



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, $(\text{CH}_3(\text{C}_6\text{H}_4)\text{O})_3\text{P}=\text{O}$, has been the most commonly studied vapor

phase lubricant, owing to its high thermal stability and wide use as an antiwear 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 $D_{\text{P-O}} = 86\text{-}92 \text{ kcal mol}^{-1}$ 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 ($(\text{CH}_3\text{O})_3\text{P}$). The authors recent studies of trimethylphosphite decomposition on Ni(111) and oxidized Cu(111) surfaces revealed that one of the initial steps in trimethylphosphite 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) trimethylphosphite 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 aryloxy 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 aryloxy 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 [Rufael]. Thus, the signal originally assigned to P=O might in fact be due to an aryloxy species produced by the cleavage of P-O bonds in tricresylphosphate. The point is that the authors model compound, trimethylphosphite, 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 trimethylphosphite, that in the phosphates it is the P-O bonds that break to generate alkoxy or aryloxy 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 (RCH₂-O-) and secondary alkoxides (R'RCH-O-) is β -hydride elimination to form aldehydes (RCH=O) or ketones (R'RC=O) which desorb rapidly from the surfaces [Gellman, Friend]. Tertiary alkoxides (R''R'RC-O-) have no β -hydrogen atoms for elimination. They can react by C-O bond cleavage, at much higher temperatures, to form tertiary alkyl groups (R''R'RC-) which would then have β -hydrogen atoms which could be eliminated to yield olefins [Brainard (1989a), Brainard (1989b)]. By contrast the phenoxy groups (C₆H₅O-) have no comparable mechanistic pathways which lead to reaction products that can desorb from the surface. Because they have no β -hydrogen atoms they cannot undergo β -hydrogen elimination. One possible mechanism would be the cleavage of

the C-O bond to produce adsorbed phenyl groups. A study of the surface chemistry of iodobenzene on the Ni(100) surface suggests that this ought to be accompanied by the observation of benzene desorption [Tjandra]. However, this was not observed in a study of the surface chemistry of phenol on the Ni(110) surface [Russell (1995)]. Instead there is some evidence that phenoxy decomposition occurs by cleavage of a C-C bond and the only observed decomposition products were CO and H₂. This is accompanied by the deposition of carbon onto the Ni(110) surface. For these mechanistic reasons the decomposition of phenoxy groups is likely to be more efficient at carbon deposition onto surfaces than decomposition of alkoxy groups and it may be that this is the reason for the superior performance of aryl phosphates over alkyl phosphates as vapor phase lubricants.

In this study cyclohexanol (C₆H₁₁OH), t-butanol ((CH₃)₃COH), and phenol (C₆H₅OH) were chosen as models for the ligands used on alkyl and aryl phosphate vapor phase lubricants. 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 cyclohexanoxo group (C₆H₁₁O-). This is a secondary alkoxy and can react by β -hydrogen elimination to yield cyclohexanone (C₆H₁₀=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-butanoxo intermediate ((CH₃)₃CO-) 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-butanoxo intermediates. The chemistry of t-butanol on the pre-oxidized Ag(110) and Cu(110) surfaces generates isobutylene ((CH₃)₂C=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)₃C-CH₂-) on the Ni(100) surface [Zaera]. These react by cleavage of the C-C bond adjacent to the surface to produce adsorbed tertiary butyl groups ((CH₃)₃C-) which then react by β -hydrogen elimination to yield isobutylene desorption. By comparing the surface chemistry of phenoxy, cyclohexanoxo, and t-butanoxo groups the authors have gained insight into the relative efficiency of carbon deposition by the different alkyl and aryl phosphates used for vapor phase lubrication.

