Reaction of Tributyl Phosphite with Oxidized Iron: Surface and Tribological Chemistry

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Received March 3, 2004. In Final Form: June 15, 2004

The surface chemistry of a model lubricant additive, tributyl phosphate (TBPi), is investigated on FeO₄ in ultrahigh vacuum. A portion of the TBPi desorbs molecularly following adsorption at ~200 K, the remainder decomposing either by C–O bond scission to form 1-butyl species or by P–O bond cleavage to from butoxy species. Adsorbed butyl species either undergo β-hydride elimination to desorb 1-butene or decompose to deposit carbon and hydrogen on the surface. The resulting adsorbed hydrogen reacts with the oxide to desorb water or with the butoxy species to form 1-butanol. Butoxy species are stable up to ~600 K at which temperature they also undergo β-hydride elimination to form butanal and the released hydrogen reacts with other butoxy species to form 1-butanol. Only a small amount of carbon is deposited onto the surface following adsorption at ~200 K, which then desorbs as CO above ~750 K. Adsorbing TBPi at 300 K results in the deposition of more carbon and an Auger depth profile reveals that the carbon is located predominantly on the surface, while the phosphorus is rather uniformly distributed throughout the oxide film. This result is in accord with previous near-edge X-ray absorption fine structure measurements, which show the formation of phosphates and polyphosphate glasses. The resulting tribological film appears to be composed of a relatively hard polyphosphate glass formed by rapid diffusion of PO₄ species into the oxide, covered by a low shear strength graphitic layer.

Introduction

Phosphorus-containing molecules are dissolved in base oils to function both as extreme-pressure (EP) and as antiwear (AW) additives.1–7 Phosphorus forms an active component of perhaps the most widely used antiwear additive, zinc dialkyl dithiophosphate (ZDDP). The chemistry that leads to antiwear films is relatively complicated; this is not surprising, given the complexity of the molecules. However, the consensus is that one of the most important components formed in the antiwear film is a relatively hard polyphosphate glass, obviously derived from the phosphorus in the additive. Chlorine,8,9 sulfur,10,11 and phosphorus-containing12–16 molecules are commonly used as EP additives. Chlorine-containing additives are generally chlorinated hydrocarbons and operate by reactively forming an FeCl₂ film8,9,17–19 at the high temperatures (about 1000 K and above20) encountered at the solid–solid interface during EP applications such as ferrous metal machining or forming. Sulfur-containing additives are generally molecules that contain sulfur–sulfur linkages and, for disulfide bonds, cleave to form surface thiocarbonylates that rapidly decompose to form FeS under EP conditions10,11 and FeS₃ at the lower temperatures encountered in typical antiwear applications.21 Phosphorus-containing EP additives are generally more complicated and consist of phosphate or phosphates that form P(OR)₃ or O=P(OR)₂, respectively, where R is a hydrocarbon species (at least one) or hydrogen.2,12–16 At least one role of the hydrocarbon groups is to render the molecule oleophilic allowing it to dissolve in the base oil. One of the most commonly used aromatic forms is tricresyl phosphate, although alkyl substituents are common. The chemistry of tributyl phosphate has been studied on clean iron surfaces.22,23 This work suggested that the initial surface reaction would be dominated either by cleavage of the P–O bonds to yield surface alkoxo species or alternatively by the cleavage of C–O bonds to yield surface alkyl groups. It was found on clean iron that the alkyl chemistry dominated the surface reaction.22,23 While it is true that the interface is likely to be relatively clean under true EP conditions since the oxide layer will be rapidly removed from the surface, under AW conditions a surface oxide is still likely to be present. Moreover, in some EP applications, such as grinding, air is rapidly entrained with the lubricating fluid allowing oxygen to access the surface. This is likely to allow the surface to reoxidize so that, even in these cases, the chemistry of the oxide surface may be more relevant than that of the clean surface. The following therefore explores the surface chemistry of tributyl phosphate on oxidized iron in

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ultrahigh vacuum. The butyl version of the phosphate is chosen since it is relatively easy to introduce into ultrahigh vacuum, it is a reasonable facsimile of commercial alkyl-containing phosphate additives, and would allow rather direct comparison with the chemistry on the clean (reduced) surface. To assist in understanding the surface chemistry of the phosphate, both 1-butanol and 1-iodobutane are also studied here since these are expected to form 1-butoxy and 1-buty1 species, respectively, identical to those likely to be formed from decomposition of the phosphate.

