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Behavior of a Thioether
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National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

Summary

An electrochemical cell was constructed to explore the possible radical anion forming behavior of a thioether liquid lubricant. The electrochemical behavior of the thioether was compared with the electrochemical behavior of biphenyl, which is known to form radical anions. Under controlled conditions biphenyl undergoes a reversible reaction to a radical anion, whereas the thioether undergoes an irreversible reduction yielding several products. These results are discussed in relation to boundary lubrication.

Introduction

Advanced aircraft will place increased thermal stresses on liquid lubricants and hydraulic fluids. Maximum fluid temperatures in excess of 316° C have been estimated for future applications (refs. 1 to 3). The C-ethers (aromatic thioethers) were developed as a promising class of fluids for some of these applications (ref. 4). They are thermally stable to 390° C, as evidenced by isoteniscope measurements, and oxidatively stable to 260° C. They have a -29° C pour point, low vapor pressure, and a high surface tension. Some of their drawbacks include poor boundary lubricating ability and poor wetting characteristics. Other drawbacks of the C-ethers are the high wear they cause and the excessive formation of an insoluble deposit under boundary lubricating conditions. The high wear and deposit formation are especially prevalent when lubricating conditions take place in a low-oxygen, low-moisture environment. The deposits may degrade the boundary lubricating properties, which reduces the useful life of the fluid.

The presence of oxygen or moisture in the fluid environment improves the boundary lubricating properties of polynuclear aromatics (ref. 5) as well as that of C-ethers. Goldblatt (ref. 6) proposed a radical anion model to explain the lubricating behavior of polynuclear aromatic fluids. The C-ethers, although polyaromatic, are not polynuclear, but their lubricating behavior is similar to that of polynuclear aromatics. It was this similarity that led to an electrochemical study of the C-ethers to ascertain any radical anion behavior.

A common method for generating polynuclear radical anions is the chemical reagent method (refs. 7 and 8),

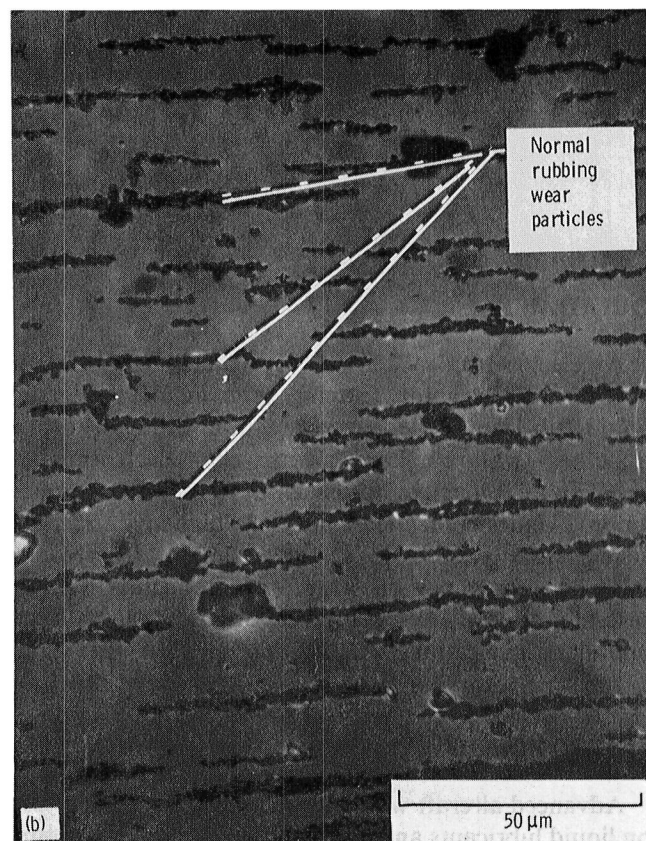
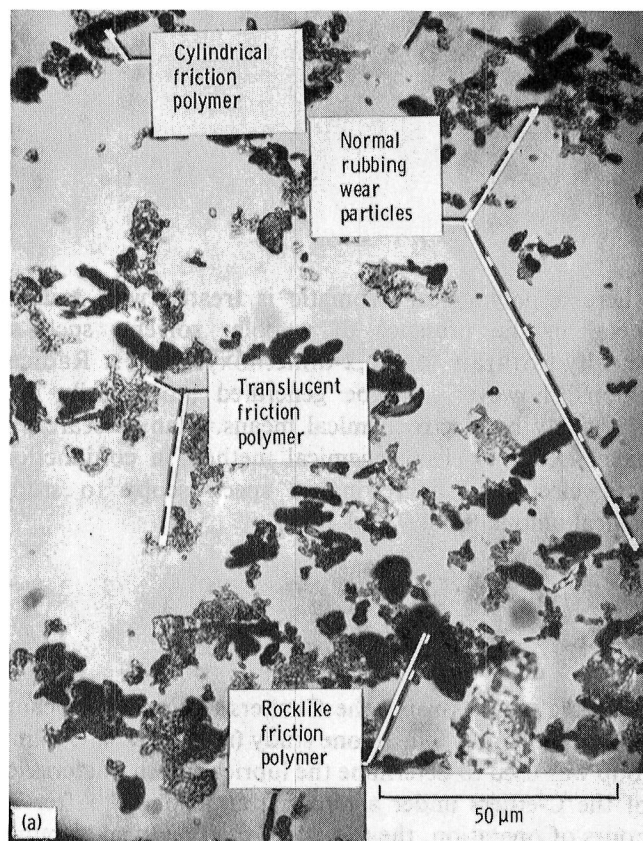
where a polynuclear aromatic is treated with sodium metal in the presence of a polar solvent, such as tetrahydrofuran or 1,2-dimethoxyethane. Radical anions, however, can be generated more easily and effectively by electrochemical means. Many researchers have used this electrochemical method in conjunction with electron spin resonance spectroscopy to study radical anions (refs. 9 and 10).