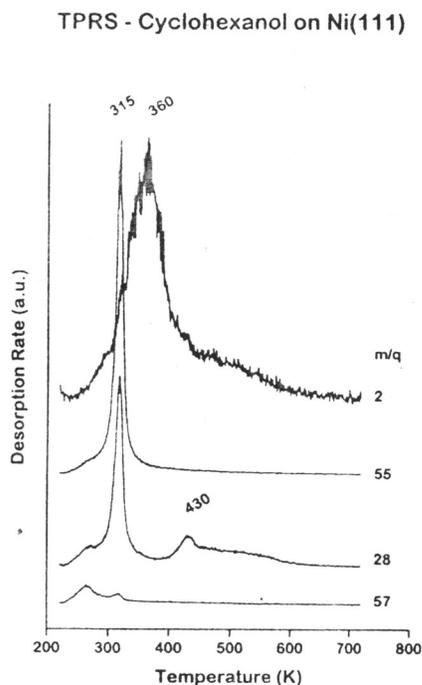


Fig. 1—Selected TPRS spectra of cyclohexanol on a Ni(111) surface. Cyclohexanol reacts to form cyclohexanoxo, the majority of which decomposes by β -hydrogen elimination to yield cyclohexanone desorption at 318 K. Some fraction decomposes completely to hydrogen, carbon and oxygen to yield H_2 and CO desorption at higher temperatures. Only the representative fragments for hydrogen ($m/q = 2$), cyclohexanone ($m/q = 28, 55$ and 57) and carbon monoxide ($m/q=28$) are shown. The relative intensity of fragments with $m/q = 55$ and 57 discriminates cyclohexanone from cyclohexanol. The heating rate was 2 K/s .

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 cyclohexanoxo intermediates and then desorbs as cyclohexanone 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-butanoxo groups produced on the surface desorb as isobutylene. The remainder underwent decomposition to yield carbidic carbon on the surface and H_2 and CO desorbing into the gas phase. Although some carbidic 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 phenoxo which then decomposed completely to yield graphitic carbon deposits on the Ni(111) surface and desorption of H_2 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.

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^+ ion 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 $>1000\text{K}$ 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+%), t-butanol (99.5+%) and phenol (99+%) (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 cyclohexanoxo intermediate. This would then be followed by β -hydrogen elimination to yield adsorbed cyclohexanone.

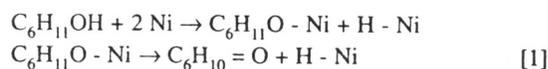


Figure 1 shows selected TPRS spectra of cyclohexanol adsorbed at 230 K on Ni(111) and then heated at 2K/s . The main desorption feature appears at 315 K as is seen in the desorption spectrum of the fragment at $m/q = 55$ and has been identified as desorption of cyclohexanone. Other fragments were monitored 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 cyclohexanoxo 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 H_2

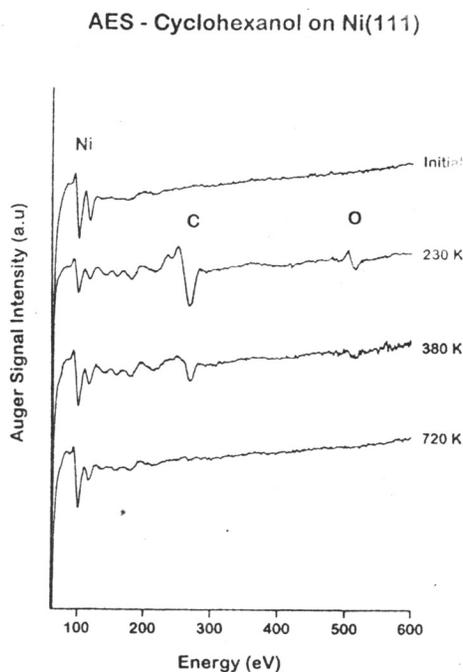


Fig. 2—AES spectra of a Ni(111) surface following.

- (a) Ar⁺ sputtering and annealing
- (b) saturation adsorption of cyclohexanol at 230 K
- (c) heated to 380 K
- (d) heated to 720 K.

The spectrum taken at 380K reveals that a large fraction of the carbon initially present in the form of cyclohexanol desorbs in the form of cyclohexanone. The carbon film that remains after cyclohexanone desorption reacts to desorb as CO and dissolves into the bulk of the Ni sample during heating to 720K.

desorption is observed following adsorption of hydrogen or methanol on the clean Ni(111) surface [Van Treuren, Christmann (1979)]. The implication is that the majority of the C-H bonds have dissociated at or below 360K. In addition there is a small amount of residual H₂ desorption that is coincident in temperature with the desorption of CO (*m/q* = 28) in the temperature range 400-600K. The high temperature desorption of H₂ may be due to the dissociation of hydrocarbon fragments produced during the course of cyclohexanoxy decomposition.