**Experimental Section**

Experiments were carried out in a stainless steel, ultrahigh vacuum chamber operating at base pressures of $\sim 2 \times 10^{-10}$ Torr following bakeout, which has been described in detail elsewhere. The chamber is equipped with a Dycor quadrupole mass spectrometer for temperature-programmed desorption (TPD) measurements and a single-pass, cylindrical-mirror analyzer for Auger analysis of the surface. An iron foil (Johnson-Matthey, 99.99% purity) is mounted on a steel plate (1 mm thick) as a support and a K-type thermocouple is mounted to the back of the support plate to allow the temperature to be monitored.

The tributyl phosphate (Fluka, >95% purity), 1-butanol (Fluka, >99% purity), and 1-iodobutane (Aldrich, 99% purity) were transferred to glass bottles and attached to the gas-handling line of the vacuum system and further purified by several freeze-pump-thaw cycles, and their purity monitored by mass spectrometry.

The iron foil was bombarded with argon ions ($\sim 1 \mu\text{A}/\text{cm}^2, 2 \text{keV}$) and annealed to 1000 K several times to remove surface contaminants (mainly C, S, and N). It was then oxidized using $5 \times 10^{-7}$ Torr of O$_2$ for 1 h at 800 K. This procedure also completely removes any residual carbon. Langell and Somorjai found that, for an Fe(110) single

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Figure 1. Temperature-programmed desorption spectra following various exposures of 1-butanol adsorbed onto Fe$_3$O$_4$ at 200 K, taken using a heating rate of 10 K/s. Spectra are shown for 56, 72, 43, and 44 amu.
crystal, an oxygen exposure of \(~ 600\) langmuirs at \(~ 770\) K is required to saturate the oxygen Auger signal. This implies that, since much larger oxygen exposures were used in this work, the surface region of the polycrystalline sample is fully oxidized.

The oxidation state of the iron was gauged using Auger spectroscopy. The line shapes of high-kinetic-energy LMM iron Auger signals do not change with oxidation state. However, the line shapes of the lower-energy M\(_{2,3}VV\) Auger signals are sensitive to the iron oxidation state. \(^{25-28}\) In the case of pure iron, the MVV transition has a kinetic energy of 46.5 eV, which is also found for FeO. However, for Fe\(_3O_4\), the 52 eV transition becomes the strongest and is accompanied by features at 46.5 and 44 eV, which are relatively weak. In the case of Fe\(_2O_3\), the 46.5 eV signal disappears completely and the 44 eV signal is as intense as the 52 eV signal. Comparison of these fingerprint data with the Auger spectrum of the oxidized foil used in this work showed it to be Fe\(_3O_4\). It has also been found that heating bulk \(\alpha\)-Fe\(_2O_3\) to \(~ 770\) K in ultrahigh vacuum induces a phase transition from Fe\(_2O_3\) to Fe\(_3O_4\). Since our sample is annealed to 1000 K, this observation is consistent with the assignment of our films to Fe\(_3O_4\).

The peak-to-peak amplitude ratio of O (KLL, 510 eV)/Fe (LMM, 702 eV) for our sample is \(2.7 \pm 0.3\). Values of \(~ 1.3\) have been measured previously for an Fe\(_3O_4\) thin

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Figure 2. Temperature-programmed desorption spectra following various exposures of 1-butanol adsorbed onto Fe\(_3O_4\) at 250 K, taken using a heating rate of 10 K/s. Spectra are shown for 31, 2 (H\(_2\)), 18 (H\(_2O\)), and 28 (CO) amu.
film, and a ratio of 4.5 was measured for a thick Fe$_3$O$_4$ film containing 10% of Fe$_2$O$_3$ prior to ion bombardment, which decreased to ~2.1 after the first 50 Å of the film was removed. A measured ratio of O (KLL, 510 eV)/Fe (LMM, 651 eV) for bulk Fe$_3$O$_4$ yielded 3.75 (0.10, and an estimated value of the O (KLL, 510 eV)/Fe (LMM, 702 eV) ratio is 3.1.\textsuperscript{25} The O/Fe Auger ratio appears therefore to depend on film thickness suggesting that a relatively thick film was formed in this work.

