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Reaction of tributyl phosphate with oxidized iron: surface chemistry and tribological significance

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The chemistry of tributyl phosphate on Fe_3O_4 was studied in ultrahigh vacuum using temperature-programmed desorption (TPD) and Auger spectroscopy. A portion of the tributyl phosphate desorbs intact with an activation energy of ~120 kJ/mol. The remainder decomposes either by P—O bond scission to deposit surface butoxy species or appears to dehydrogenate desorbing C_2 or C_3 compounds and depositing hydrogen and carbon on the surface. The resulting hydrogen reacts either with the oxide to desorb water or with butoxy species yielding 1-butanol. The remaining butoxy species are stable up to ~600 K where they decompose to desorb butanal via hydride elimination where again the hydrogen reacts with butoxy species to form 1-butanol or with the oxide to form water. The carbon deposited onto the surface further reduces the oxide to desorb as CO above ~750 K, although a small amount of carbon is detected on the surface using Auger spectroscopy. Substantially larger amounts of carbon are deposited onto the surface when Fe_3O_4 is exposed to tributyl phosphate at 300 K, where an Auger depth profile reveals that the carbon is located at the surface while the PO_x species formed by tributyl phosphate decomposition diffuse rapidly into the oxide layer, leading to a film structure in which graphitic carbon is deposited onto a phosphorus-containing oxide layer.

KEY WORDS: tributyl phosphate, iron oxide, temperature-programmed desorption, Auger depth profile, surface chemistry

1. Introduction

Lubricants that incorporate phosphorus-containing molecules are used both as extreme-pressure (EP) and anti-wear (AW) additives [1–7]. Phosphorus is also an active component of zinc dialkyl dithiophosphate (ZDDP), which is extensively used as an AW additive in engine oils. It is generally agreed that AW films containing a relatively hard polyphosphate glass are formed by reaction with the phosphorus in the additive. Chlorine- [8,9], sulfur- [10,11] and phosphorus-containing [12–16] molecules are all used as EP additives. It has been demonstrated previously that chlorinated hydrocarbons function by reactively forming a $FeCl_2$ film [17–19] at the high temperatures (>1000 K [20]) encountered at the solid-solid interface during EP applications. Sulfur-containing additives decompose to form FeS under EP conditions, and FeS_2 at the lower temperatures found in less severe AW applications [21]. Phosphorus-containing EP additives often consist of phosphite or phosphate esters with formulae $P(OR)_3$ or $O{=}P(OR)_3$ respectively, where R is a hydrocarbon species or hydrogen [12–16]. One role of the hydrocarbon functionalities is to solubilize the molecule in the base oil.

The chemistry of tributyl phosphate has been investigated previously on clean iron surfaces in ultrahigh vacuum [22,23]. It was proposed that the surface reaction could be initiated either by cleavage of the P—O bond to yield a surface alkoxy species or alternatively by the cleavage of the C—O bond to yield a surface alkyl group. It was found on clean iron that the alkyl chemistry dominated the surface reaction. Since any oxide layer is likely to be rapidly removed under EP conditions [24], the interface is likely to be relatively clean. However, under AW conditions, a surface oxide is still likely to persist so that, in the following, the chemistry of tributyl phosphate is explored on an Fe_3O_4 surface. The chemistry of tributyl phosphite has been previously explored on oxidized iron [24], where it was found that both P—O bond cleavage (to form surface alkoxides) and C—O bond scission (to form surface alkyl species) occurred at or below ~400 K. Both of these subsequently decomposed via a hydride elimination reaction to form butanal and 1-butene, respectively. This chemistry was confirmed by adsorbing 1-butanol or 1-iodobutane onto the surface [25,26]. It was also found that the adsorbed butyl species (either formed from 1-iodobutane or tributyl phosphite) could also decompose to deposit carbon onto the surface. A depth profile of the resulting film revealed that the resulting carbon was predominantly located at the surface, while the phosphorus rapidly diffused into the oxide layer.

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2. Experimental

Experiments were carried out in a stainless-steel, ultrahigh vacuum chamber operating at a base pressure of $\sim 2 \times 10^{-10}$ Torr following bakeout, which has been described in detail elsewhere [27]. 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. In a TPD experiment, tributyl phosphate is initially adsorbed onto the surface at a temperature at which no reaction occurs (in this case ~100 K). The sample is then placed close to, and in line of sight of the ionizer of a quadrupole mass spectrometer and the sample heated such that the temperature varies linearly with time. The resulting mass spectrometer intensities at various masses are recorded and plotted versus temperature to yield the TPD spectrum.