The desorption of CO (*m/q* = 28) occurs over the temperature range 400-600K. Although there is a fragment with *m/q* = 28 that appears in the desorption spectrum at 315K this is associated with the fragmentation of cyclohexanone. In the temperature range 400-600 K the only fragments observed in the mass spectrometer have *m/q* = 2, 12, 16, and 28. Molecular CO adsorbed on the Ni(111) surface desorbs in the temperature range 380-430K [Zhang, Miller, Froitzheim, Christmann (1974)]. The small peak observed at the low temperature side of the CO desorption feature observed in Fig. 1 may be due to molecularly adsorbed CO present either as a product of cyclohexanol decomposition or simply adsorbed from the chamber background. On the other hand the CO desorbing in the temperature range above 450K must come from the recombination of C and O atoms produced as a result of the decomposition of cyclohexanoxy on the Ni(111) surface. The

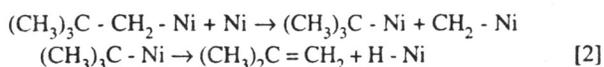
recombination of atomic C and O is known to occur in this temperature range [Madden, Erley, Russell (1987)].

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 cyclohexanoxy. An analogous species for which the reaction mechanism is known on the Ni(100) surface is the neopentyl group, (CH₃)₃C-CH₂-Ni. This undergoes cleavage of the α C-C bond to form an adsorbed t-butyl group. These then react by β -hydrogen elimination to produce isobutylene [Zaera].



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

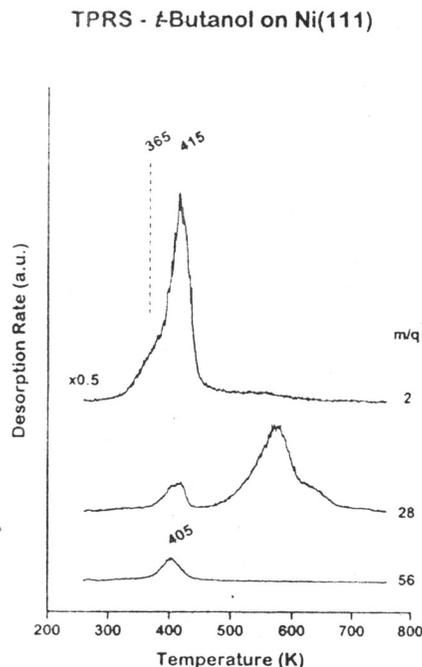


Fig. 3—Selected TPRS spectra of *t*-butanol on a Ni(111) surface. A small fraction of the *t*-butanol reacts to form isobutylene while the remained completely decomposes to hydrogen, carbon and oxygen by 450K. Desorption of isobutylene ($m/q = 2, 28$ and 56) occurs at 405K. The hydrogen has desorbed from the surface by 450K while the C and O recombine to desorb as CO between 500 and 650K. The heating rate was 2 K/s.

of hydrogen alone by exposure to H_2 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*-butanoxo groups undergo complete dissociation to deposit carbon and oxygen on the Ni(111) surface.

The TPRS 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*-butanoxo groups which are the species of primary interest in this study. The desorption of isobutylene is consistent with a mechanism in which the $(CH_3)_3C-O-Ni$ bond is broken to form adsorbed *t*-butyl groups which then undergo β -hydrogen elimination to produce the isobutylene.

