Formation of High Molecular Weight Products from Benzene During Boundary Lubrication

Wilfredo Morales
Lewis Research Center
Cleveland, Ohio

April 1985
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DURING BOUNDARY LUBRICATION

Wilfredo Morales
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Organic electrochemistry was used to elucidate the mechanism by which benzene forms polyphenyl ether type products during boundary lubricating conditions. The results indicate that an electron transfer process occurs leading to the formation of the polyphenyl ether type products by means of an intermediate, phenol.

INTRODUCTION

In a previous study (ref. 1) an electrochemical procedure was developed to simulate and explain certain aspects of the boundary lubricating behavior of a thioether liquid lubricant. That study was based on work performed by Goldblatt (ref. 2) who proposed a radical anion theory to explain the boundary lubricating behavior of polynuclear aromatics. Although the thioether is not a polynuclear aromatic, its lubricating behavior was observed to be similar to that of polynuclear aromatics, and it was this similarity that led to an electrochemical study of the thioether to ascertain any radical anion behavior. In this study, organic electrochemistry was used to help elucidate a possible mechanism by which benzene seems to form polyphenyl ether type products when benzene was used as a boundary lubricant in a sliding friction and wear apparatus. The results of this study, where benzene was electrochemically hydroxylated to phenol, give evidence of an electron transfer process that is fundamental to boundary lubricating behavior.

BACKGROUND

The electrochemical study of the thioether liquid lubricant rested on the interaction of the lubricant with freshly abraded nascent metal surfaces. One of the first experimentalists to investigate nascent metal surfaces was Russell (ref. 3). He was able to show that the abraded surfaces of certain metals evolved a gas that produced an image on photographic plates. Although he did not identify the gas, he found that hydrogen peroxide vapors produced similar images on the photographic plates. It was Churchill (ref. 4) who showed that hydrogen peroxide is formed on freshly abraded surfaces. Shaw (ref. 5) observed that certain organic fluids (used as lubricants for metal cutting studies) reacted vigorously with the nascent surface of a metal cut.

It was Kramer (ref. 6) who reported that abraded metal surfaces emit electrons. Grunberg (ref. 7) showed that measurable amounts of hydrogen peroxide are produced when certain metals are cut (producing a nascent metal surface) under water. He explained his results by invoking the Kramer effect.
More recently Rosenfeld (ref. 8) reported the formation of gas bubbles in mineral lubricating oil (and other liquids) during sliding wear experiments and that mass spectroscopic analysis gave evidence the gas was hydrogen. Rosenfeld concluded that the gas formation is the result of a chemical reaction which occurs between the fluids and the nascent metal surfaces.

As was stated earlier, it was Goldblatt who proposed a radical anion theory to account for the anomalous lubricating behavior of polynuclear aromatics; but it was Appeldoorn and Tao (ref. 9) who first observed that, in the absence of oxygen (argon atmosphere, <0.005 percent oxygen) and moisture (<20 ppm water), these fluids cause extreme wear (scuffing) at low loads. They also observed that the presence of small amounts of oxygen or moisture decreased this wear. They pointed out that this is in contrast to the behavior of nonaromatics, such as alkanes, where high wear occurs in the presence of oxygen and moisture. Goldblatt theorized that during the wear process where nascent metal surfaces are formed, the polynuclear aromatics adsorb on the metal surfaces where an electron transfer occurs from the metal surface to the adsorbate. According to Suhrmann (ref. 10) a process like this only requires that the metal be able to deliver electrons coming from "s" or "p" bands.

Much research has been carried out in the study of nascent metal surface reactions during the abrasion of the metal surfaces. Trying to understand the heterogeneous surface reactions involving oxygen, water, lubricant, and metal is very difficult. However, due to the success of the thioether electrochemical study, it was felt that organic electrochemistry could be useful in elucidating boundary lubricating reactions.