Background

Several studies using the C-ethers as liquid lubricants have been conducted. In one study (ref. 11) a vane pump loop was used to determine the lubricating characteristics of the C-ethers under a nitrogen atmosphere. After 32 hours of operation, the test was halted because of pump pressure loss. Deposit formation had jammed the pump vanes and rotor and caused high pressure drops across system filters.

In another study (ref. 12) a ball-on-disk sliding friction apparatus was used to investigate the lubricating characteristics of the C-ethers. Greater quantities of a deposit, referred to as *friction polymer* were formed in a low-oxygen atmosphere. This is illustrated by ferrographic analysis of a used C-ether tested in dry nitrogen (fig. 1(a)) and dry air (fig. 1(b)).

The C-ether liquid lubricant was also examined in full-scale, high-temperature tests of M-50 steel bearings; test details and results are reported in reference 13. All bearing tests were marred by excessive deposit formations and repeated filter pluggings. Lubricant samples were collected after each bearing run, and these samples were delivered to the NASA Lewis Research Center and analyzed by high-pressure liquid chromatography (HPLC) in the size exclusion mode using chloroform as the mobile phase solvent (ref. 14). The lubricant sample from a 111-hour bearing test had the appearance of a black viscous sludge. Figure 2 is the chromatogram comparing the unused C-ether lubricant with the chloroform soluble portion of the used C-ether lubricant from the 111-hour bearing test. There has been an obvious loss in the amount of the three-phenyl-ring component and an apparent increase in the amount of the four-phenyl-ring components. This is probably caused by preferential volatilization of the three-phenyl-ring



(a) Dry nitrogen.

(b) Dry air.

Figure 1. — Photomicrographs of wear debris generated by C-ether at 100° C (ref. 12).

component. In addition, there is the appearance of some higher molecular weight material in the molecular weight range from 400 to 1000.

Although the HPLC analysis of the chloroform soluble portion of the 111-hour bearing test sample revealed some degradation of the C-ether lubricant, it did not reveal the extreme amount of degradation product that

was expected from visual inspection of the bearing oil sample. This stems from the inability of the chloroform solvent to dissolve the deposit for HPLC analysis. The deposit also proved insoluble in other solvents which included tetrahydrofuran, acetonitrile, and methanol, as well as other solvents.

In a related study at NASA (ref. 14) the C-ether lubricant was tested using a micro-oxidation test (refs. 15 and 16). This micro-oxidation test is a simple, quick, bench test. It was used in an attempt to correlate laboratory C-ether liquid-lubricant oxidation and thermal degradation results with the full-scale, high-temperature bearing test results.

An M-50 steel catalyst was chosen for the micro-oxidation tests. Both the temperature and the length of time for the micro-oxidation tests, conducted under an air atmosphere, were varied in order to reproduce the bearing test chromatogram result. A test run for 60 minutes at 350° C gave the best reproduction (fig. 3). The preferential volatilization of the three-phenyl-ring component occurred, and the slight appearance of a higher molecular weight product was detected at a molecular weight of 450. Examination of the catalyst surface and the sample lubricant at the end of the run revealed no deposit formation.

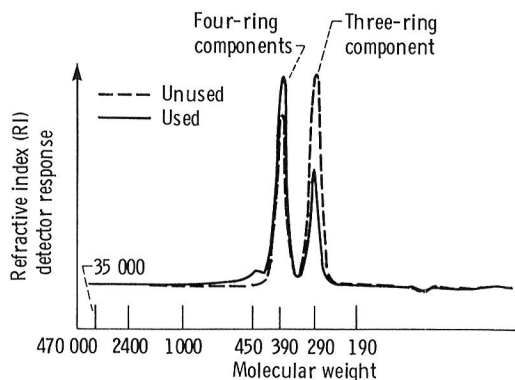


Figure 2. — Size exclusion chromatogram comparing unused C-ether lubricant and 111-hr-bearing-test C-ether lubricant (ref. 14). RI(8x) chloroform mobile phase; flow rate, 1.0 ml/min.

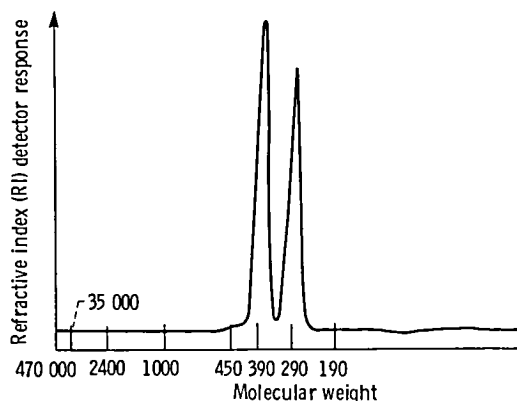


Figure 3.—Size exclusion chromatogram of C-ether lubricant from micro-oxidation test (350° C, 60 min). Catalyst, M-50 steel; test atmosphere, dry air. RI(8x) chloroform mobile phase; flow rate, 1.0 ml/min.