**Results**

**1-Butanol Adsorption.** Figures 1 and 2 display a series of temperature-programmed desorption (TPD) spectra collected at various masses following adsorption of various exposures of 1-butanol on Fe$_3$O$_4$ (in langmuirs, 1 langmuir = 1 × 10$^{-6}$ Torr s) at 200 K. Note that doses are not corrected for ionization gauge sensitivities and the exposures are marked adjacent to the corresponding spectrum. Figures 1a–d and 2a are due to the desorption of molecular C$_4$ species and exhibit two features centered at ~260 and 590 K. Figure 2b–d displays a corresponding series of TPD data collected at 2 (H$_2$), 18 (H$_2$O), and 28 (CO) amu. The mass spectra of both 1-butanol and butanal were measured with the same mass spectrometer that was used to collect TPD data. These reveal that 1-butanol has a reasonably intense feature at 31 amu, which is virtually nonexistent in the butanal spectrum, while butanal has a feature at 72 amu, which is essentially absent in the 1-butanol spectrum. Figure 2a then indicates that both the 260 and 590 K desorption states contain 1-butanol, while spectrum 1b also reveals that they also contain butanal, where the proportion of each is different.

**Figure 3.** Temperature-programmed desorption spectra following various exposures of 1-iodobutane adsorbed onto Fe$_3$O$_4$ at 200 K, taken using a heating rate of 10 K/s. Spectra are shown for 44, 55, 56, and 57 amu.
for the low- and high-temperature desorption states. No butanal is formed at low exposures (up to 0.2 langmuirs) below 500 K (Figure 1b), while a broad 1-butanol state is evident in this temperature and exposure range (Figure 2a).

Negligible hydrogen desorption is detected (Figure 2b), while water desorbs almost coincident with the low-temperature (≈260 K) butanal and 1-butanol desorption state (Figure 2c), and a weak water desorption state is also detected at ≈590 K at high 1-butanol exposures. The 28 amu trace (Figure 2d) has weak peaks at ≈260 and 590 K due to some fragmentation of 1-butanol and butanal. The 28 amu signal increases substantially above ≈750 K, and this is ascribed to the formation of CO rather than hydrocarbon fragments since it has no corresponding intensity at 26 and 27 amu (not shown). The CO therefore arises due to reaction between carbon formed by 1-butanol decomposition and the iron oxide.

**1-Iodobutane Adsorption.** The corresponding desorption data for 1-iodobutane are shown in Figures 3, 4, and 5. The majority of the features in the mass spectra of 1-butene and 1-iodobutane are common to both species except for an intense feature at 57 amu in the 1-iodobutane spectrum, which is not detected in 1-butene. Thus, the data of Figure 3d indicate that the low-temperature (≈290 K) desorption feature is due to 1-iodobutane desorption. Apparently at very low exposures, a small amount of 1-iodobutane also desorbs at higher temperatures (≈360 K). It is also evident from the spectra in Figures 3b and 4a and 4b that there is an additional desorption state at ≈370 K, which generally appears as a shoulder on the 290 K state. Since this is clearly not due to 1-butanol at this

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**Figure 4.** Temperature-programmed desorption spectra following various exposures of 1-iodobutane adsorbed onto Fe₃O₄ at 200 K, taken using a heating rate of 10 K/s. Spectra are shown for 18 (H₂O), 28 (CO), 41, and 43 amu.
higher temperature, but has intensity at masses due to 1-butene, it is assigned to the desorption of 1-butene formed by β-hydride elimination from 1-butyl groups formed from 1-iodobutane. A signal is also detected at 430 K at 43 (Figure 4b) and 41 (Figure 4a) amu. Note that this temperature is close to that at which 1-butanol and butanal desorb. TPD spectra were therefore collected at 72 (butanal) and 74 (1-butanol) amu, and the results are displayed in Figure 5. Figure 5a shows a feature at 600 K with intensity at 72 but not at 74 amu indicating that this is due to a small amount of butanal desorption at this temperature. A weak feature is also detected at 300 K at both 72 and 74 amu suggesting that a small amount of 1-butanol is formed at this lower temperature.