**APPARATUS**

**Sliding Friction and Wear Apparatus**

Figure 1 represents a simple drawing of the sliding friction and wear apparatus used in this study. A metal disk is connected to the shaft of a variable speed motor. A metal rider, which is connected to a stationary holder, rests against the metal disk surface. The holder is part of a counter weight connection so that placing a 1 kg load on the counter weight connector will result in the rider exerting a 1 kg load on the disk.

**Electrochemical Cell**

The electrochemical cell used in this study is shown in figure 2. It consisted of a single pyrex glass compartment which was filled with 15 ml electrolyte. Iron wire served as both the anode and cathode electrodes and were electrically connected to a dc power supply. The cell has a gas inlet and outlet thus enabling one to carry out experiments in a nitrogen or air atmosphere.

**High Pressure Liquid Chromatograph (HPLC)**

A Waters model 244 liquid chromatograph was used for chromatographic analysis of the electrolyte and its contents at the end of an experiment. The unit was combined with an ultraviolet (UV) absorbance detector. The UV detector
monitors the absorbance at a wavelength of 254 nm at sensitivities ranging from 0.005 to 2.0 absorbance units full scale (AUFS).

For these studies, the liquid chromatograph was set up in the size exclusion mode where two micro-styragel columns were used together with a chloroform mobile phase. In the size exclusion mode, components of a mixture separate according to their different molecular sizes which is a function of their molecular weights. Thus by separating known standards of different molecular weights, and noting their retention times, one can set up a calibration chart where the molecular weight of the components will be a function of their retention times.

HPLC, although an excellent separatory technique, does not, by itself, identify the separated components of an injected sample. In order to analyze separated components many HPLC systems incorporate a "collect mode" whereby an operator can collect fractions of the mobile phase at a detector output; each collected fraction hopefully containing a single component. Each collected fraction can then be analyzed using an appropriate analytical instrument such as an infrared spectrophotometer, NMR or UV-visible spectrophotometer.

The success of using this "collected fraction" method depends on the operator being able to judge or calculate when to collect the mobile phase (containing the component to be analyzed) and how much of it to collect. This method is complicated by the fact that the sample size of the separated component is very small.

The utility of HPLC can be enhanced if an analytical instrument, capable of analyzing very small quantities of substances, is connected to the output line of an HPLC system providing a continuous analysis of the mobile phase contents.

In this study a dual diode array UV-visible spectrophotometer was connected on-line to the output of the HPLC system. This UV-visible spectrophotometer makes an excellent analytical complement to HPLC by providing a semi-continuous analysis of the mobile phase and its contents.

**UV-VISIBLE SPECTROPHOTOMETER**

An HP 8450 UV/VIS spectrophotometer was used. This is a general purpose dual diode array instrument providing a full 200 to 800 nm wavelength measurement in 1 sec. The instrument is equipped with five detachable cell holders (four sample cells and one reference cell) designed to accommodate rectangular cells with path lengths of 0.1 to 1.0 cm. An adjustable cell holder accommodates the flow cell.

The spectrophotometer can be programmed to take a full UV-visible spectrum (200 to 800 nm) of the flow cell contents every 3 sec thus providing a semi-continuous analysis of the effluent liquid chromatograph.

The UV-visible spectrophotometer is connected to a flexible disc drive thus allowing the immediate storage of all spectra.
SAMPLE PREPARATION FOR CHROMATOGRAPHIC ANALYSIS

At the conclusion of a test involving the sliding friction and wear apparatus, 4 ml of chloroform were used to rinse the entire wear track of the disk. The rinse was filtered to eliminate any insoluble material, and the filtered rinse was passed through a silica sep-pak cartridge in order to eliminate highly polar compounds such as water. Fifty micro-liters of the prepared rinse were injected into the liquid chromatograph.

