Gillibrand and B. Halliwell, *J. Inorg. Nucl. Chem.*, **34**, 1143 (1972).

# The Anodic Oxidation of Galena in a Cationic Surfactant-Aqueous Sodium Hydroxide Emulsion

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## ABSTRACT

A study was made of the electro-oxidation of galena in Hyamine 2389 surfactant systems. It was found that during the oxidation, one could observe four oxidation waves in voltammetric curves. These were concluded to be the oxidation of the galena to (i) PbO and S, (ii) PbO and $SO_3^=$, (iii) $PbSO_4$, and (iv) $PbO_2$ and $SO_4^=$. A study of the effect of the relation between the amount of galena in a suspension and the height of the highest peak in the voltammetric curve showed a complex relationship. At low concentrations of galena, the height varied with a regular periodicity indicating the formation on the electrode of multilayers of the Hyamine-galena micelle complex with the layers arranged in a manner similar to Langmuir-Blodgett films, alternating in nature from hydrophobic to hydrophilic to hydrophobic, etc. At higher concentrations of galena, it behaves as if one has simple monolayer adsorption.

In a recent study of the electro-oxidation of iron pyrite in a cationic surfactant-styrene-aqueous sodium hydroxide emulsion (1) it was shown that the filming of the electrode allowed one to observe a series of reactions not observable in normal aqueous solutions. In addition it was shown that the surfactant solubilized the iron pyrite making it possible to obtain a wave that was sensitive to the concentration of iron pyrite (2). However, because of the formation of multilayers of surfactant on the electrode, the height of the voltammetric peak was a complicated function of the concentration.

This is a report on a similar study of the oxidation of galena (lead sulfide) made in order to determine whether these techniques are of general use for the study of sulfide minerals. In connection with studies of mineral flotation processes, there have been a variety of studies of the electro-oxidation of a number of sulfide minerals. These studies have been reviewed and discussed in the papers by Hayes *et al.* (3) and by Richardson *et al.* (4, 5). Their summaries of the results for the sulfide minerals including galena are that initial oxidation removes lead from the surface producing a sulfur rich film which upon further oxidation eventually produces sulfur. Electrochemical studies in basic solutions (6-10) have led to the conclusion that the first stable products are sulfur and PbO, $Pb(OH)_2$, or $HPbO_2^-$, with secondary reactions that produced thiosulfate and sulfate.

In this investigation, similar to the iron pyrite work, studies were made in a surfactant induced suspension of the galena in order to determine the relation between the amount of sulfide mineral and the height of the voltammetric peak. Studies were also made in a sandwich cell to delineate the reactions that are occurring.

## Experimental

*Surfactant suspensions in a beaker cell.*—Similar to previous studies (11) the emulsion contained 35 ml of a 2N sodium hydroxide solution, containing 3.5 ml of styrene and 3.5 mls of Hyamine 2389 (predominantly methyldodecylbenzyltrimethylammonium chloride) obtained from Rohm and Haas. Weighed samples of naturally occurring galena which had been ground in a mortar and sieved in a 279 (53 μm) mesh screen were added to the emulsion after the residual voltammetric curves had become constant. The suspension was stirred with a magnetic stirrer and the sample was allowed to stand for 25 min in the stirred suspension before obtaining the voltammetric curve. Some voltammetric studies were done with lead sulfide prepared

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