The micro-oxidation test was repeated under a nitrogen atmosphere. Figure 4 is the size exclusion chromatogram of the C-ether sample tested in the nitrogen atmosphere. The preferential volatilization of the three-phenyl-ring component again occurred, and the appearance of at least three higher molecular weight products was detected. Deposit formation did not occur.

The size exclusion analysis (fig. 3) of the micro-oxidation sample tested in an air atmosphere revealed the excellent oxidative stability of the C-ethers under the static conditions of extreme temperature and time in the presence of a catalyst. It was the analysis of the micro-oxidation test sample tested in a nitrogen atmosphere which revealed the surprising result—the detection of at least three higher molecular weight products. A calculation using the molecular weight calibration curve indicates that the molecular weights of the three degradation products correspond approximately to five-, six-, and seven-phenyl-ring products. It is possible that the C-ether liquid lubricant may slowly polymerize under certain conditions and that the presence of oxygen tends to inhibit this process.

The possible polymerization of the C-ether lubricants was investigated further in a study (ref. 14) using a free radical source, diphenyl disulfide. One weight percent of diphenyl disulfide was added to the C-ethers, and 10 milliliters of this solution were heated in glassware at 350° C for 4 hours in a nitrogen atmosphere. A sample was then withdrawn and prepared for size exclusion analysis. Figure 5 is the chromatogram of this sample. In addition to the primary C-ether peaks, there are four other peaks. Based on the calibration curve, these peaks correspond to two-, five-, six-, and possibly seven-phenyl-ring products. At 350° C, the diphenyl disulfide will cleave to free radicals (fig. 6), which then attack the C-ethers and cause a slow polymerization process to occur. This result and the results of the micro-oxidation tests substantiate the polymer forming properties of the C-ethers.

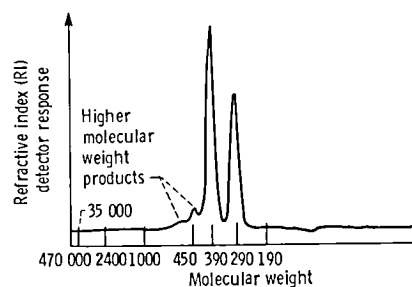


Figure 4.—Size exclusion chromatogram of C-ether lubricant from micro-oxidation test (350° C, 60 min). Catalyst, M-50 steel; test atmosphere, dry nitrogen. RI(8x) chloroform mobile phase; flow rate, 1.0 ml/min.

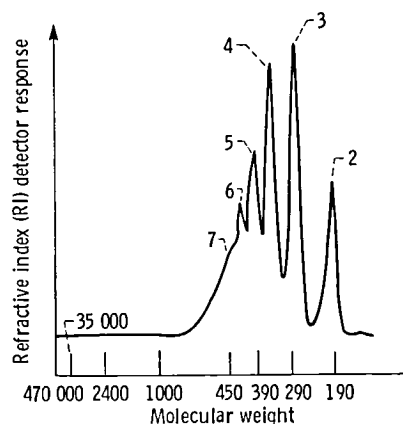


Figure 5.—Size exclusion chromatogram of C-ether lubricant containing 1 wt% diphenyl disulfide (350° C, 4 hr). Test atmosphere, dry nitrogen (no catalyst). RI(8x) chloroform mobile phase; flow rate, 1.0 ml/min.

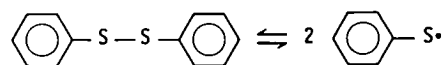


Figure 6.—Free radical formation from diphenyl disulfide.

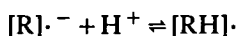
Several things become apparent at this point. The problems associated with the C-ethers are not due to oxidative degradation. The static microoxidation test, while providing valuable information, did not duplicate the results found in the bearing test samples, especially the formation of insoluble deposits.

The formation of the insoluble deposit appears to be the result of a dynamic condition, something that the micro-oxidation test cannot simulate. Chemical analysis shows the deposits have a very high iron content, which indicates possible corrosive wear where the debris is likely to be a mixture of insoluble organometallics and inorganic iron compounds such as iron sulfides and oxides.

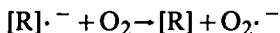
In several of the C-ether studies it was noted that high wear and deposit formation were especially prevalent when lubrication was taking place in a low-oxygen, low-moisture environment. This behavior is similar to the lubricating behavior of polynuclear aromatics.

Appeldoorn and Tao (ref. 5) reported that these fluids, in the absence of oxygen (argon atmosphere, <0.005 percent oxygen) and moisture (<20 ppm), caused 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 alkanes (nonaromatics), where high wear occurs in the presence of oxygen and moisture.