At the conclusion of an electrochemical test, 2 ml of the electrolyte, taken from the cell, were added to a test tube containing 5 ml chloroform and 8 ml water. The bulk of the acetic acid and the iron acetate separated into the water layer. Chloroform soluble organic compounds separated into the chloroform layer. Four milliliters of the chloroform layer were then withdrawn from the test tube and passed through a silica sep-pak cartridge. Fifty micro-liters of the prepared sample were injected into the liquid chromatograph.

TEST PROCEDURE

Sliding Friction and Wear Apparatus

For this study, an iron disk and iron rider were used. The iron disk was ground and lapped to a surface finish of 10x10^-8 to 20x10^-8 m (4 to 8 μm), rms. The iron rider tip was machined and polished to a surface finish of 5x10^-8 to 10x10^-8 m (2 to 4 μm), rms. Both disk and rider were scrubbed with a paste of levigated alumina and water, rinsed with distilled water, then placed in a desicator until needed.

The benzene used was of analytical grade, thiophene free, where 5 ml of the benzene were saturated with distilled water at room temperature.

The disk and rider were assembled in the sliding friction and wear apparatus and a syringe was filled with the water saturated benzene. The test chamber was continuously purged with dry air at a flow rate of 3.5x10^-2 m³/hr. The rider was loaded against the disk with the 1 kg dead weight and the syringe placed in a position so that benzene could be added, drop by drop, onto the wear track of the disk. The disk speed was set at 20 rpm. The test began by adding a few drops of benzene onto the disk surface before switching on the motor, and adding two drops of benzene per minute onto the disk surface for 30 min before the test was stopped.

Electrochemical

The organic electrolyte was prepared by adding 0.1 g iron (II) acetate into 15 ml glacial acetic acid. This was followed by adding 2 ml distilled water and 2 ml benzene to the electrolyte. The electrolyte was then placed in the electrochemical cell. The cell electrodes were then connected to a variable dc power supply, and an air line connected to the gas inlet where the air flow rate was set at 40 ml/min. The test was conducted by turning on the power supply and adjusting the potential to 3.0 V. The potential was left at 3.0 V until the test was concluded. All test runs lasted 30 min. A sample was then collected and prepared for HPLC analysis.
RESULTS

Sliding Friction and Wear Apparatus

Figure 3 represents the HPLC chromatogram of the benzene standard showing a retention time of 18.30 min. Figure 4 is the HPLC chromatogram of the chloroform-soluble residue collected from the iron disk at the end of the sliding friction and wear experiment. Two peaks were detected, one having a retention time of 13.20 min and the second peak having a retention time of 14.60 min.

In order to estimate the molecular weights of these two unknown peaks a calibration chart was constructed. Since benzene was the test fluid all standards were taken to be derivatives of benzene. Figure 5 is the HPLC chromatogram of the standards. The natural log of the molecular weights of the standards were then plotted against their retention times resulting in figure 6, the calibration chart.

According to the calibration chart, peak one has a molecular weight of 665, and peak two has a molecular weight of 354. The calibration data shows that the molecular weight of peak two corresponds exactly to the molecular weight of the four phenyl-ring polyphenyl ether standard, and that the molecular weight of unknown peak one, 665, is close to the molecular weight of a seven phenyl-ring polyphenyl ether, 630. This observation led to the question if unknown peaks one and two might have the general structure of polyphenyl ethers.

UV data were obtained on peaks one and two and compared to the UV spectra of the four and six phenyl-ring polyphenyl ether standards (a seven phenyl-ring polyphenyl ether standard was unavailable). Figure 7 is the UV spectrum of the mixed four phenyl-ring polyphenyl ether and figure 8 is the UV spectrum of unknown peak two. The near identical spectra coupled with the retention time data gives evidence that unknown peak two is a four phenyl-ring polyphenyl ether type product. The UV spectrum of unknown peak one, figure 9, also has the same UV pattern of the four and six phenyl-ring (fig. 10) polyphenyl ethers thus also giving evidence that it is a polyphenyl ether type product.