Water desorption is found in a broad feature between 250 and 550 K (Figure 4c), while no hydrogen desorption is detected (not shown). This indicates that, similar to the behavior found for 1-butanol, hydrogen resulting from butyl decomposition reacts with the surface oxide to form water. The spectra displayed in Figure 4d show that the corresponding carbon desorbs above 750 K, as found above. The low-temperature features in the 28 amu spectra are due to some 1-iodobutane fragmentation in the mass spectrometer ionizer.

Figure 5. Temperature-programmed desorption spectra following various exposures of 1-iodobutane adsorbed onto Fe$_3$O$_4$ at 200 K, taken using a heating rate of 10 K/s. Spectra are shown for 72 and 74 amu.

Higher temperature, but has intensity at masses due to 1-butene, it is assigned to the desorption of 1-butene formed by β-hydride elimination from 1-butyl groups formed from 1-iodobutane. A signal is also detected at 600 K at 43 (Figure 4b) and 41 (Figure 4a) amu. Note that this temperature is close to that at which 1-butanol and butanal desorb. TPD spectra were therefore collected at 72 (butanal) and 74 (1-butanol) amu, and the results are displayed in Figure 5. Figure 5a shows a feature at 600 K with intensity at 72 but not at 74 amu indicating that this is due to a small amount of butanal desorption at this temperature. A weak feature is also detected at 300 K at both 72 and 74 amu suggesting that a small amount of 1-butanol is formed at this lower temperature.

Tributyl Phosphite Adsorption. The TPD spectra of tributyl phosphite (TBPI) adsorbed on Fe$_3$O$_4$ at 180 K as a function of exposure for various masses are displayed in Figures 6 and 7. Clearly substantial reaction has occurred on the surface although some molecular desorption takes place as evidenced by the 83 amu spectrum (Figure 7c), which is exclusively due to tributyl phosphite. This occurs in a broad feature with a peak temperature of 450 K at low exposures (0.05 langmuir), which grows and shifts slightly to lower temperatures with increasing exposure and is centered at 430 K following an exposure of 1.0 langmuir. A sharp feature appears at 240 K for an exposure of 1.0 langmuir, which is assigned to the desorption of second-layer tributyl phosphite indicating that the surface is saturated by a 1.0 langmuir exposure.

No hydrogen desorption (2 amu, not shown) is detected at all doses, and perhaps a small amount of CO is formed at higher temperatures (spectra not shown). Water (18 amu, Figure 7a) is formed at low temperatures in a broad feature at 350 K at low exposures, shifting to 260 K at saturation (Figure 7a), and an additional feature is found at 640 K, which grows with increasing tributyl phosphite coverage. It should be noted that no water is observed without tributyl phosphite adsorption.

The desorption spectra due to potential decomposition products are relatively complex indicating a number of surface decomposition pathways. The spectrum collected at 72 amu (Figure 6d), a mass that is due exclusively to butanal, shows an intense feature at 630 K, close to the temperature found by adsorbing 1-butanol directly onto the surface (Figure 1b) indicating that the source of butanal is identical in both cases. In this case, 1-butanol was also found to desorb (Figure 2a, 31 amu), and a feature at 630 K in the 31 amu spectrum following tributyl phosphite adsorption (Figure 6a) indicates that 1-butanol is also formed at this temperature. A small amount of water was also found at 630 K when 1-butanol was adsorbed on iron oxide (Figure 2c), while substantially more water is found following tributyl phosphite adsorption (Figure 7a). Water also desorbs at low temperatures when tributyl phosphite is adsorbed on Fe$_3$O$_4$ (Figure 7a), as also found following 1-butanol (Figure 2c) and 1-iodobutane (Figure 4c) adsorption. An additional 1-butanol desorption state is detected at 450 K (Figure 6a) which is not associated with the formation of butanal. This is close to the desorption temperature of tributyl phosphite (Figure 7c). However, tributyl phosphite has negligible fragmentation intensity at 31 amu. In addition, the 450 K 1-butanol desorption state decreases in intensity with increasing tributyl phosphite exposure, while it would increase if it were due to tributyl phosphite fragmentation.

