The Carbon Deposition Mechanism in Vapor Phase Lubrication

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The study of various alkoxy species on metal surfaces has provided insight into the mechanism by which carbon is deposited into the lubricating films of polyphosphate glass generated by arylphosphate vapor phase lubricants. Previous work using trimethylphosphite has suggested that one of the initial steps in the decomposition of organophosphorus compounds on metal surfaces is cleavage of P-O bonds to produce adsorbed alkoxy species. In the case of alkyl alkoxy groups (poor ligands for vapor phase lubrication) there are reaction mechanisms such as β-hydride elimination which efficiently remove hydrocarbons from the surface. In the case of the aryl alkoxy groups (good ligands for vapor phase lubricants) such mechanisms cannot be active due to the lack of β-hydrogen atoms. Experiments using various alkoxy species demonstrate these differences and reveal that phenoxy groups deposit carbon onto the surface quite efficiently while cyclohexanoxy and t-butanoxy groups do not.

KEYWORDS
Vapor Phase Lubrication; Carbon; Nickel; Lubricant Properties

INTRODUCTION

Development of new lubrication techniques for high temperature applications has been an important area of research over the past decade. Among those techniques under development, vapor phase lubrication (VPL) has been one of the most promising for overcoming the limitations of current liquid lubrication systems [Rao, Hanyaloglu (1995), Makki]. In vapor phase lubrication, lubricants in vapor form are delivered by hot vaporized fuels or inert carrier gases to the hot sliding surfaces. Tricresylphosphate, \((\text{CH}_3(\text{C}_6\text{H}_5\text{O})_3\text{P})=\text{O}\), has been the most commonly studied vapor phase lubricant, owing to its high thermal stability and wide use as an antwear additive. Other aryl and alkyl phosphates have also been studied, but the aryl phosphates appear to be more effective than the alkyl phosphates [Groeneweg, Forster]. Current understanding of the mechanism of vapor phase lubrication is that the lubricants react with hot sliding surfaces to form thin lubricating films. These films are not well characterized but are thought to be composed of polyphosphate glass which serves as a binder for carbonaceous deposits possibly in the form of small graphitic particles [Forster]. Another approach to high temperature lubrication is being developed in parallel to vapor phase lubrication and relies upon lubrication by catalytic carbon deposition [Sawyer, Smith, Lauer]. In some sense catalytic carbon deposition is another form of vapor phase lubrication in which lubricating graphitic particles are generated on hot surfaces by catalytic decomposition of hydrocarbons transported to the surface through the vapor phase. Both vapor phase lubrication by phosphates and lubrication by catalytic carbon deposition have been demonstrated to work on numerous metal and ceramic surfaces and at temperatures above 650°C [Lauer, Graham, Hanyaloglu (1993)]. Vapor phase lubrication by organophosphates has advanced recently to the stage of being demonstrated for practical applications [Van Treuren]. Although carbon deposits are common to both schemes, the phosphate component of the vapor lubrication films are critical to some applications. For example, tricresylphosphate has been shown to be a poor vapor phase lubricant under conditions in which little phosphate is deposited with the graphitic films [Hanyaloglu (1993)]. Understanding the carbon deposition mechanism is an important issue in the further development of vapor phase lubrication technology.

The goal of this investigation has been to understand some of the fundamental surface chemistry involved in vapor phase lubrication, particularly the carbon deposition mechanism. One of the initial questions to be addressed has been the relative surface reactivities of the P-O-C bonds in compounds such as the arylphosphates. These are the two weakest bonds in the aryl phosphates with bond strengths of \(D_{\text{P-O}} = 86-92 \text{ kcal mol}^{-1}\) and \(D_{\text{C-O}} = 84 \text{ kcal mol}^{-1}\). The initial reactions of such species could involve P-O bond cleavage to produce alkoxy groups or O-C bond cleavage to...
give adsorbed aryl groups. The authors have chosen to study these reactions initially by using the simplest possible compound containing these bonds: trimethylphosphite (CH₃O)₃P. The authors recent studies of trimethylphosphate decomposition on Ni(111) and oxidized Cu(111) surfaces revealed that one of the initial steps in trimethylphosphate decomposition on these surfaces is P-O bond cleavage to produce methoxy intermediates. These methoxy intermediates react in the same fashion as methoxy intermediates produced by methanol deprotonation on the Ni(111) and Cu(111) surfaces [Ren]. Similarly, on the Fe(110) trimethylphosphate reacts by cleavage of P-O bonds to produce methoxy groups [Holbert]. These findings suggest that during the decomposition of organophosphates it may well be that the P-O bonds break first to form alkoxy or arylxox intermediates, which then undergo further thermal decomposition on the metal surfaces to deposit carbon.