Goldblatt (ref. 6) theorized that the lubricating behavior of polynuclear aromatics could be accounted for if these fluids formed radical anions at a rubbing surface. In the absence of oxygen and moisture, the radical anion can attack the surrounding metal or metal oxide and lead to accelerated wear. On the other hand, almost all radical anions can be quenched by moisture or oxygen. Quenching by moisture involves hydrolysis of the radical anion



whereas quenching by oxygen involves an electron-transfer process



Apparatus

Electrochemical Cell

The electrochemical cell used in this study is shown in figure 7. It consists of two Pyrex glass compartments, a cathode compartment and an anode compartment, separated by a Teflon membrane. A pool of mercury (0.5 ml) sits at the bottom of the cathode compartment, and the cell is filled with 20 milliliters of an electrolyte. A platinum foil serves as the anode, and the pool of mercury serves as the cathode. Another platinum wire is used to make electrical contact between the mercury and a dc power source. The cell has both a gas inlet and a gas outlet thus enabling one to carry out experiments in a nitrogen or an air atmosphere.

Liquid Chromatograph

A Waters model 244 liquid chromatograph was used for chromatographic analysis. The unit was combined with an ultraviolet (UV) absorbance detector and a differential refractive index (RI) detector, or refractometer. The UV detector monitors the absorbance at a wavelength of 254 nanometers at sensitivities ranging from 0.005 to 2.0 absorbance units full scale (AUFS). The refractometer is sensitive to all compounds that differ in refractive index from the mobile phase. It detects changes in the RI as small as 10^{-7} RI units

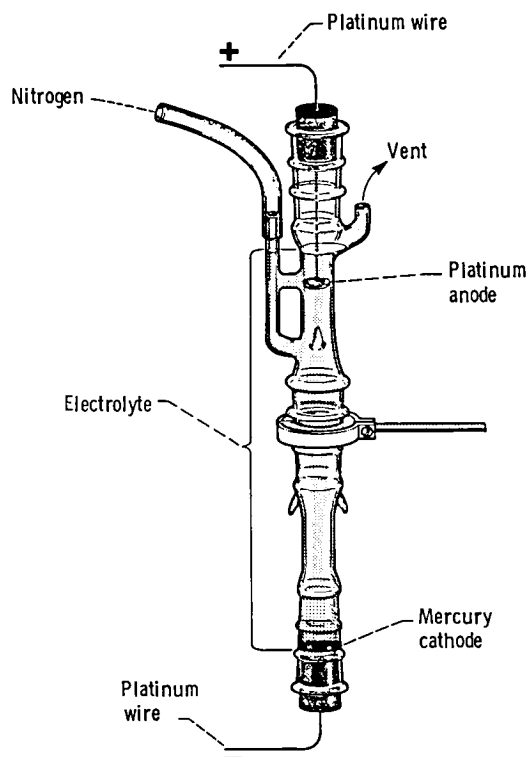


Figure 7. - Electrochemical cell.

throughout the RI range 1.00 to 1.75. For these studies, the liquid chromatograph was set up in the normal phase mode, which is a CN column (an intermediate polarity column made by chemically bonding a cyano group to silica) and a heptane mobile phase.

Ultraviolet-Visible Spectrophotometer

A diode array UV-visible spectrophotometer was connected to the liquid chromatograph output (fig. 8). Separated samples were eluted from the column to a flow cell installed in the spectrophotometer. The spectrophotometer was programmed to take a full UV-visible spectrum (200 to 800 nm) of the flow cell contents every 3 seconds with a 1-second measurement time. The resulting data were immediately stored on floppy disks for subsequent study.

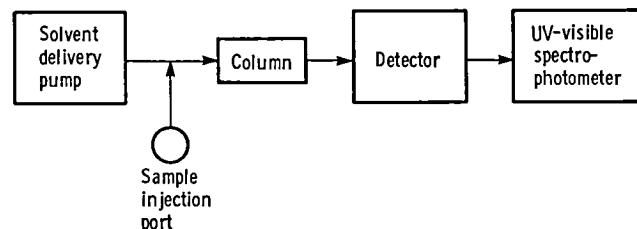


Figure 8. - HPLC system with UV-visible spectrophotometer.

Test Procedure

Electrochemical Cell Preparation

Before each test, the two glass compartments of the electrochemical cell were cleaned by rinsing first with chloroform and then with methanol. They were then placed in an oven heated to 120° C and dried overnight. Both electrodes were constructed by inserting a platinum wire through a rubber stopper (fig. 7). The cathode stopper was then inserted into the outer ground joint of the cathode glass compartment and a small volume of mercury (0.5 ml) was injected into the cathode compartment. The mercury formed a pool which covered the small length of platinum wire which protruded from the stopper.

The electrolyte used for these tests was a 0.1 M solution of tetrapropyl-ammonium perchlorate in acetonitrile. The solution was prepared by dissolving 0.4 gram of the perchlorate in 20 milliliters of acetonitrile. All chemicals were of reagent grade purity. Next 0.25 gram of the aromatic sample under study was dissolved in the solution, and the solution was then introduced into the electrochemical cell. Finally, the anode stopper was inserted into the outer ground glass joint of the anode compartment, and a nitrogen line was connected to the gas inlet. A continuous flow of nitrogen purged the cell of air.