An iron foil (Johnson–Matthey, 99.99% purity) is mounted on a steel plate (1 mm thick) as a support and a Type K thermocouple is attached to the plate to allow the temperature to be monitored. The tributyl phosphate (Aldrich, 99% purity) was transferred to a glass bottle, attached to the gas-handling line of the vacuum system, further purified by several freeze-pump-thaw cycles and its purity monitored by mass spectroscopy. The sample was dosed by backfilling the chamber and exposures in Langmuirs ($1 \text{ L} = 1 \times 10^{-6}$ Torr s) are uncorrected for ionization gauge sensitivity.

The iron foil was bombarded with argon ions ($\sim 1\ \mu\text{A/cm}^2$, 2 keV) and annealed to 1000 K several times to remove surface contaminants (mainly C, S and N). It was then oxidized using 5×10^{-7} Torr of O_2 for 1 h at 800 K to form an oxide film on the iron. It has been shown previously that this procedure leads to the formation of an Fe_3O_4 film deposited onto the iron substrate [24,28–30].

3. Results

Figure 1 displays a series of TPD spectra following various exposures of tributyl phosphate (TBP) on Fe_3O_4 collected at 99, 72, 31 and 56 amu, where exposures are marked adjacent to the corresponding spectra. The 99 amu trace (figure 1(a)) is exclusively due to tributyl phosphate, which therefore desorbs molecularly at ~470 K. It should be noted that the sensitivity of the quadrupole mass spectrometer decreases with increasing mass. An additional, higher-temperature state is detected at ~540 K at the highest exposure (0.5 L). A Redhead analysis [31] of the TPD data, assuming a pre-exponential factor of $1 \times 10^{13}\ \text{s}^{-1}$, yields a desorption activation energy of ~120 KJ/mol. This value is approximately the same as that for tributyl phosphite (~110 KJ/mol [24]), indicating that the extra oxygen on the phosphorus has only a marginal effect on the heat of adsorption.

Figure 1(b) shows the corresponding 72 amu spectra. The mass spectra of 1-butanol, butanal and 1-butene have been measured with the mass spectrometer used to collect the TPD data displayed in figures 1–3, and these reveal that the signal at 72 amu is predominantly due to butanal, with negligible contributions from 1-butanol and TBP. The predominant feature in the spectrum is a feature at ~600 K that grows with increasing TBP exposure. A similar feature has been detected following the adsorption of both tributyl phosphite (TBPi) and 1-butanol on Fe_3O_4 [24] and arises from a hydride elimination reaction from adsorbed butoxy species, in this case formed by P—O bond scission of TBP. In principle, butoxy species can also form by reaction of butyl species with surface oxygen, but it has been shown that the yield of butoxy by this pathway is low [24]. A lower-temperature butanal desorption state is evident at ~300 K, not detected following the adsorption of 1-butanol nor TBPi [24].

The 31 amu spectra in figure 1(c) are due to 1-butanol desorption with very little contribution from other species. These spectra are more complex than those due to TBP (figure 1(a)) and butanal (figure 1(b)). Several features can be identified, the first being a ~600 K peak, coincident with the butanal desorption state (figure 1(b)). A similar feature has been detected following the adsorption of both 1-butanol and TBPi on Fe_3O_4 [24] and is due to butoxy rehydrogenation by the hydrogen supplied by the hydride elimination reaction that gives rise to butanal (figure 1(b)). A small feature is also detected at ~300 K, coincident with the 300 K, butanal feature observed in figure 1(b), and finally a broad feature is detected at ~500 K, which is due exclusively to the desorption of 1-butanol and which is also detected following TBPi adsorption [24].

While there are no masses exclusively due to 1-butene desorption, the 56 amu fragment, although it does contain intensity due to 1-butanol and butanal, has a relatively large contribution from 1-butene. These spectra are displayed in figure 1(d) and show high-temperature peaks due to 1-butanol and butanal desorption. When TBPi and 1-iodobutane are adsorbed onto iron oxide, the resulting 1-butene appears at just above ~200 K in the case of TBPi and at ~350 K following 1-iodobutane adsorption [24]. The weak feature detected at ~230 K is therefore assigned to the desorption of a very small amount of 1-butene. The relative amount found following the adsorption of TBP is substantially less than that detected from TBPi suggesting that the presence of the additional oxygen on the phosphorus favors P—O bond rather than C—O bond cleavage [24].

Figure 2(a) and (b) display the corresponding 2 (H_2) and 18 (H_2O) amu spectra respectively.