It should be pointed out that there is an early study that used XPS to study the decomposition of tricresylphosphate itself on a polycrystalline iron surface [Wheeler]. The mechanistic model presented to explain the results of that work was one in which the O-C bonds dissociate to produce a surface aryl species, some fraction of which is lost from the surface during heating. The evidence for this was based the loss of O(1s) signal at 533.7 eV (assigned to P-O-C species) and the increase in intensity of the O(1s) signal at 531.5 eV (assigned to P=O species). During heating the loss of carbon from the surface was observed as a decrease in the C(1s) signal. A model proposing the intermediate formation of arylxy species (Fe-O-C) could also explain the data in that the O(1s) binding energy for methoxy on Fe(110) (Fe-O-CH₃) is now known to be 531.8 eV [Ruffell]. Thus, the signal originally assigned to P=O might in fact be due to an arylxy species produced by the cleavage of P-O bonds in tricresylphosphate. The point is that the authors model compound, trimethylphosphate, although much simpler than tricresylphosphate may exhibit reactivity that is different from a phosphate. This issue requires further investigation and the surface chemistry of the phosphates will be studied in the future.

The experiments described in this paper begin with the assumption, based on previous work with trimethylphosphate, that in the phosphates it is the P-O bonds that break to generate alkoxy or arylxy species on the surface and that it is the decomposition of these species that deposits carbon onto the surface [Ren, Holbert]. According to current understanding there are three possible pathways for these alkoxy groups to react. One reaction mechanism which is prevalent in primary (RCH₂O-) and secondary alkoxydes (R"R'CH-O-) is β-hydride elimination to form aldehydes (RCH=O) or ketones (R"R'C=O) which desorb rapidly from the surfaces [Gellman, Friend]. Tertiary alkoxydes (R"R'R'CH-O-) have no β-hydride atoms for elimination. They can react by C-O bond cleavage, at much higher temperatures, to form tertiary alkyl groups (R"R'R-) which would then have β-hydride atoms which could be eliminated to yield olefins [Brainard (1989a)]. The mechanism may be the same as that of an analogous species, neo-pentyl groups (CH₃)₂C⋅CH₂⋅C-(CH₃) which which then react by β-hydride elimination to yield isobutylene desorption. By comparing the surface chemistry of phenoxy, cyclohexanox, and t-butanox intermediate the authors have gained insight into the relative efficiency of carbon deposition by the different alkyl and aryl phosphates used for vapor phase lubrication.

In this study cyclohexanol (C₆H₁₁OH), t-butanol (CH₃CH₂COH), and phenol (C₆H₅OH) were chosen as models for the ligands used on alkyl and aryl phosphate vapor phase lubri- cants. Their thermal decomposition on the Ni(111) surface was studied because data are available for the surface chemistry of many alkoxy groups produced by the adsorption of alcohols on this surface. Phenol has been studied on Ni(110), Ni(111), and many other metal surfaces [Russell (1995), Myers]. The primary observation of thermally programmed reaction studies has been that phenol decomposition occurs to yield H₂ and CO desorption. Since most vapor phase lubricants examined to date have been aryl phosphates, it is important to include phenol in the authors study.

For comparison with the decomposition of phenol we have chosen to study cyclohexanol decomposition on the Ni(111) surface. The chemistry of small primary and secondary alcohols on Ni(111) and many other surfaces is quite well understood [Gellman, Friend], however, the surface chemistry of larger cyclic alcohols such as cyclohexanol is not nearly as well studied. Based on the authors knowledge of the smaller linear alcohols one would expect that cyclohexanol would form a cyclohexanol group (C₆H₁₁O-). This is a secondary alkoxy and can react by β-hydro- gen elimination to yield cyclohexanone (C₆H₅C=O).