The positive potential of a dc power supply was connected to the anode platinum wire, and the negative potential to the cathode platinum wire. All tests were conducted by turning on the dc power supply and increasing the voltage in increments of 2 volts up to a maximum 10 volts. At test conclusion, the power supply was turned off, and samples were collected from the cell for chromatographic analysis (HPLC).

Sample Preparation for Chromatographic Analysis

At the conclusion of a test, the cathode contents of the cell were withdrawn and placed in an evaporating disk, where the acetonitrile was allowed to evaporate, leaving behind a residue. The residue was treated with 5 milliliters of heptane. The resulting mixture was filtered to separate the insoluble tetrapropylammonium perchlorate salt. A CN column was used to analyze the heptane solution.

Experimental Samples

Biphenyl

Biphenyl (fig. 9) is a nonpolynuclear aromatic which can be reduced, by using the chemical reagent method, to a stable radical anion (ref. 12). An electron from the sodium metal is transferred to the biphenyl molecule,

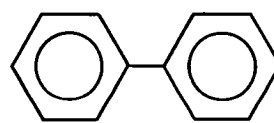


Figure 9. – Biphenyl.

where it is delocalized. Because of the known radical anion forming property of biphenyl, it was used as the reference sample in the electrochemical cell.

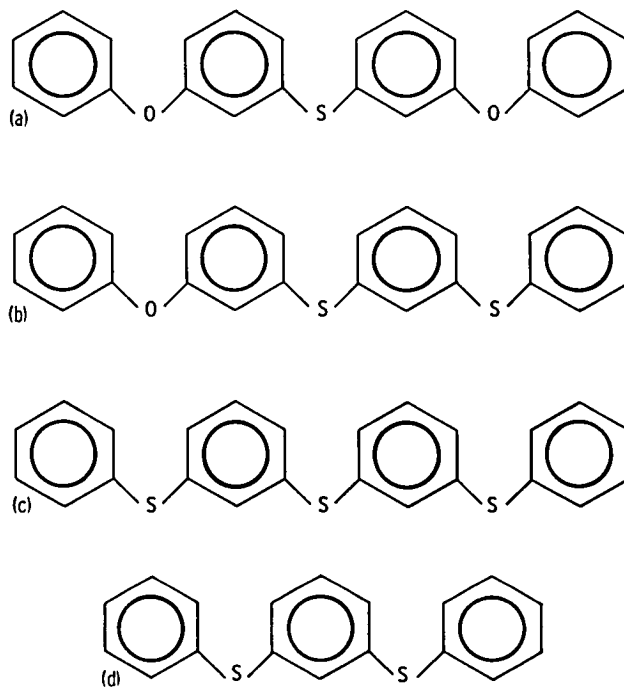
C-ethers

The C-ethers (fig. 10) are a mixture of four nonpolynuclear aromatics. One of the four components (the three-phenyl-ring component (d) 1,3-bis (phenylthio) benzene) was used as the test sample in the electrochemical cell in order to simplify analysis.

Results

Biphenyl

After the electrochemical cell was prepared and purged with nitrogen, the biphenyl sample was introduced into the cathode compartment. A dc power supply and an ammeter were connected to the cell electrodes. The



- (a) 1,1-thiobis[3-phenoxybenzene]; molecular weight, 370.
(b) 1-phenoxy-3-[[3-(phenylthio)phenyl]thio]benzene; molecular weight, 386.
(c) 1,1-thiobis[3-(phenylthio)benzene]; molecular weight, 402.
(d) 1,3-bis(phenylthio)benzene; molecular weight, 294.
- Figure 10. – Chemical components of C-ether base fluid.

voltage to the cell was slowly increased at approximately 1 minute intervals in 2-volt increments until an intense blue color started to form above the mercury surface. This occurred at 10 volts (3.5 mA). All aromatics which are reduced to stable radical anions, either chemically or electrolytically, are deeply colored; for instance, the naphthalene radical anion is green, the anthracene radical anion is blue, and the benzonitrile radical anion is red-orange (ref. 8).

The power supply was left at 10 volts for 1 hour. With continued nitrogen purge, the power supply was disconnected and the blue color immediately disappeared. The contents of the cathode compartment were collected and a sample was prepared for HPLC analysis.

Figure 11 is the HPLC chromatogram of biphenyl standard. Figure 12 is the chromatogram of the electrolyzed biphenyl sample collected from the cell. It reveals a single peak with a retention time of 6.96 minutes compared to the biphenyl standard retention time of 7.05 minutes. This is within the calibration accuracy of the system (0.1 min.) and indicates no change in composition. The UV analyses of the biphenyl standard (fig. 13) and the electrolyzed sample (fig. 14) also show no change in composition.

C-ether

After preparing the cell, the C-ether sample was introduced into the cathode compartment, and the power supply and ammeter were connected to the cell. The power supply voltage was again increased in 2-volt intervals.

At 10 volts a bright red color started to form over the mercury surface. The voltage was maintained at 10 volts for 1 hour. When the power supply was disconnected the red color did not disappear as the blue had done when the power supply was disconnected from the biphenyl sample. The cell was left undisturbed in order to determine the persistence of the red color. After 3 hours the color was still intense. A sample of the colored solution was then taken for HPLC analysis. Approximately 5 milliliters of the cathode contents were withdrawn using a long tip syringe. As the red solution entered the air-filled syringe chamber the color disappeared. This sample was prepared for HPLC analysis.