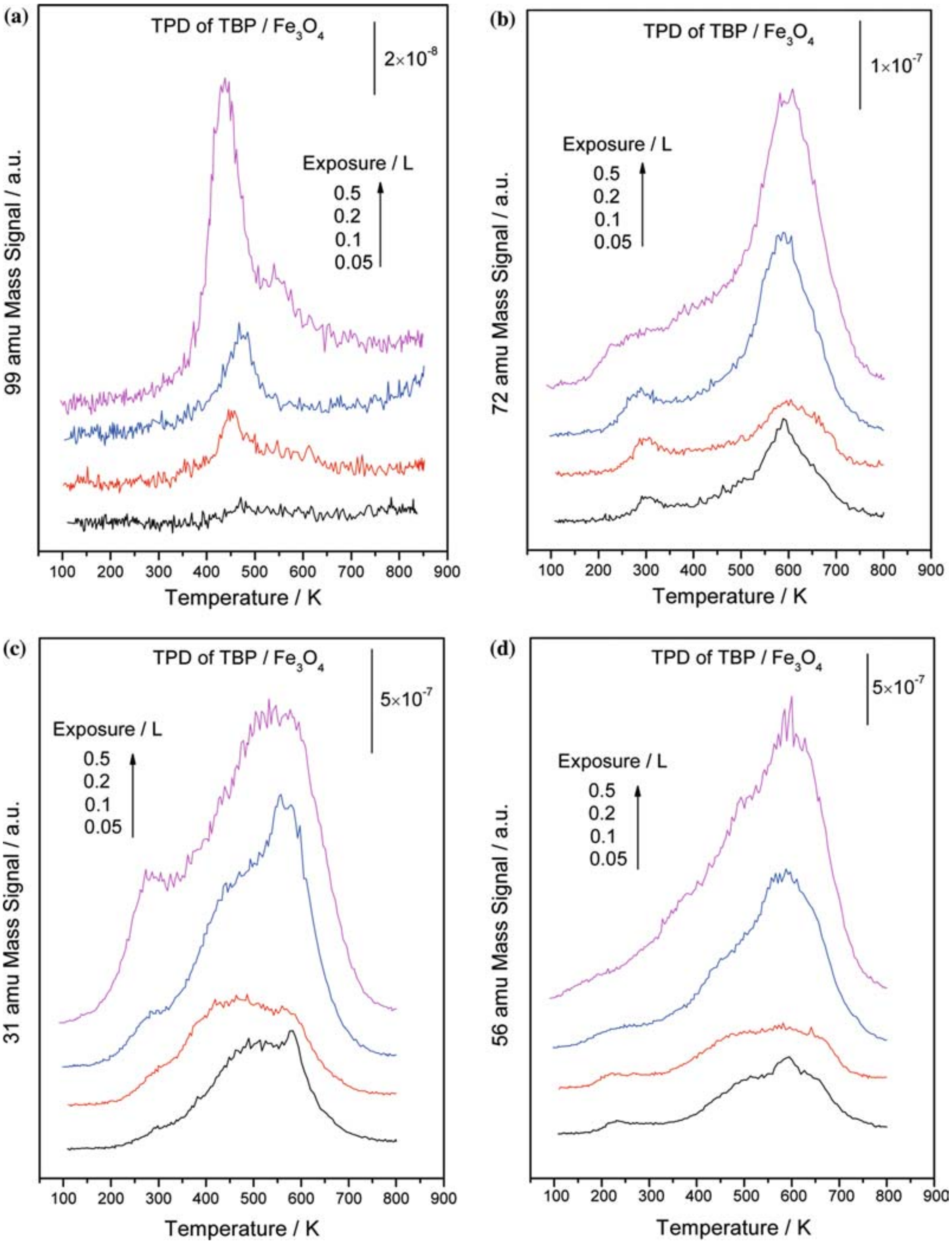


Figure 1. Temperature-programmed desorption spectra of various exposures of tributyl phosphate on Fe_3O_4 at ~100 K, taken using a heating rate of 10 K/s collected at (a) 99, (b) 72, (c) 31 and (d) 56 amu.

Essentially no hydrogen desorbs from the surface since it all reacts with the oxide to form water. Water desorbs in two states at ~650 and between ~220 and ~280 K (figure 2(b)). It has been shown that water desorbs from oxidized iron below ~200 K [32] indicating that the water formation rate from TBP is reaction-rate limited. The high-temperature water desorption state is due to hydrogen released from adsorbed butoxy species via a hydride elimination reaction to yield butanal (figure 2(b)), which then either reacts with other butoxy species to form 1-butanol (figure 1(c)) or with the oxide to form water (figure 1(b)). It has been shown previously that the carbon deposited onto the surface from the decomposition of 1-butanol, 1-iodobutane or TBPi desorbs as CO (28 amu) at above 750 K by reaction with the oxide [24]. The increase in background at above 700 K observed in figure 2(c) is due to a similar effect following TBP adsorption. Figure 2(d) shows spectra collected at 44 amu and confirms that the carbon reacts exclusively at high temperatures to form CO without forming CO_2. The weak features observed in figure 2(c) and (d) between