There are no masses that are exclusively due to 1-butene. It has intense fragments at 56 (Figure 6b) and 41 (Figure 7b) amu, but butanal, 1-butanol, and tributyl phosphite also have fragments at these masses. However, the majority of the desorption products arising from butyl decomposition desorb at low temperatures (Figures 3 and
4). Thus, the 41 (Figure 7b) and 56 (Figure 6b) amu spectra exhibit features above 400 K due to 1-butanol and butanal desorption, while small features are detected at 240 K in both spectra, which are assigned to the desorption of a small amount of 1-butene. Note that this temperature is lower than that found for the desorption of 1-butene from butyl species formed from iodobutane (≈370 K). The sharp feature seen in both spectra following a 1 langmuir tributyl phosphite exposure may be due to second-layer tributyl phosphite desorption. The weakness of these features, particularly those at 41 amu, which is the most intense mass in the mass spectrum of 1-butene, implies that only small amounts of 1-butene are formed from tributyl phosphite. Finally, the 57 amu spectra (Figure 6c) are due to 1-butanol and butanal desorption at high temperatures (≈630 K), and the features below this temperature are due to the desorption of tributyl phosphite.

To gauge the extent of decomposition of the hydrocarbon fragments from tributyl phosphite on Fe₃O₄, Auger spectra were collected of the surface after repeatedly adsorbing TBPi and heating to 800 K and the results are displayed in Figure 8 after each cycle. Auger spectra were collected only after heating to 800 K to avoid electron-beam-induced decomposition of molecular fragments present at lower temperatures. This confirms that the iron and oxygen signals remain constant between experiments and that only a very small amount of carbon is deposited onto the surface, while the amount of phosphorus continues to grow. However, tribological interfaces are generally substantially hotter than 200 K so that a similar experiment was carried out, now by adsorbing tributyl phosphite (10 langmuirs) at 300 K. The data of Figures 6 and 7 indicate that some tributyl phosphite has desorbed by this temperature and some 1-butene and water have formed. The resulting Auger spectra are shown in Figure

**Figure 6.** Temperature-programmed desorption spectra following various exposures of tributyl phosphite adsorbed onto Fe₃O₄ at 200 K, taken using a heating rate of 10 K/s. Spectra are shown for 31, 56, 57, and 72 amu.
9 and reveal the presence of substantially more carbon, while the phosphorus signal is relatively smaller.

A depth profile of the selvedge was measured by bombarding the sample with argon ions (3 keV energy, \( \sim 1 \mu \text{A/cm}^2 \)), and the results are displayed as a function of bombardment time in Figure 10 after exposing Fe\(_3\)O\(_4\) to 10 langmuirs of tributyl phosphite and then heating it to 800 K. The peak-to-peak intensities of the features due to oxygen (O KLL, 520 eV kinetic energy), carbon (C KLL, 272 eV kinetic energy), and phosphorus (P KLL, 120 eV kinetic energy) were ratioed to the most intense iron Auger feature (Fe LMM, 703 eV kinetic energy). This clearly indicates the presence of a substantial amount of carbon at the surface, while the surface phosphorus Auger signal is relatively small. The phosphorus, however, penetrates quite far into the oxide film, and the phosphorus Auger signal diminishes only slightly after 15 min of bombardment.

To gauge the effect of surface carbon on the reactivity of tributyl phosphite, Fe\(_3\)O\(_4\) was repeatedly dosed with 10 langmuirs of tributyl phosphite and a TPD spectrum was obtained by heating to 800 K at a heating rate of 8 K/s. The resulting 83 amu (tributyl phosphite) TPD spectra are displayed in Figure 11 and show that the amount of molecular desorption increases substantially from its initial amount after the first dose, slightly more after the second dose, and remains constant after the fourth dose.
implying that the presence of surface carbon deactivates the oxide surface for tributyl phosphite decomposition.