Figure 15 is the normal phase chromatogram of the three-phenyl-ring C-ether standard having a retention time of 6.10 minutes. Figure 16 is the normal phase chromatogram of the sample collected from the cathode compartment. In addition to the original C-ether peak, two other peaks are detected, one peak with a 5.30-minute retention time and the other with a 7.10-minute retention time. The thioether sample, unlike the biphenyl sample, apparently undergoes a change in composition.

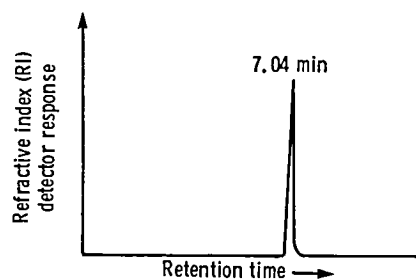


Figure 11. – HPLC (normal phase) chromatogram of biphenyl standard. Conditions: Heptane mobile phase; CN Column.

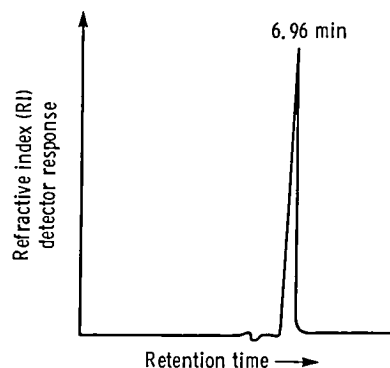


Figure 12. – HPLC (normal phase) chromatogram of electrolyzed cathode sample (biphenyl). Conditions: Heptane mobile phase; CN column.

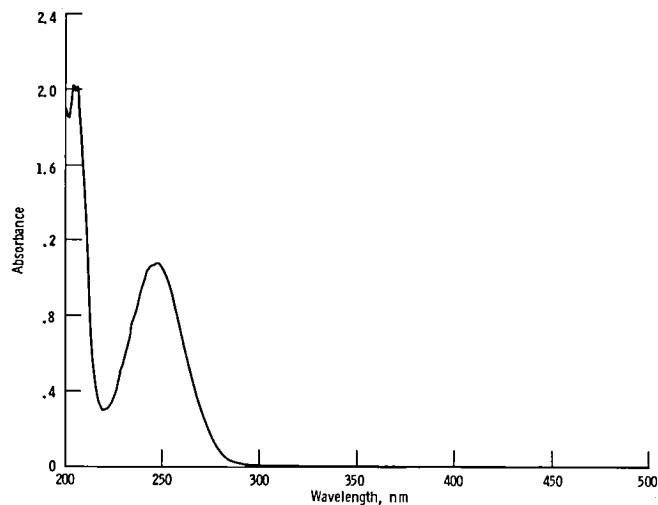


Figure 13. – Ultraviolet spectrum of biphenyl.

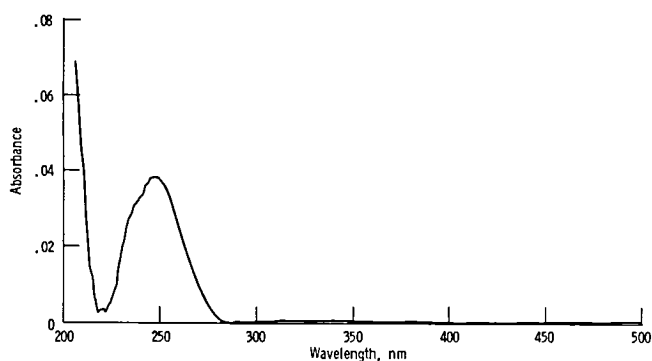


Figure 14. – Ultraviolet spectrum of electrolyzed biphenyl.

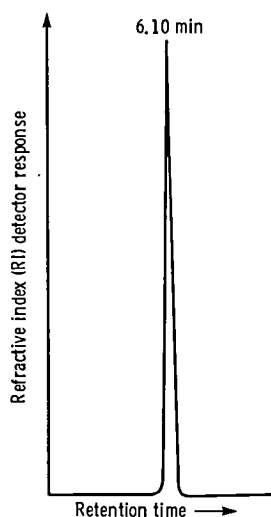


Figure 15. – HPLC (normal phase) chromatogram of three-phenyl-ring thioether standard. Conditions: Heptane mobile phase; CN column.

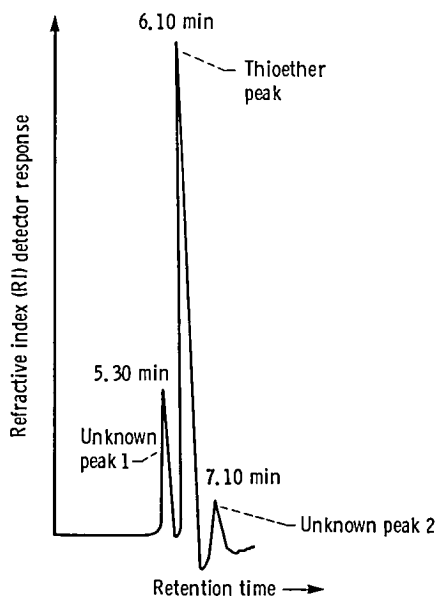


Figure 16. – HPLC (normal phase) chromatogram of electrolyzed sample (three-phenyl-ring thioether) from cathode compartment. Conditions: Heptane mobile phase; CN column.