The third species studied in this investigation was t-butanol and the authors results can be compared with previous work using this molecule on the Ag(110) and Cu(110) surfaces [Brainard (1989a)], Brainard (1989b)]. The t-butanox intermediate (CH₃CH₂CO-) produced by deprotonation of the t-butanol has been found to be more stable than either the primary or the secondary alkoxy groups. This is presumably due to the fact that there is no active β-hydrogen in the t-butanox intermediates. The chemistry of t-butanol on the pre-oxidized Ag(110) and Cu(110) surfaces generates isobutylene (CH₃CH₂C=CH₂) and isobutylene oxide, which desorb into the gas phase [Brainard (1989a), Brainard (1989b)]. The mechanism may be the same as that of an analogous species, neo-pentyl groups (CH₃)₂C⋅CH₂⋅C-(CH₃) which which then react by β-hydride elimination to yield isobutylene desorption. By comparing the surface chemistry of phenoxy, cyclohexanox, and t-butanox intermediate the authors have gained insight into the relative efficiency of carbon deposition by the different alkyl and aryl phosphates used for vapor phase lubrication.
EXPERIMENTAL

The majority of the experiments described in this paper were performed in an ultra-high vacuum (UHV) surface analysis chamber equipped with an Ar⁺ sputtering gun for surface cleaning, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), and a quadrupole mass spectrometer for detecting desorbing species during temperature programmed reaction spectrometry (TPRS). The X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) experiments were performed in a second UHV chamber. Both chambers were equipped with standard leak valves for introducing vapor for adsorption onto the Ni(111) surface. The same Ni(111) single crystal sample was used in both chambers. The Ni(111) surface could be cooled to below 160K and heated resistively to >1000K on the sample manipulators.

The Ni(111) surface was cleaned by cycles of Ar⁺ ion sputtering and annealing using procedures that were identical to those of earlier work [Van Treuren, Wheeler]. The cyclohexanol (99.9+%), t-butanol (99.5+%) and phenol (99.9+) (Aldrich Chemical Co) were further purified by freeze-pump-thaw cycles before introduction into the UHV chambers for adsorption onto the Ni(111) surface. All three alcohols have reasonably high vapor pressures at room temperature. No special care was needed except that the phenol was kept in dark when not in use [Russell (1995)].

RESULTS

Cyclohexanol Decomposition

The primary mechanism that is expected for cyclohexanol decomposition on the Ni(111) surface is initiated by deprotonation to form a stable cyclohexanoyl intermediate. This would then be followed by β-hydrogen elimination to yield adsorbed cyclohexanone.

As expected, the three molecules used in this investigation will be shown to reveal three distinct mechanisms of alkoxy decomposition on the Ni(111) surface. Cyclohexanol adsorbs on the Ni(111) surface to form cyclohexanoyl intermediates and then desorbs as cyclohexanol upon heating to 315 K. A small fraction of the adsorbed cyclohexanol decomposes completely giving rise to desorption of CO at temperatures above 400 K. Residual carbon dissolved into the bulk of the Ni crystal at temperatures below 730 K, leaving the Ni(111) surface clean. Some of the t-butanol groups produced on the surface desorb as isobutylene. The remainder underwent decomposition to yield carbodic carbon on the surface and H₂ and CO desorbing into the gas phase. Although some carbodic carbon was deposited onto the Ni(111) surface during thermal decomposition of t-butanol, the Ni(111) surface was clean after heating to 730 K. Finally, phenol adsorbed to form phenoxy which then decomposed completely to yield graphitic carbon deposits on the Ni(111) surface and desorption of H₂ and CO. The graphitic carbon remained on the surface to temperatures in excess of 730K. These findings reveal fundamental differences between the surface chemistry of various alkoxy species and reveal the mechanisms by which the molecular structure of the ligands used in vapor phase lubricants can influence their tribological behavior.

\[ C_6H_{11}OH + 2 \text{Ni} \rightarrow C_6H_{10}O - \text{Ni} + H \cdot \text{Ni} \]
\[ C_6H_{10}O - \text{Ni} \rightarrow C_6H_{10} = O + H \cdot \text{Ni} \]