Electrochemical

It was believed that the initial step in the formation of peaks one and two was the production of phenol from benzene, since phenols have been used successfully as starting materials in the preparation of polyphenyl ethers (ref. 11).

A literature search revealed that the electrochemical formation of phenols from benzene and other aromatics has been investigated by many researchers (refs. 12 and 13) but all the hydroxylations were carried out in aqueous media.

Organic electrochemistry was used to see if benzene could be hydroxylated to phenol in a nonaqueous environment hopefully simulating the boundary lubricating conditions of the sliding friction and wear apparatus which consist of iron, benzene, dissolved oxygen, and water. Experimentation lead to an electrochemical system consisting of iron electrodes and an organic electrolyte composed of iron (II) acetate dissolved in glacial acetic acid. This electrolyte has the capability of completely dissolving both benzene and water.
Dissolved oxygen was introduced into the system by bubbling air into the electrolyte.

Figure 11 is the HPLC chromatogram of the sample taken from the electrochemical cell at the end of the test. In addition to the benzene peak, four unknown peaks were detected. It was found that unknown peaks one, two, and three are small quantities of acetic acid (which was not totally extracted from the injected sample since acetic acid is soluble in chloroform) where the acetic acid seems to form dimers, trimers, and so forth, of itself.

Unknown peak four was found to be phenol. Its retention time of 21.2 min is the same as the phenol standard (fig. 12) retention time and its UV spectrum (fig. 13) matches the UV spectrum (fig. 14) of the phenol standard.

Three other experiments were conducted using the electrochemical cell. In the first experiment the hydroxylation test was repeated but with nitrogen, instead of air, bubbling through the electrolyte. In the second experiment the test was repeated with air but with no potential at the electrodes. In the third experiment, the test was repeated with air and a potential but without the iron (II) acetate. In all three cases phenol was not detected.

DISCUSSION

The electrochemical experiment gives evidence that polyphenyl ether type products could be formed from benzene, during boundary lubricating conditions, via the formation of phenol. The electrochemical hydroxylation of benzene in the electrochemical cell is initiated by the electro-reduction of molecular oxygen to hydrogen peroxide (ref. 12),

\[ O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \]  (1)

The hydrogen peroxide is decomposed by the ferrous cations,

\[ H_2O_2 + Fe^{2+} \rightarrow HO^- + HO + Fe^{3+} \]  (2)

The hydroxy radical then reacts with benzene to form phenol,

\[ HO^- + \text{C}_6H_6 \rightarrow \text{C}_6H_5OH \]  (3)

The ferric cations are reduced at the cathode to ferrous cations,

\[ Fe^{3+} + e^- \rightarrow Fe^{2+} \]  (4)

Recalling from the Background section that it has been shown that hydrogen peroxide can be formed on freshly abraded metal surfaces, and utilizing the electrochemical test results, then it can be suggested that the initial step in the formation of hydrogen peroxide on abraded metal surfaces is the electro-reduction of molecular oxygen.

The process by which oxygen is electro-reduced at rubbing metal surfaces can only be speculated at this point. Based on the substantial work conducted on the flash temperatures associated with metal rubbing processes, it seems...
plausible that the flash temperatures occurring at very localized surface areas may be high enough to overcome the work function of the metal leading to electron emission. Research work in this area is needed to pinpoint how oxygen can be electron reduced at rubbing metal surfaces.

The electro-reduction of oxygen can take one of two paths depending on the environment of the abraded metal surface. If a source of protons is readily available i.e., water, then the electro-reduction of oxygen would lead to hydrogen peroxide.

\[ \text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \]

If a source of protons is not available, lets say that the metal is abraded in the presence of mineral oil void of water, then the electro-reduction of oxygen could lead to the formation of the superoxide radical ion,

\[ \text{O}_2 + \text{e}^- \rightarrow \text{O}_2^- \]

Randin (ref. 14) suggested that this ion may be stable enough in paraffinic oil to be detected.