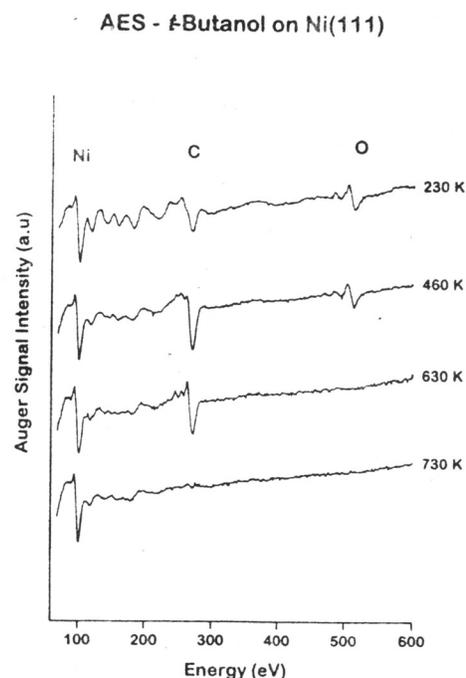
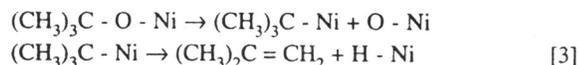


Fig. 4—Auger electron spectra of a Ni(111) surface following saturation of *t*-butanol.

- (a) at 230 K followed by heating to
 (b) 480 K
 (c) 630 K
 (d) 730 K

Deposition of carbidic carbon is revealed in (c) by the features in the range of 240 and 260 eV. This carbidic carbon dissolves into the bulk of the Ni sample during heating to 730K.



This then is a mechanism by which carbon is removed 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*-butanoxo 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 carbidic 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 1s 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-

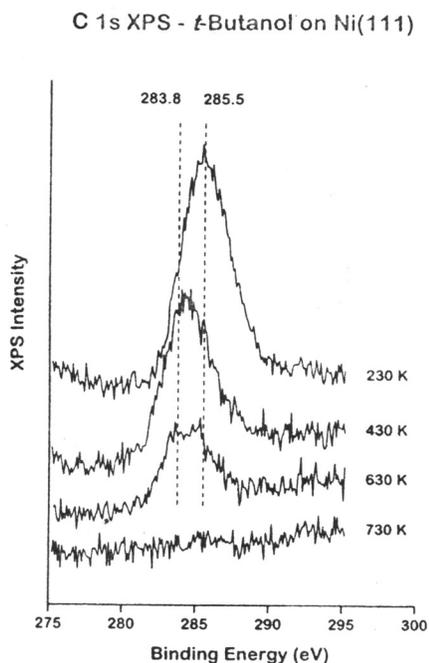


Fig. 5—C 1s XP spectra following adsorption of *t*-butanol on a Ni(111) surface and then annealing to increasing temperatures. The spectra were obtained with the sample cooled to 230 K after heating to the indicated temperatures. There are clear shifts in the C 1s line during *t*-butanol decomposition. At 630K the surface appears to have two types of carbon species, possibly both carbidic (283.8 eV) and graphitic (285.5 eV). The pass energy was 140 V.

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 $(\text{CH}_3)_3\text{C}-\text{ONi}$ 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 $\text{C}_6\text{H}_5-\text{ONi}$ bond would result in the formation of a phenyl group which

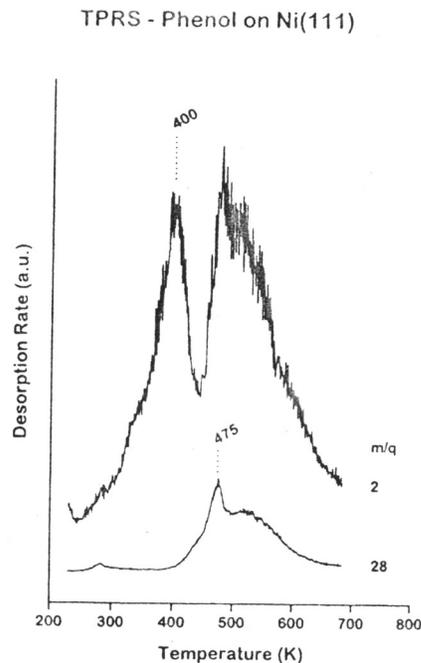


Fig. 6—TPR spectra of phenol on a Ni(111) surface. Only two desorbing species H_2 ($m/q = 2$) and CO ($m/q = 28$) were detected. The appearance of hydrogen desorption at $T > 450\text{K}$ indicates the presence of intact C-H bonds at temperatures much higher than those achieved using either cyclohexanol or *t*-butanol. Phenol was adsorbed at 230K and the heating rate was 2 K/s.

also cannot produce any stable product by β -hydrogen elimination. Phenyl groups on the Ni(100) surface produce benzene and H_2 desorption [Tjandra]. Figure 6 shows the TPR spectra of adsorbed phenol on Ni(111). The only species observed desorbing from the surface are H_2 ($m/q = 2$) 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.