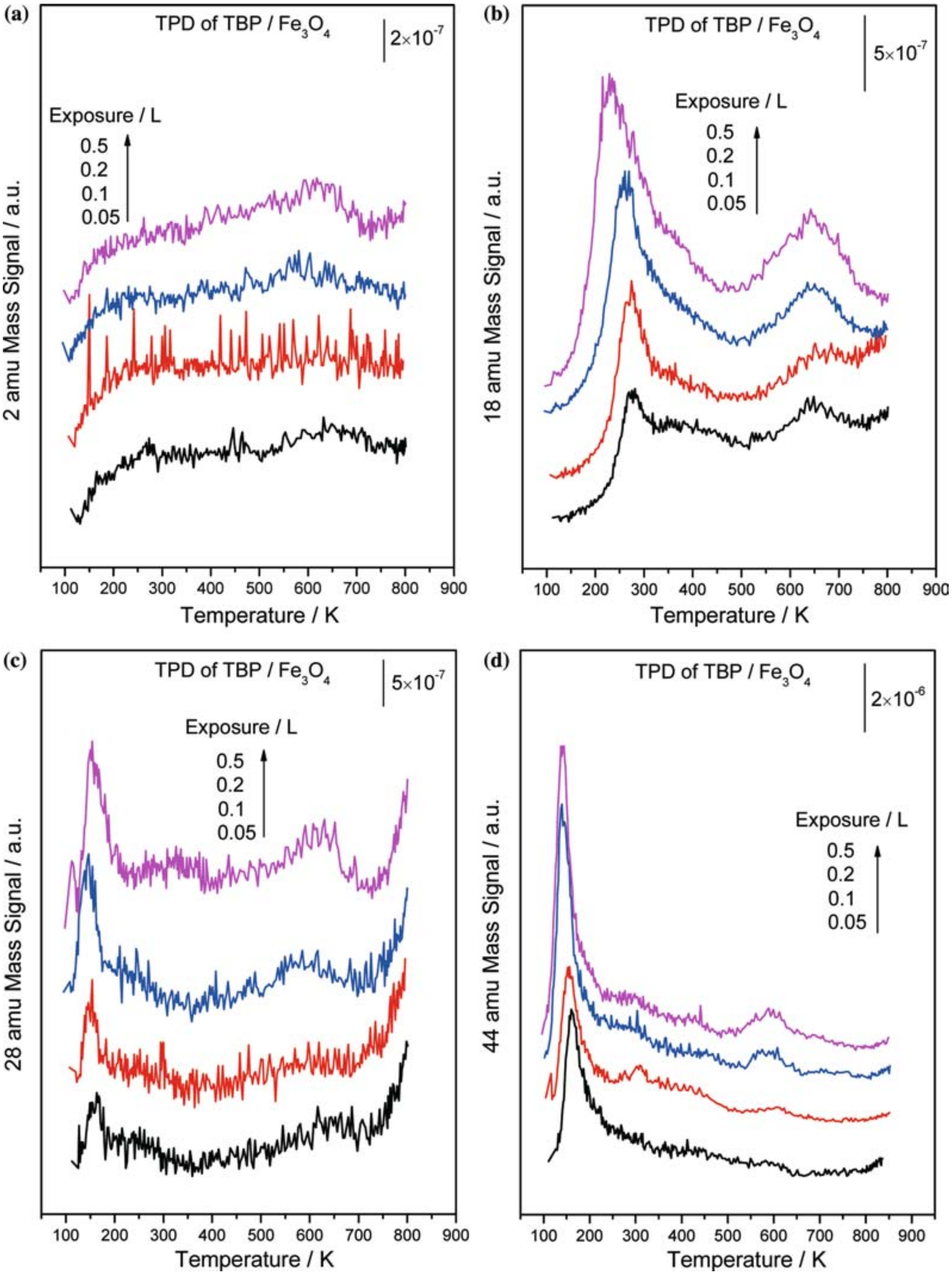


Figure 2. Temperature-programmed desorption spectra of various exposures of tributyl phosphate on Fe_3O_4 at ~100 K, taken using a heating rate of 10 K/s, collected at (a) 2, (b) 18, (c) 28 and (d) 44 amu.

200 and 700 K are due to fragments of 1-butanol and butanal and an additional feature is detected at ~180 K in both spectra. This will be discussed in greater detail below.

Finally, the spectra collected at the various other most prominent masses are displayed in figure 3. These masses are predominantly due to fragments of 1-butanol and butanal. 43 amu is mainly due to butanal and has features at ~300 and ~600 K. The general shapes of the profiles in figure 3 resemble those in figure 1. The ~180 K feature, observed at 28 and 44 amu (figure 2 (c) and (d)) is exclusively present at 43 amu in figure 3(c).