[1]

Figure 1 shows selected TPR spectra of cyclohexanol adsorbed at 230 K on Ni(111) and then heated at 2K/s. The main desorption feature appears at 315 K as is seen in the desorption spectrum of the fragment at m/q = 55 and has been identified as desorption of cyclohexanone. Other fragments were monitored during TPRS experiments. The fragmentation pattern matches that of a standard cyclohexanone spectrum which, as in Fig. 1, has a significantly higher intensity at m/q = 55 than at m/q = 57 [Heller]. In comparison, when adsorption was performed at 170K, multilayers of adsorbed cyclohexanol desorbed at 197 K. Cyclohexanol is identified by its fragmentation pattern which has a higher intensity at m/q = 57 than at m/q = 55. Desorption of cyclohexanone is consistent with the expected β-hydrogen elimination in cyclohexanoyl but this is not the only decomposition pathway since additional species are observed desorbing from the surface at higher temperatures.

Some fraction of the cyclohexanol adsorbed on the Ni(111) surface undergoes complete decomposition to adsorbed hydrogen, carbon and oxygen. Hydrogen (m/q = 2) desorbs in a peak centered at 360 K. This is the same temperature range at which H₂
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recombination of atomic C and O is known to occur in this temperature range [Madden, Erley, Russell (1987)].

The observation of CO desorption at 450-600K during cyclohexanol decomposition implies that some fraction of the carbon in the adsorbed molecule does end up on the Ni(111) surface at high temperatures. Surface carbon was monitored by taking Auger spectra of the surface after heating to increasing temperatures (Fig. 2). The cyclohexanol was adsorbed at 230K which is above the multilayer desorption temperature and thus allows the adsorption of a saturated monolayer. Heating to 380K results in the desorption of the fraction of the cyclohexanol that reacts to form cyclohexanone. The Auger electron spectra indicate that roughly 60 percent of the adsorbed carbon and oxygen present at 230K is removed in the form of cyclohexanone during heating to 380K. Surface analysis using XPS shows the same results and suggests that about 70 percent of the carbon is removed from the surface in the form of cyclohexanone. The carbon and oxygen remaining on the Ni(111) surface at 380K are completely removed by heating to 720K. In part this is a result of the desorption of CO in the temperature range 400-600K. However, the decomposition of cyclohexanol presumably deposits carbon and oxygen in a six to one ratio while the desorption of CO results in removal of only one carbon atom per oxygen atom. There must be some carbon deposited onto the Ni(111) surface that is removed during heating by dissolution into the bulk of the crystal.

As expected the decomposition of cyclohexanol on the Ni(111) surface follows a mechanism that is consistent with that observed for primary and secondary alcohols on a number of metal surfaces. A stable alkoxy intermediate is produced which can react by β-hydrogen elimination resulting in cyclohexanone desorption. This illustrates the relatively efficient removal of carbon from the surface by ligands with β-hydrogen atoms. As a result the use of alkyl phosphates with primary or secondary alkoxy groups as vapor phase lubricants might be expected to lead to low carbon content in the lubricating films of polyphosphate glass.

t-Butanol Decomposition

The deprotonation of t-butanol on a metal surface results in the formation of a t-butoxy group that has no β-hydrogen atoms and hence cannot decompose by the simple one-step β-hydrogen elimination observed in primary or secondary alkoxy groups such as cyclohexanoxo. An analogous species for which the reaction mechanism is known on the Ni(100) surface is the neopentyl group, (CH₃)₂C-CH₂-Ni. This undergoes cleavage of the α-C-C bond to form an adsorbed t-buty1 group. These then react by β-hydrogen elimination to produce isobutylene [Zaera].

\[
(\text{CH}_3)_2\text{C} \cdot \text{CH}_2 \cdot \text{Ni} + \text{Ni} \rightarrow (\text{CH}_3)_2\text{C} \cdot \text{Ni} + \text{CH}_2 \cdot \text{Ni}
\]

\[
(\text{CH}_3)_2\text{C} \cdot \text{Ni} \rightarrow (\text{CH}_3)_2\text{C} = \text{CH}_2 + \text{H} \cdot \text{Ni}
\]  [2]