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

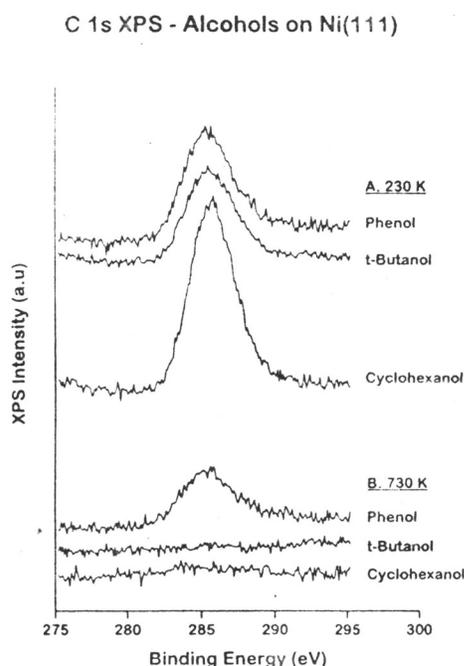


Fig. 7—Comparison of C 1s XP spectra of cyclohexanol, t-butanol, and phenol obtained at identical experimental conditions.

(a) the Ni(111) surface was saturated with adsorbate at 230K
(b) the adsorbed alcohols were heated to 730K.

The spectra clearly reveal that the phenol deposits carbon onto the surface far more efficiently than either the cyclohexanol or the t-butanol. The passing energy was 140 V.

phenoxy groups are clearly much lower than in the cyclohexanoxy or t-butanoxy 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(110) surface remain intact during the reaction producing CO [Russell (1995)]. In other words the decomposition process is not initiated by cleavage of the $\text{C}_6\text{H}_5\text{-ONi}$ 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 $\text{C}_6\text{H}_5\text{-ONi}$ 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-butanoxy groups is the efficiency of carbon deposition onto the surface. In the cases of cyclohexanoxy or t-butanoxy 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.

Carbon AES on Ni(111)

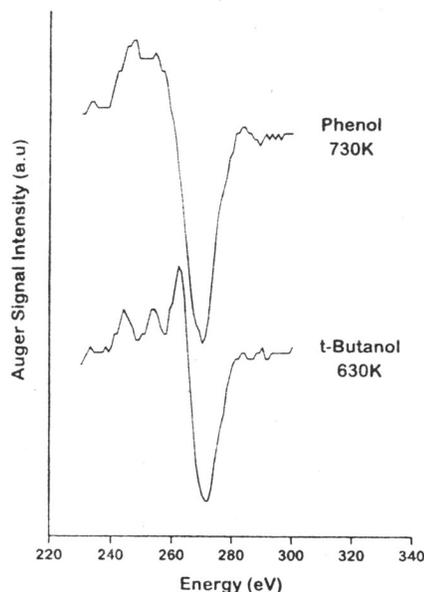


Fig. 8—A direct comparison of AES lineshape of carbon deposited on the surface by adsorption of phenol on Ni(111) followed by annealing to 730K and adsorption of t-butanol followed by annealing to 630K. The features in the energy range 240-260 eV of the t-butanol spectrum are distinctive of carbidic carbon. The spectrum taken following the decomposition of phenol is characteristic of graphitic carbon.

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-butanoxy 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 carbidic 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.