Discussion

**1-Butanol.** The main desorption states found following 1-butanol adsorption on iron oxide are at ~260 and 590 K (Figures 1 and 2). The low-temperature state (at ~260 K) has a tail that appears at higher temperatures (Figure 2a) and extends up to ~450 K. Since a substantial amount of water is formed between 250 and 450 K following adsorption of 1-butanol (Figure 2c), this clearly indicates that a portion of the 1-butanol dehydrogenates. Given that the hydroxy hydrogen is the most labile, it is likely that 1-butanol decomposes to form adsorbed 1-butoxy species and coadsorbed hydrogen. In addition, a significant proportion of the adsorbed 1-butanol desorbs molecularly at ~260 K. The broad state centered at ~260 K with a high-temperature tail extending to ~450 K is thus assigned to a combination of molecular desorption (at ~260 K) and reaction between adsorbed hydrogen and 1-butoxy species to produce the high-temperature tail. A simple Redhead analysis, assuming a pre-exponential factor of \(1 \times 10^{13} \text{s}^{-1}\) yields a molecular desorption activation energy of ~65 kJ/mol.\(^{30}\) A large proportion of the resulting hydrogen also reacts with the surface oxide to form water at between 300 and 450 K (Figure 2c). A previous study of water on iron oxide\(^{31}\) revealed two water desorption states at ~250 K for the monolayer and ~170 K for multilayer desorption. This implies that the water desorbing between 300 and 450 K in this study is reaction

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\(^{30}\) Redhead, P. A. *Vacuum* 1962, 12, 203.

rate limited and not due to water desorption from the background. This is confirmed by carrying out blank experiments. The remaining 1-butoxy species appear to be remarkably stable on the oxide surface and persist up to ~590 K. Under tribological conditions such a monolayer may act as a boundary lubricating layer. The ~590 K desorption state includes both 1-butanol (Figure 2a) and butanal (Figure 1b). The proportion of each is estimated for each exposure from the intensity of the 590 K features using the mass spectrometer ionizer fragmentation patterns and the intensities of the desorption features. To precisely calculate these proportions, the absolute mass spectrometer sensitivities of the most intense peaks (at 41 amu for 1-butanol and 43 amu for 1-butanol in our spectrometer) are required. These are difficult to measure precisely, so it is assumed that they are identical for 1-butanol and butanal. With this assumption, between 35 and 45% of the 590 K feature may act as a boundary lubricating layer.

The TPD spectra of Figure 5 also indicate that a small amount of butanal is formed at ~600 K. This presumably arises because a small portion of the butyl species that are formed on the surface adsorbs onto oxygen sites on the iron oxide forming 1-butoxy species as found above. It is interesting to note that, in this case, no significant 1-butanol is formed. This may just be because the 1-butoxy coverage in this case is so low that the hydrogen formed by \(\beta\)-hydride elimination does not encounter other 1-butoxy species before it reacts with the surface oxide.

**Tributyl Phosphite.** Tributyl phosphite adsorbs on FeO at ~200 K with a portion desorbing molecularly at between ~450 and 430 K, depending on coverage, the remainder decomposing. The surface saturates when exposed to ~1 langmuir of tributyl phosphite and second layers desorb at ~240 K (Figure 7c). A simple Redhead analysis gives a desorption activation energy for tributyl phosphite adsorbed on the iron oxide surface of between 115 and 109 kJ/mol, depending on coverage.

A number of desorption products are found. A combination of 1-butanol and butanal is formed at ~630 K. This behavior is similar to that found when 1-butanol is adsorbed onto the oxide (Figures 1 and 2) and indicates that identical surface chemistry occurs in both cases; adsorbed 1-butoxy species undergo \(\beta\)-hydride elimination to form butanal and the resulting hydrogen reacts rapidly with other 1-butoxy species to form 1-butanol. Substantially more water is formed from tributyl phosphite (Figure 7a) than from 1-butanol (Figure 2c) at ~600 K. It has been shown that water desorbs from oxidized iron below ~250 K, indicating that the water formation from TBPI is reaction rate limited. Since only a small amount of water was formed at the highest 1-butanol coverages, it may be that higher 1-butoxy coverages are attained when tributyl phosphite adsorbs onto the surface.

A weak 1-butanol desorption feature is also detected at ~450 K. A similar feature was evident following adsorption of 1-butanol (Figure 2a) as a shoulder on the ~260 K molecular desorption state and was ascribed to reaction with the \(\ce{O-H}\) hydrogen released when 1-butoxy species are first formed. However, no hydroxy groups are present in tributyl phosphite. In this case, however, butyl species can be formed by \(\ce{C-O}\) bond scission. The detection of a small amount of 1-butene at ~240 K (Figures 6b and 7b) indicates that this does occur to some extent. Adsorbed butyl species do thermally decompose and evolve substantial amounts of water between 300 and 500 K when formed from 1-iodobutane (Figure 4e), which suggests another possible origin for the hydrogen. This is not necessarily the only source of hydrogen at low temper-