A series of Auger spectra collected after dosing 1 L of TBP at 150 K and heating to ~800 K are displayed in figure 4(a). This procedure was repeated several times without cleaning the surface between each experiment, and the number adjacent to each Auger spectrum indicates the number of times this experiment was performed. In each case, only a small amount of carbon (yielding a feature at ~270 eV kinetic energy) is depos-

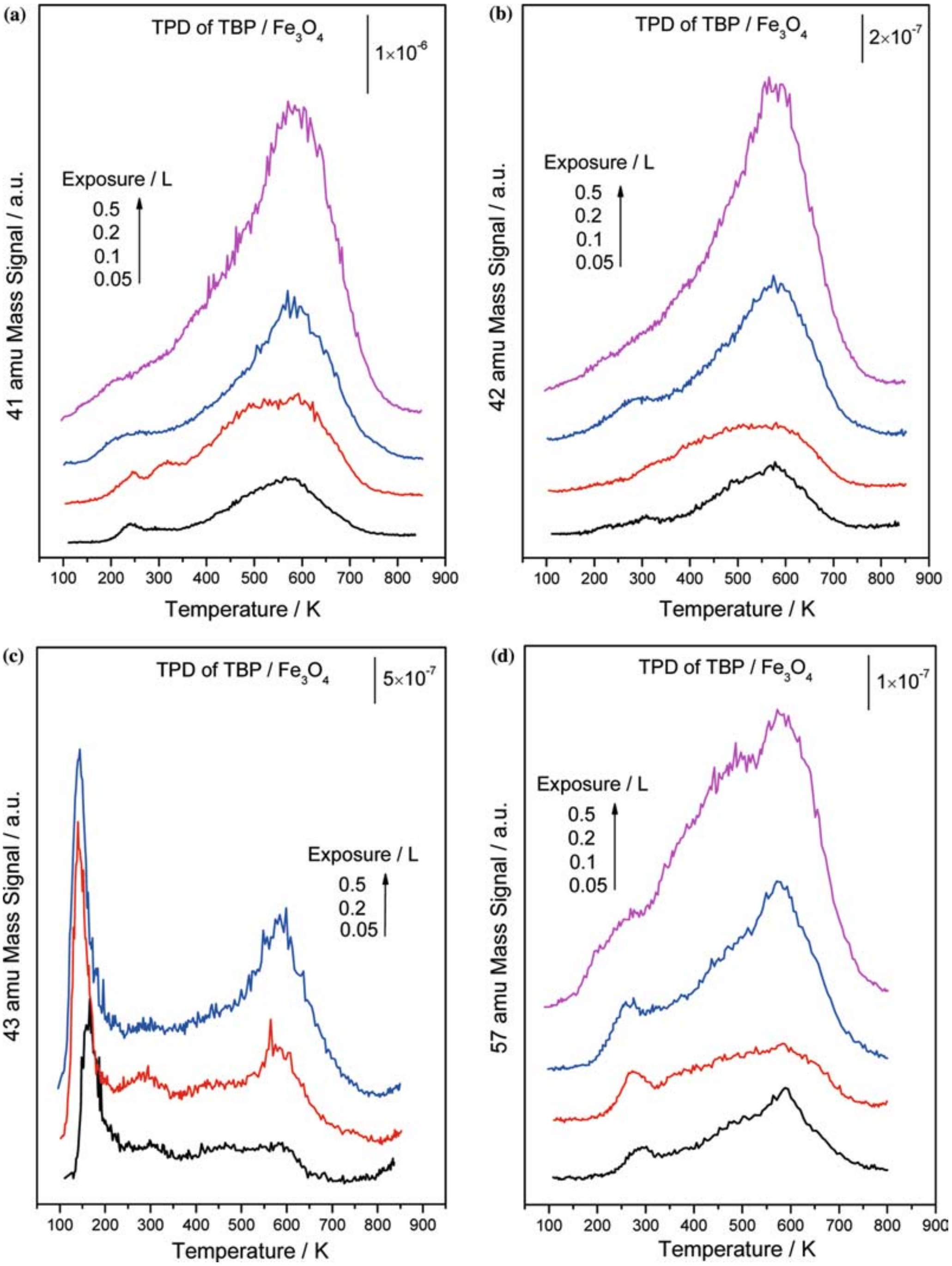


Figure 3. Temperature-programmed desorption spectra of various exposures of tributyl phosphate on Fe_3O_4 at ~100 K, taken using a heating rate of 10 K/s, collected at (a) 41, (b) 42, (c) 43 and (d) 57 amu.

ited onto the surface, in accord with the CO TPD data (figure 2(c)). The carbon Auger signal grows slightly with repeated TBP dose, while the phosphorus signal (at ~120 eV kinetic energy) remains approximately constant. Since tribological reactions of TBP take place at 300 K or above, the adsorption of TBP on the iron oxide surface was also examined at 300 K. Figures 1–3 indicate that reaction takes place at this temperature and the resulting TPD spectra obtained by dosing at 300 K (not shown) are essentially identical to those shown in figures 1–3 above 300 K. The resulting Auger spectra are displayed in figure 4(b) where the surface was exposed to 10 L of TBP to ensure that the surface was saturated. In this case, substantially more carbon is deposited onto the surface, while the phosphorus Auger signal is much weaker. The amount of carbon on the surface increases for the first three adsorption-heating cycles and changes little in the fourth cycle.