A reaction like this does indeed occur in the case of t-butoxy groups. Figure 3 shows selected TPR spectra of t-butanol adsorbed on Ni(111) illustrating the desorption of three species: H₂, CO, and isobutylene. Hydrogen desorbs in the temperature range of 350-450 K with a dominant peak centered at 415 K and a low temperature shoulder at 365K. This is roughly the feature which one observes in the desorption of H₂ following adsorption
of hydrogen alone by exposure to H₂ gas [Christmann (1979)].
This hydrogen may be contributed by deprotonation of the hydroxyl protons of the adsorbed t-butanol and dehydrogenation of the methyl moieties. As shown in Fig. 3, in the same temperature range (405K) one observes the desorption of isobutylene (m/q = 56) and a feature with m/q = 28 which may be due in part to the fragmentation of isobutylene and in part to the desorption of molecularly adsorbed CO. Other m/q ratios were monitored using the mass spectrometer in order to identify other possible products of t-butanol decomposition. These included the dominant ionization fragments of t-butanol itself (m/q = 59), isobutylene oxide (m/q = 42), and acetone (m/q = 58), however, none of these species were observed [Brainard (1989a), Brainard (1989b)]. Finally in the temperature range 500-650K there is a large CO desorption feature indicating that some fraction of the t-butanoxy groups undergo complete dissociation to deposit carbon and oxygen on the Ni(111) surface.

The TPR spectra of Fig. 3 suggest that the t-butanol decomposition occurs in several steps and that there are two parallel decomposition pathways. They are consistent with a mechanism that is initiated by low temperature deprotonation to produce adsorbed t-butanoxy groups which are the species of primary interest in this study. The desorption of isobutylene is consistent with a mechanism in which the (CH₃)₂C-ONi bond is broken to form adsorbed t-butyl groups which then undergo β-hydrogen elimination to produce the isobutylene.

\[
\text{(CH₃)₂C - O - Ni \rightarrow (CH₃)₂C - Ni + O - Ni}
\]

\[
\text{(CH₃)₂C - Ni \rightarrow (CH₃)₂C = CH₂ + H - Ni}
\]

This then is a mechanism by which carbon is remove from the Ni(111) surface. However, not all the adsorbed t-butanol generates desorbing organic compounds. Some fraction undergoes complete dehydrogenation at temperatures below 420K to release hydrogen and leave carbon and oxygen atoms on the surface. These then recombine and desorb as CO in the temperature range 500-650K [Madden, Erley, Russell (1987)]. Given the stoichiometry of the t-butanoxy groups, however, these reactions must leave some carbon on the Ni(111) surface.

The evolution of the carbon on the Ni(111) surface during the decomposition of t-butanol has been monitored using both AES and XPS. Auger analyses revealed that t-butanol deposits carbodic carbon on the Ni(111) surface, but the carbon easily dissolved into the Ni bulk. Figures 4 and 5 illustrate the Auger spectra and the C Is X-ray photoemission line as the adsorbed layer of t-butanol was heated. The spectra collected after the sample was heated to 460K correspond to the condition after desorption of isobutylene and hydrogen. Of the carbon initially adsorbed on the surface as t-butanol at 230K, roughly 33 percent has been removed in the form of isobutylene (and some CO). During heating to 630K an additional 33 percent is removed by recombination of C and O to des-
orb as CO. Further heating to 730K results in the disappearance of the carbon from the Ni(111) surface, presumably due to dissolution into the bulk of the Ni sample.

In contrast to the primary and secondary alcohols, t-butanoxo groups cannot undergo β-hydrogen elimination since there is no β-H. Thus, the t-butanoxo intermediate is more stable than the alkoxy groups formed by primary and secondary alcohols. This enhanced stability can be readily observed by comparing Figs. 1 and 3. The isobutylene desorption temperature is about 100K higher than that of cyclohexanone. This is due to the higher activation barrier for cleavage of the (CH₃)₂C-ONi bond which must be the rate limiting step in the appearance of isobutylene. This observation is consistent with previous studies of alcohol decomposition on pre-oxidized Ag(110) and Cu(110) surfaces [Brainard (1989a), Brainard (1989b)]. The combined facts that some of the carbon can be removed from the surface as isobutylene and that the remainder desorbs as CO or dissolves into the bulk indicate that none of the forms of carbon generated by decomposition of t-butanoxo groups on the Ni(111) surface are stable to high temperatures.