Comparison of Carbon XPS

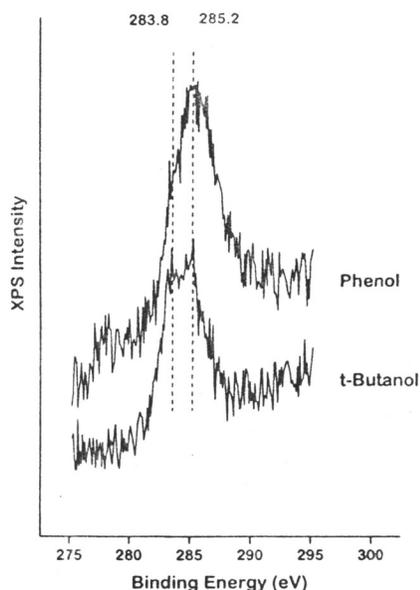


Fig. 9—Comparison of the C 1s XP spectra of carbon deposited on the surface by adsorption of phenol on Ni(111) followed by annealing to 730K and adsorption of t-butanol followed by annealing to 630K. The peak due to phenol decomposition is centered at 285.2 eV. The peak due to t-butanol decomposition appears to have two features with the lower energy having a binding energy of 283.8 eV. The splitting between the two is close to that observed for the difference between graphitic carbon (phenol) and carbidic carbon (t-butanol).

Graphitic and carbidic carbon on surfaces can be distinguished spectroscopically using either Auger spectroscopy or X-ray photoemission spectroscopy. Figure 8 shows the C_{272} Auger peaks of the carbon films produced by adsorption of t-butanol and phenol followed by heating to 630K and 730K, respectively. The lineshapes are quite distinct and the lineshape for the carbon deposited from phenol in particular is characteristic of that commonly assigned to graphitic carbon [Hutson, Houston]. A previous study has established that phenol decomposition also deposits graphitic carbon onto the Ni(110) surface at 650K [Russell (1995)]. In contrast, the Auger lineshape for carbon deposited by t-butanol decomposition (Fig. 8) is quite different and exhibits a couple of peaks in the energy range 240-260 eV which are characteristic of a carbidic state.

Further insight into the nature of the carbon can be obtained by comparing the C(1s) binding energies of the two types of carbon. As can be seen in Fig. 9, the C(1s) binding energy for carbon deposited from phenol is at 285.2 eV while the C 1s spectrum from t-butanol appears to be composed of two peaks, the lower energy one being positioned at 283.8 eV. A previously reported value for the C(1s) binding energy in graphite is 284 eV [Hutson, Outka]. For comparison the value for the C(1s) binding energy of carbidic carbon on the Ni(100) surface is 282.9 eV [Hutson, Koel]. The difference in the reported binding energies of 1.1 eV is close to the 1.4 eV difference between the C(1s) binding energies that the authors observe for carbon deposited from t-butanol and phenol.

This suggests that these 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 carbidic.

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 ($(CH_3C_6H_4O)_3P=O$) and triphenyl phosphate ($(C_6H_5O)_3P=O$). Each phosphate molecule can be viewed as a P=O group bonded to three aryloxy ligands. Using trimethylphosphite, $(CH_3O)_3P$, as a model compounds 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 alkoxy species and that these then decompose in the same manner as alkoxy groups produced by alcohol decomposition. Thus, the current investigation of the surface chemistry of alkoxy and aryloxy 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 alkoxy groups.

Previous studies of vapor phase lubrication have shown that the aryl phosphates give better performance than the alkyl phosphates [Groeneweg, 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 alkoxy species generated by phosphate decomposition. The aryloxy groups such as phenoxy can deposit more carbon onto the surface than the alkoxy groups because their chemistry does not allow removal of carbon from the surface in the form of hydrocarbon intermediates. In the cases of the alkoxy 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 graphitic films more readily than the alkoxy groups. Alkoxy groups produced carbidic carbon films that dissolved in the bulk of the Ni sample at much lower temperatures than the graphitic films. These two features of the surface chemistry of the aryloxy and alkoxy groups are consistent with the observed differences in the performance of the organophosphates used as vapor phase lubricants. They suggest that the phosphates with aryloxy ligands will decompose to produce lubricating films that are higher in graphitic carbon content than organophosphates based on alkoxy 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 trimethylphosphite decomposition the authors have worked on the basis that the relevant intermediates are alkoxy and aryloxy species. The alkoxy 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 graphitic carbon on the surfaces. The ability to decompose to deposit graphitic 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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