Since the sliding friction and wear apparatus was run with water-saturated benzene in air, the formation of hydrogen peroxide is to be expected. Hydrogen peroxide is decomposed in the electrochemical cell, by ferrous cations. The hydroxylation of benzene in the sliding friction and wear apparatus requires the decomposition of hydrogen peroxide, but it is uncertain whether the decomposition occurs due to the presence of soluble ferrous cations in the benzene or due to an iron surface reaction. Grunberg (ref. 11) conducted experiments where he abraded a variety of metals under water. He measured the quantity of hydrogen peroxide formed at the end of each experiment, and reported that for zinc, aluminum, magnesium, and nickel he detected essentially the same quantity of hydrogen peroxide, but that for copper he detected very little hydrogen peroxide while for iron the only thing he could detect and measure was ferric ions (Fe$^{3+}$).

This is not to say that the abrasion of copper and iron under water did not produce hydrogen peroxide but that the formation of hydrogen peroxide during the abrasion of copper or iron was rapidly followed by its decomposition. Grunberg's observation with the copper experiment is in accord with observations by Saeland (ref. 15) and Dowden and Reynolds (ref. 16) that hydrogen peroxide is quickly decomposed by copper via a surface reaction. Grunberg's detection of ferric ions suggests that during the abrasion process, ferrous cations are produced which then decompose hydrogen peroxide,

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}^- + \text{HO}^+ + \text{Fe}^{3+} \]

This is the same reaction as occurs in the electrochemical cell. These observations can therefore suggest that the decomposition of hydrogen peroxide, in the sliding friction and wear apparatus, occurs due to the presence of ferrous cations, although experimental detection of ferric cations is needed to confirm this hypothesis.

The decomposition of hydrogen peroxide is followed by the formation of phenol which is then followed by a reaction process leading to the formation of the polyphenyl ether type products.
Further work is needed to elucidate the reaction mechanism by which the polyphenyl ether type products are formed from phenol.

**SUMMARY OF RESULTS**

An electrochemical cell was used to help elucidate a possible mechanism by which polyphenyl ether type products are formed from benzene when benzene was used as a boundary lubricant. The electrochemical results, where benzene was hydroxylated to phenol via the electro-reduction of oxygen, gives evidence that an electron transfer process occurs during boundary lubrication that leads to the formation of polyphenyl ether type products from benzene.

**REFERENCES**


Figure 1. - Sliding friction and wear apparatus

Figure 2. - Electrochemical cell.
Figure 3. - HPLC chromatogram of benzene standard.

Figure 4. - HPLC chromatogram of the chloroform-soluble residue from the sliding friction and wear apparatus.
Six phenyl ring polyphenyl ether 13.60 min

Four phenyl ring polyphenyl ether 14.60 min

Biphenyl 17.0 min

Figure 5. - HPLC chromatogram of standards.

Natural log of molecular weights

Retention time, min

Figure 6. - Calibration chart LN (molecular weight) versus retention time.
Figure 7. - UV spectrum of mixed four phenyl ring polyphenyl ether.

Figure 8. - UV spectrum of unknown peak two.
Figure 9. - UV spectrum of unknown peak one.

Figure 10. - UV spectrum of six phenyl ring polyphenyl ether.
Figure 11. - HPLC chromatogram of electrochemical cell sample.

Figure 12. - HPLC chromatogram of phenol standard.
Figure 13. - UV spectrum of unknown peak four.

Figure 14. - UV spectrum of phenol standard.
High molecular weight products were detected on the wear track of an iron disk at the end of a sliding friction and wear test using benzene as a lubricant. Size exclusion chromatography in conjunction with UV analysis gave evidence that the high molecular weight products are polyphenyl ether type substances. Organic electrochemistry was used to elucidate the possible surface reaction mechanisms.
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