**Phenol Decomposition**

As in the case of the t-butanoxo group the phenoxy groups produced by phenol adsorption on a metal surface have no β-hydrogen atoms for elimination. Furthermore the cleavage of the C₆H₄-ONi bond would result in the formation of a phenyl group which also cannot produce any stable product by β-hydrogen elimination. Phenyl groups on the Ni(100) surface produce benzene and H₂ desorption [Tjandra]. Figure 6 shows the TPR spectra of adsorbed phenol on Ni(111). The only species observed desorbing from the surface are H₂ (m/q = 2) and CO (m/q = 28). No desorption signals were observed while monitoring m/q = 15, 18, 39, 63, possible cracked fragments from phenoxy, benzene, or m/q = 94. the parent phenol molecule. Phenol decomposes completely to deposit carbon on the surface with the only reaction channel for carbon removal being the desorption of CO.

\[
C₆H₄O - Ni + Ni → C - Ni + H - Ni + O - Ni
\]  

[4]

Hydrogen desorption during phenol decomposition gives rise to two peaks in Fig. 6. The first peak centered at 400K is evidently due to desorption of atomic H adsorbed on the Ni(111) surface since the peak position is in the range found by adsorbing hydrogen on a clean Ni(111) surface [Christmann (1979)]. In contrast with the decomposition of either cyclohexanoxo or t-butanoxo groups on the Ni(111) surface, the C-H bonds in phenoxy remain intact to much higher temperatures. The second hydrogen desorption peak in Fig. 6 extends from 450 to 650K. This is a much higher temperature range than the intrinsic desorption of hydrogen from the Ni(111) surface and must be rate limited by the dehydrogenation of intermediates in the decomposition of phenoxy on the surface. The rates of the dehydrogenation reaction in the adsorbed
phenoxy groups are clearly much lower than in the cyclohexanoxy or t-butanox groups.

The desorption of CO during phenoxy decomposition on the Ni(111) surface occurs over the temperature range 450-600K (Fig. 6). The production of CO can occur by a mechanism in which there is complete decomposition of the phenoxy followed by recombination of atomic C and O on the Ni(111) surface. Alternately there may be a mechanism which results in the production of CO without the intermediate dissociation of the C-O bond. Previous work using $^{13}$C isotope labeling and infrared spectroscopy has suggested that some fraction (~60%) of the C-O bonds in phenoxy adsorbed on the Ni(111) surface remain intact during the reaction producing CO [Russell (1995)]. In other words the decomposition process is not initiated by cleavage of the $C\equiv H_\text{2}$-ONi bond but by some other reaction such as either C-H or C-C bond breaking. The lack of any benzene desorption also suggests that the reaction mechanism is not one which produces a stable phenyl intermediate [Tjandra]. It is not clear from the authors data whether the formation of CO from phenoxy on the Ni(111) surface occurs by a mechanism involving cleavage of the C-O bond in the $C\equiv H_\text{2}$-ONi or by a mechanism that leaves it intact.

The important difference between the surface chemistry of the phenoxy groups and that of the cyclohexanoxy or t-butanox groups is the efficiency of carbon deposition onto the surface. In the cases of cyclohexanoxy or t-butanox there are mechanisms by which carbon is removed from the surface in the form of hydrocarbon species. This does not occur in the case of phenoxy.

An equally important difference is the nature of the carbon that is left on the surface. There are significant differences between the carbonaceous deposits left by these three species. The most important is that the carbon deposits produced by phenoxy decomposition are stable on the surface to higher temperatures than those generated during cyclohexanoxy or t-butanox decomposition. Figure 7 compares the C 1s XP spectra of the adsorbed monolayers of all three species as deposited on the surface at 230K and after heating to 730K. It is quite apparent that the carbon film produced by decomposition of phenol is the only one that survives annealing to 730K.