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**References**


with PO to deposit primarily 1-butoxy species onto the surface along K, the major reaction pathway involves P is summarized in Scheme 1. Following adsorption at temperature is higher than that found for 1-butoxy species species are derived from tributyl phosphite, this reaction the remainder of the 1-butoxy species are stable up to 630 K where they decompose to form 1-butanol and butanal. It should be mentioned that, when the 1-butoxy species are derived from tributyl phosphite, this reaction temperature is higher than that found for 1-butoxy species formed from 1-butanol (~590 K), implying that the 1-butoxy species may be stabilized by coadsorbed PO groups.

Since tribological reactions take place at 300 K or above, we also examined the adsorption of tributyl phosphite on the iron oxide surface at 300 K. Evidently, some decomposition takes place at this temperature since 1-butene (Figure 6b) and water (Figure 7a) are formed and some tributyl phosphite desorbs (Figure 7c). Iron oxide was therefore exposed to 10 langmuirs of tributyl phosphite (Figure 11). A layered graphitic structure, of course, would correspond to graphitic rather than "carbidic" carbon where it is relatively uniformly distributed. While the chemical state of the resulting phosphorus species is not known from Auger spectroscopy, near-edge X-ray absorption fine structure (NEXAFS) data have shown that these generally consist of phosphates. At the low phosphorus concentrations that would be formed in these TPD experiments, it is likely that the PO species react with the surface oxide layer to form Fe₃(PO₄)₂. In the presence of the higher tributyl phosphite concentrations in a lubricant, higher phosphorus concentrations would lead to the formation of polyphosphate glasses as found from NEXAFS analyses of lubricating films formed from phosphorus-containing additives. These materials are rather hard and protect against wear. Clearly the rate of carbon diffusion into the bulk of the sample is substantially lower than that of the PO species, leading to a film structure in which the phosphate layer forms below a carbon layer. The presence of the surface carbonaceous layer passivates the surface toward further reaction. Finally, the C KLL line fine structure (NEXAFS) data have shown that these generally consist of phosphates.

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be expected to have a low friction coefficient, in particular when deposited onto a hard polyphosphate glass substrate, and this combination of a low-shear strength material (graphite) deposited onto a hard substrate (a polyphosphate glass) may be the explanation for the efficacy of these molecules as antiwear additives.

Conclusions

A portion of the tributyl phosphite adsorbed on Fe_{2}O_{3} at \( \sim 200 \) K desorbs intact with an activation energy of between 109 and 115 kJ/mol depending on coverage. The remainder decomposes either by C–O bond scission to form adsorbed butyl groups or by P–O bond scission to form adsorbed butoxy species although some of the adsorbed tributyl phosphite might also dehydrogenate. The adsorbed butyl groups react either by \( \beta \)-hydride elimination to form a small amount of 1-butene at \( \sim 250 \) K or by decomposing to deposit hydrogen and carbon on the surface. The resulting hydrogen reacts either with the oxide to form water or with adsorbed butoxy species to form 1-butanol. The remaining 1-butoxy species are stable to \( \sim 600 \) K where they undergo \( \beta \)-hydride elimination to form butanal, and the hydrogen released by this reaction predominantly reacts with adsorbed butoxy species to form additional 1-butanol, although some water is also formed. Surface carbon reduces the oxide at above 750 K to form CO, although an Auger analysis of the sample following reaction reveals that only a small amount of carbon is deposited onto the surface when TBPi is adsorbed at 200 K and heated to 800 K. However, when tributyl phosphite is adsorbed on Fe_{2}O_{3} at 300 K and then heated, substantially more carbon is deposited. A depth profile reveals that the carbon is located predominantly at the surface, while the phosphorus is distributed relatively uniformly throughout the oxide film. This observation is in accord with previous measurements of the film structure by NEXAFS where phosphates and polyphosphates were detected in the film. This implies that the tribological film formed by reaction of tributyl phosphite with an oxide is comprised of a hard polyphosphate glass film produced by rapid diffusion of PO_{x} fragments into the oxide, covered by a low-shear strength graphitic layer.

Acknowledgment. We gratefully acknowledge support of this work by the Chemistry Division of the National Science Foundation under Grant Number CHE-9213988. LA049438T