Shown in figure 5 is a depth profile of an iron oxide surface exposed to 10 L of TBP and heated to 800 K.

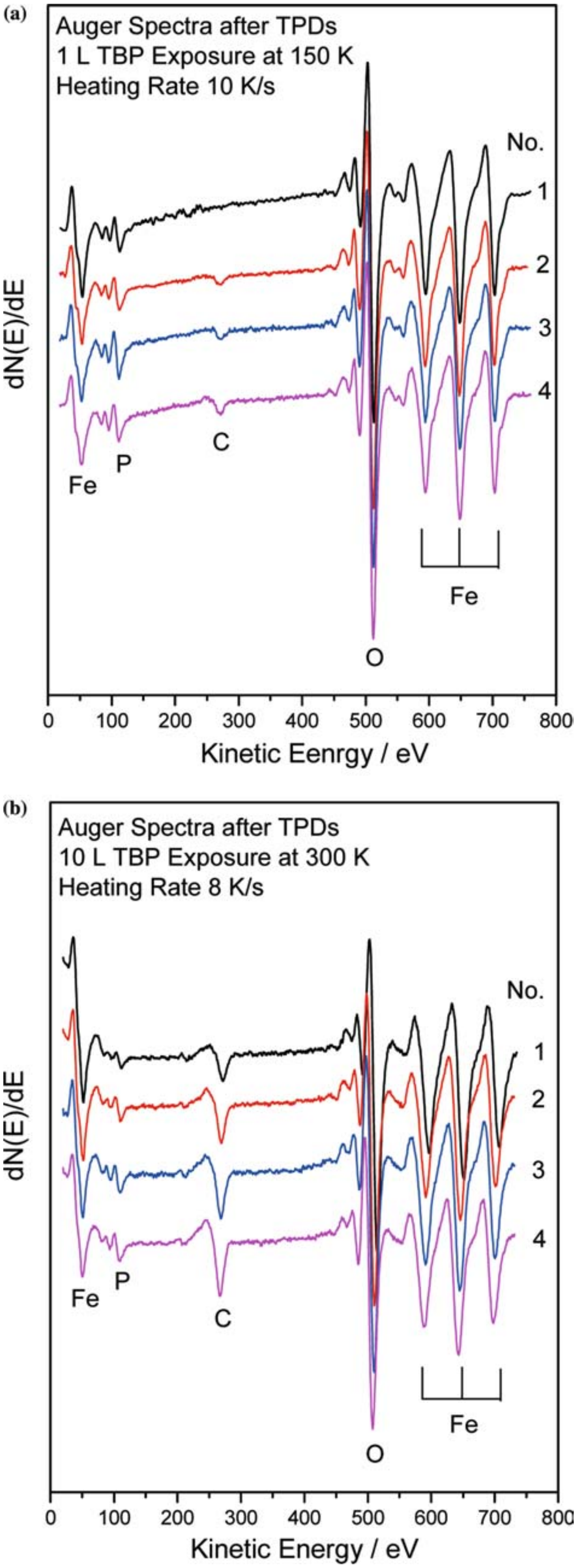


Figure 4. Auger spectra of iron oxide surfaces after (a) repeated exposure to 1 L of tributyl phosphate at 150 K with subsequent heating to 800 K, and (b) after repeated exposure to 10 L of tributyl phosphate at 300 K with subsequent heating to 800 K.