XPS and AES Analysis of Carbon on the Ni(111) Surface

Adsorbed carbon on metal surfaces is often thought to exist in either carbodic or graphitic forms. For a direct comparison of the carbon deposits on the Ni(111) surface Fig. 7 compiles together the C(1s) XP spectra obtained at identical conditions for the three alcohols adsorbed at 230K and then after heating to 730K. It reveals that after the adsorbed layers have been heated to 730K all of the carbon deposited during the decomposition of cyclohexanol and t-butanol has disappeared. In contrast, a large fraction (~60%) of the carbon initially present on the Ni(111) due to phenol adsorption at 230K remained on the surface following phenol decomposition. This residual carbon dissolved into the Ni bulk when the Ni(111) surface was heated to 900 K. Clearly there are differences in the thermal stabilities of the carbon films generated by the decomposition of the three different alcohols.
This suggests that there are of different types with the carbon generated by phenol decomposition being of the graphitic form while a large fraction of the carbon generated by the t-butanol decomposition is carbide.

**DISCUSSION**

The primary goal of the work presented here has been to obtain a fundamental understanding of the chemistry of vapor phase lubrication. In particular the authors hope to address the differences caused by using different ligands on the organophosphates used as vapor phase lubricants. The most commonly used vapor phase lubricants are aryl phosphates, such as tricresylphosphate (CH₃C₆H₅O)₃P=O and triphenyl phosphate (C₆H₅O)₃P=O. Each phosphate molecule can be viewed as a P=O group bonded to three arylxoy ligands. Using trimethylphosphate, (CH₃O)₃P, as a model compound for study on the Ni(111), Cu(111) and Fe(110) surfaces it has been shown that scission of the P-O bonds in such species results in the formation of alkoxo species and that these then decompose in the same manner as alkoxo groups produced by alcohol decomposition. Thus, the current investigation of the surface chemistry of alkoxo and aryloxo groups produced by alcohol dissociation can shed some light on the differences observed among the different phosphates used as vapor phase lubricants. It is important to point out that the mechanism of the dissociation of the phosphates has not been clearly determined and that this requires further investigation [Wheeler]. If there are substantial differences between the reactivity of the phosphates and the phosphates, then the authors may be wrong in their conjecture that the important intermediates are alkoxo groups.

Previous studies of vapor phase lubrication have shown that the aryl phosphates give better performance than the alkyl phosphates [Groenenweg, Forster]. On the basis of the work presented in this paper it seems that this can easily be understood in terms of the decomposition chemistry of the aryloxy and alkoxo species generated by phosphate decomposition. The aryloxy groups such as phenoxo can deposit more carbon onto the surface than the alkoxo groups because their chemistry does not allow removal of carbon from the surface in the form of hydrocarbon intermediates. In the cases of the alkoy groups there are intermediates in the decomposition mechanism that have β-hydrogen atoms that can be eliminated to produce stable hydrocarbons that desorb from the surface. By comparison the only carbon removed from the surface during the decomposition of the phenoxy groups was that fraction that was oxidized to form CO. A second distinguishing feature of the carbon films generated by the decomposition of the phenoxy groups is that they form graphic films more readily than the alkoxo groups. Alkoxo groups produced carbide carbon films that dissolved in the bulk of the Ni sample at much lower temperatures than the graphic films. These two features of the surface chemistry of the aryloxy and alkoxo groups are consistent with the observed differences in the performance of the organophosphates used as vapor phase lubricants. They suggest that the phosphates with aryloxyl ligands will decompose to produce lubricating films that are higher in graphic carbon content than organophosphates based on alkoxo ligands.
CONCLUSIONS

It has been shown that some of the difference in the performance of various alkyl and aryl phosphates as vapor phase lubricants can be explained by the surface chemistry of the intermediates produced in their decomposition. On the evidence produced by studies of trimethylphosphate decomposition the authors have worked on the basis that the relevant intermediates are alkoxide and arylxoy species. The alkoxide species can decompose by β-hydride elimination mechanisms that result in the removal of carbon containing species from the surfaces. Aryloxy species, on the other hand, do not contain the requisite β-hydrogen atoms in their structures and therefore decompose completely to leave graphic carbon on the surfaces. The ability to decompose to deposit graphic carbon onto the surfaces is then believed to be the reason for the superior performance of aryl phosphates as vapor phase lubricants.

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