The two unknown peaks were identified by running various known sulfur compounds through the HPLC and noting their retention times. It was found that diphenyl sulfide has a retention time of 5.30 minutes and 1,1-thiobis [3- (phenylthio)benzene] has a retention time of 7.10 minutes. Further evidence that the unknown peaks are diphenyl sulfide and 1,1-thiobis [3-(phenylthio)benzene] is provided by UV data. Figure 17 is the UV spectrum of the diphenyl sulfide standard. Figure 18 is the UV spectrum of the unknown peak having the 5.30-minute retention time. Figures 19 and 20 are the UV spectra of the 1,1-thiobis [3-(phenylthio)benzene] standard and the second unknown peak (7.10-min retention time). Comparison of the UV spectra supports the identity of the HPLC peaks.

Discussion

The electrochemical reduction of biphenyl yielded a radical anion (fig. 21) which exhibited an intense blue color. This blue color disappeared as soon as the voltage to the cell was turned off; presumably, the biphenyl radical anion reversibly oxidized back to the neutral biphenyl molecule. HPLC and UV analyses verified this reaction of the biphenyl radical anion by detecting only the original biphenyl peak.

The electrochemical reduction of the three-ring thioether, however, yielded different results. The thioether reacted to produce a product or products exhibiting an intense red color which did not disappear after the voltage to the cell was turned off. However, as soon as the product came in contact with the air in the syringe the red color disappeared. This suggests the existence of a stable free radical species. HPLC analysis revealed that the reduced thioether produced at least two reaction products, diphenyl sulfide and 1,1-thiobis [3-(phenylthio)benzene].

The following model is proposed to explain the electrochemical behavior of the thioether. The thioether is reduced at the cathode to a radical anion (fig. 22). This radical anion decomposes to an anion and a free radical. The anion can react with a proton to form diphenyl sulfide. The proton source is most likely to be water or the acetonitrile solvent. The free radical can attack a thioether molecule forming 1,1-thiobis [3-(phenylthio)benzene].

The persistence of the red color after the voltage to the cell is turned off and the disappearance of the red color when the cathode sample comes in contact with air support a free radical model.

Further supporting evidence for the formation of stable radical species is the electron spin resonance (ESR) spectrum of the electrolyzed thioether shown in figure 23. ESR is a technique which detects unpaired electrons and thus free radicals. A sample of the red solution from the

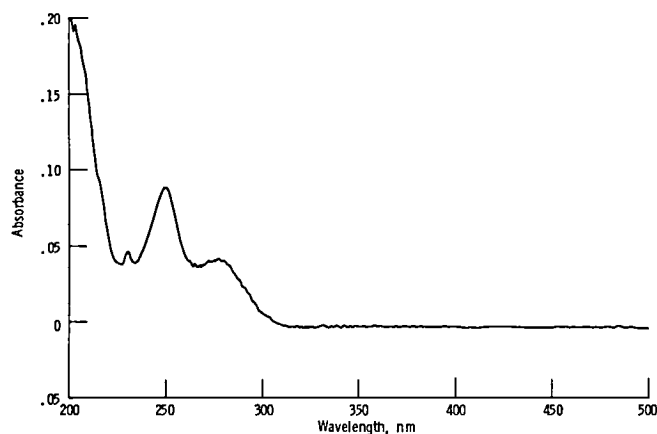


Figure 17. – Ultraviolet spectrum of diphenyl sulfide.

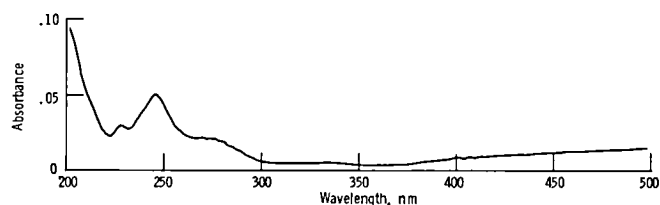


Figure 18. – Ultraviolet spectrum of unknown peak 1.

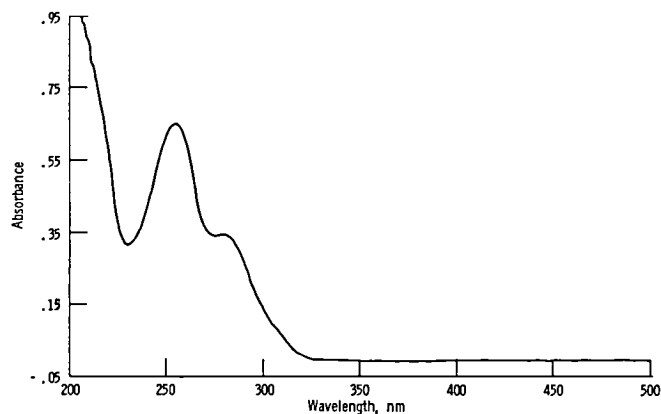


Figure 19. – Ultraviolet spectrum of 1,1-thiobis[3-(phenylthio)benzene].