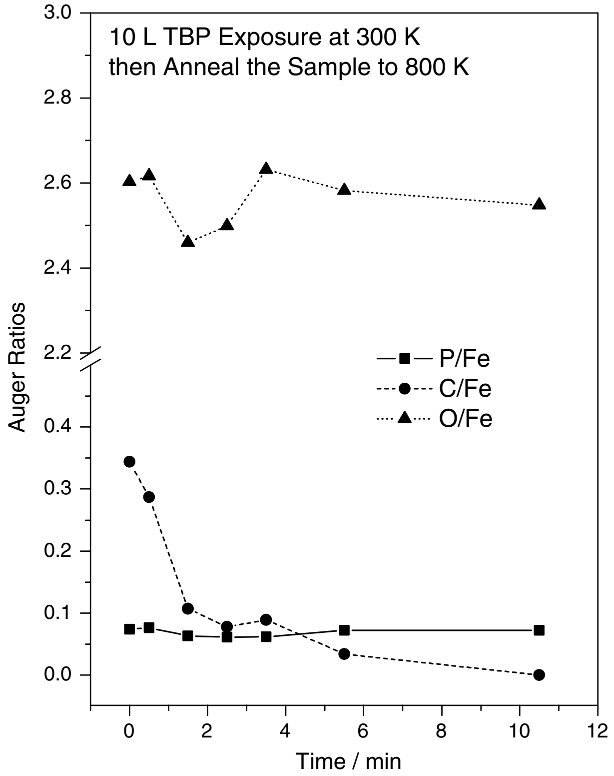
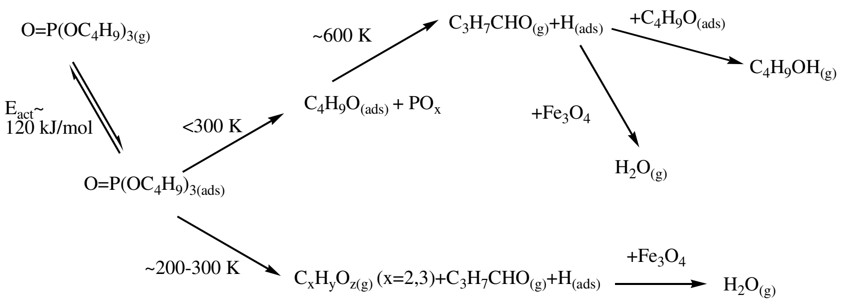


Figure 5. Depth profile of a surface obtained by adsorbing 10 L of tributyl phosphate on Fe_3O_4 at 300 K and heating to 800 K. The sample was bombarded with 3 KeV argon ions with a current density of $\sim$1 A/cm^2 for various times and the Auger spectrum collected. The peak-to-peak Auger intensities of the O KLL, C KLL and P KLL are ratioed to that of the iron LMM Auger signal at 703 eV kinetic energy.

This experiment was carried out by bombarding the surface with 3 keV Argon ions (at a current density of $\sim$1 μA/cm^2) and collecting the Auger spectrum after bombarding for various times. These data reveal that carbon is predominantly located at the surface while the phosphorus appears to be reasonably uniformly distributed throughout the oxide layer. A similar elemental distribution was found for experiments carried out using tributyl phosphite [24].

4. Discussion

The chemistry of TBP on iron oxide is very similar to that of tributyl phosphite. Tributyl phosphate adsorbs slightly more strongly than the phosphite with a heat of adsorption of $\sim$120 KJ/mol compared to $\sim$110 KJ/mol for tributyl phosphite [24]. The main difference is that very little 1-butene is detected following TBP adsorption (figure 1(d)) compared to tributyl phosphite. This suggests that P—O bond cleavage of the phosphate dominates the decomposition chemistry resulting in adsorbed butoxy species. Thus, the presence of an additional electron-withdrawing oxygen on the phosphorus weakens the P—O bonds and increases the selectivity to P—O bond scission. The butoxy species rehydrogenate to form 1-butanol in a broad



desorption state with intensity between ~200 and 700 K (figures 1(c), (d) and 3). In the case of the ~600 K desorption state, this hydrogen is supplied by hydride elimination from adsorbed 1-butoxy species to form butanal. The rate-limiting step in this reaction is therefore hydride elimination indicating that the 1-butoxy species are rather stable on the oxide surface. A portion of this hydrogen reacts with the surface oxide to form some water (figure 2(b)). A similar reaction has been found for 1-butanol and TPBi adsorbed on the oxide surface [24].

It is evident from the lower-temperature water desorption state (with a peak between ~230 and 280 K, figure 2(b)) that a substantial amount of hydrogen is released at these lower temperatures, which both reacts with the oxide to form water and with 1-butoxy species to form 1-butanol. Adsorbed 1-butyl species arising from C—O bond cleavage predominantly thermally decompose to produce hydrogen and deposit surface carbon as well as decomposing at low temperatures to yield 1-butene [24]. However, since very little 1-butene is formed by hydride elimination, it cannot account for the hydrogen in this case. It is interesting to note that some butanal is formed at ~300 K coincident with water (figure 2(b)) and 1-butanol (figure 1 (c)) desorption. No butanal is found at these low temperatures when 1-butanol or tributyl phosphite are adsorbed on the surface [24] indicating that this does not arise from 1-butoxy decomposition. This strongly suggests that the butanal formed at ~300 K arises from hydrogen elimination from adsorbed TBP itself. This therefore suggests an alternative source for the low-temperature hydrogen decomposition of TBP adsorbed onto the surface. These dehydrogenation reactions apparently result in little carbon being deposited onto the surface, suggesting that carbon-containing species desorb. Sharp, relatively intense low-temperature desorption states are detected at between ~150 and 200 K at 28 (figure 2(c)), 44 (figure 2(d)) and 43 (figure 3(c)) amu. These have no counterparts at higher masses. These desorption states suggest the formation of C_3 and C_2 compounds, although they cannot be unequivocally assigned, and imply that the alkyl groups on TBP initially decompose forming these lower-molecular-weight products. Butanal is also formed at ~300 K. The hydrogen released in these reactions forms 1-butanol suggesting that P—O bond scission also takes place at or below ~300 K and the surface chemistry is summarized in Scheme 1.

TBP adsorption at low temperatures and subsequent heating to ~800 K deposits little carbon on the surface (figure 4(a)), while substantially more carbon, but now very little phosphorus, is left on the surface when the TBP is adsorbed at 300 K and heated (figure 4(b)). The resulting film formed by reaction at 300 K and heating to 800 K (figure 5) consists of carbon preferentially located at the surface, while the phosphorus is rather uniformly distributed throughout the film. Clearly, the PO_x fragments that are formed on the surface from the decomposition of tributyl phosphate rapidly diffuse into the oxide film. A similar effect is found with tributyl phosphite [24]. While the chemical nature of the phosphorus cannot be measured using Auger spectroscopy, NEXAFS analyses of the tribological films formed from phosphorus-containing additives reveal the formation of phosphates [33–37]. At higher phosphorus concentrations and temperatures, the phosphates polymerize to form relatively hard polyphosphate glasses. Based on the elemental distribution found following TPD demonstrating that PO_x fragments rapidly diffuse into the oxide (figure 5), it is likely that the tribological film has a similar elemental distribution consisting of a (poly)phosphate layer covered by an overlayer of carbon. Measurement of the C KLL Auger lineshape (figure 4) indicates that, after having been heated to ~800 K, the carbon is graphitic. It is evident that such a structure consisting of a low-shear-strength film deposited onto a hard polyphosphate glass sublayer will lead to a wear resistant interface. Thus, in addition to solubilizing the phosphate or phosphite additive in the oil, the carbon-containing functionalities appear to play a tribological role by depositing a graphitic layer on top of a phosphorus-containing one.

In this context, it is interesting to note that P—O bond cleavage in one of the most commonly used additives, tricresyl phosphate [12–14], would deposit a substituted phenolate species, which, since it has no hydrogen, cannot desorb as an aldehyde and would lead to further carbon deposition on the surface [23]. In addition, C—O bond cleavage would result in the corresponding substituted phenyl species depositing surface carbon in a similar fashion as butyl groups do from TBP.

Phosphate esters are used as both AW and EP additives, although the interfacial temperatures in each regime are substantially different. Temperatures in excess of 1000 K can be attained during EP lubrication [20], while during AW applications, the temperatures are substantially lower. Under AW conditions (where the temperatures are likely to be lower than ~550 to 600 K), according to Scheme 1, tributyl phosphate will form stable surface 1-butoxy and PO_x species. The 1-butoxy species do not thermally decompose until the temperature exceeds ~600 K but may be worn from the surface. Above this temperature, the 1-butoxy species decompose to form 1-butanol and butanal and the oxide is reduced and evolves CO and water. These latter reactions accelerate at higher temperatures and, unless the surface is reoxidized, will result in complete reduction of the surface. In addition, since the applied loads are higher under the EP conditions at which such high temperatures are attained, significant surface wear will also remove the oxide layer. Under these conditions, the chemistry found on the clean metal surface more appropriately models EP lubrication [22, 23]. In this case, both 1-butene and CO formation are found for tributyl phosphate on clean iron. Since there is no oxide film present, the phosphorus is deposited onto the surface along with very little carbon. At the temperatures present at the EP interface, the phosphorus will oxidize the iron to form a phosphide and, at least a portion of the carbon diffuse into the bulk to form a carbide.

5. Conclusions

Tributyl phosphate adsorbs on iron oxide at ~150 K where a portion desorbs molecularly with an activation energy of ~120 KJ/mol. It decomposes by P—O bond cleavage to form adsorbed butoxy species, while the C—O bond remains substantially intact. 1-butanol and water are initially formed where the hydrogen for these reactions appears to come from the decomposition of adsorbed tributyl phosphate. The remaining butoxy species are stable up to ~600 K where a portion undergoes hydride elimination to form butanal. The hydrogen released by this process can either react with the oxide to form water or with other butoxy species to desorb 1-butanol. The carbon deposited onto the surface reduces the oxide to form CO above ~750 K. Adsorption of tributyl phosphate at 300 K and annealing to 800 K results in larger carbon coverages, where a depth profile reveals that the carbon is located predominantly at the surface while the PO_x species diffuse rapidly into the oxide. Previous NEXAFS results have demonstrated the formation of phosphates and polyphosphate glasses, suggesting that the resulting film comprises a phosphate/polyphosphate sublayer covered by carbon.

Acknowledgments

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