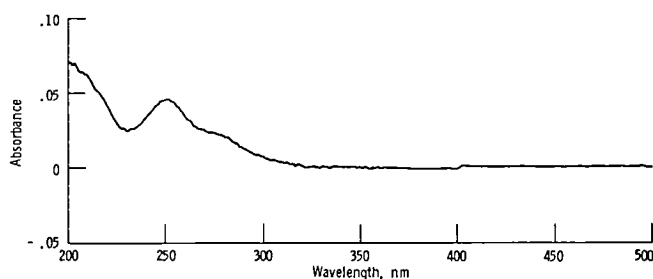


Figure 20. – Ultraviolet spectrum of unknown peak 2.

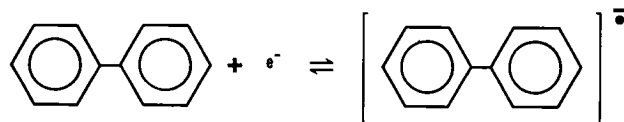


Figure 21. – Electrochemical reduction of biphenyl.

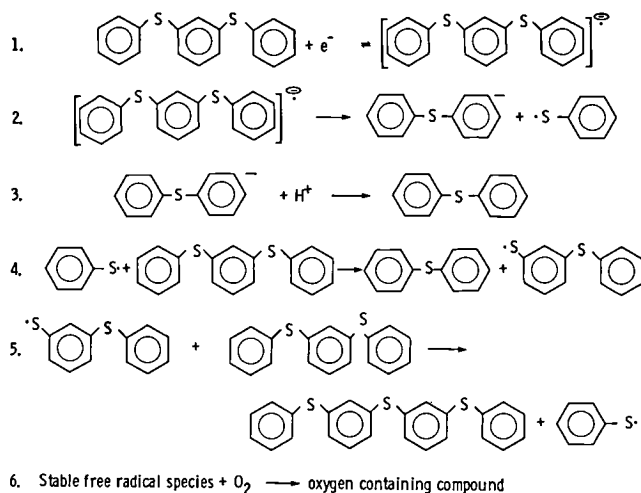


Figure 22. – Model for electrochemical breakdown of thioether.

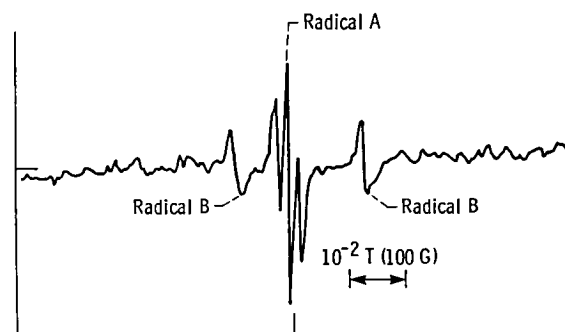


Figure 23. – ESR spectrum of a three-ring thioether from electrochemical cell.

cathode compartment of the electrochemical cell was carefully withdrawn under a nitrogen atmosphere and placed in an ESR cell. The spectrum obtained indicates the presence of two stable free radicals (labeled A and B). Radical B appears as a 1:1 doublet with a splitting of about 250×10^{-4} tesla (250 G); Radical A appears as a 1:2:1 triplet pattern with a splitting of approximately 40×10^{-4} tesla (40 G). Both are very stable species is attested to by the fact that a spectrum taken 1 hour later reveals the same pattern. However, the concentration of radical A had diminished more than that of B, which indicates that A is somewhat less stable.

The final step in the model is a reaction between the stable free radical species and oxygen (contact of the cathode contents with air) which forms an oxygen-

containing compound or compounds. These products were not isolated using the HPLC normal phase mode because oxygen compounds tend to be polar and polar compounds tend to be heptane insoluble.

The discussion in the **Background** section shows that the C-ether class of lubricants behaves according to the Goldblatt polynuclear aromatic radical anion model. The results from the electrochemical cell support this theory to the extent that radical anions are produced which subsequently decompose to an anion and a free radical. These species then react with their surroundings to produce a variety of products. The electrochemical results, the high-temperature bearing test results, and the radical-initiator results suggest that during boundary lubrication the C-ether liquid lubricant decomposes, by a radical anion mechanism, and generates a free radical which can cause a rapid polymerization reaction leading to an insoluble product. The decomposed C-ether may also be responsible for the easy formation of iron sulfides, insoluble organo metallics, iron oxides, and hydrates. These compounds are continuously worn away from the surface and may be considered the debris of corrosive wear.

Summary of Results

An electrochemical cell was used in conjunction with high-pressure liquid chromatography (HPLC), a UV-visible spectrophotometer, and electron spin resonance spectrometer (ESR) to study the radical anion forming behavior of a C-ether lubricant component. The results may be summarized as follows:

1. Biphenyl, a known radical anion precursor, reversibly yields a radical anion at the cathode in the electrochemical cell.

2. The C-ether component [1,3 bis(phenylthio)benzene] undergoes an irreversible reduction at the cathode and yields at least two known products, diphenyl sulfide and 1,1-thiobis [3-(phenylthio)benzene] by means of two unknown stable free radical species.

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National Aeronautics and Space Administration
Cleveland, Ohio, March 2, 1984

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