

Thermal decomposition of tricresylphosphate isomers on Fe

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Tricresylphosphate (TCP) $[(\text{CH}_3-\text{C}_6\text{H}_4\text{O})_3\text{P}=\text{O}]$ is the most commonly tested vapor phase lubricant and is readily available as a mixture containing all three isomers (*ortho*-, *meta*-, and *para*-) of the cresyl groups. The surface chemistry of *ortho*-, *meta*- and *para*-TCP on Fe foil was studied in order to examine the possible differences in decomposition mechanisms among the isomers. All three TCP isomers decomposed by the same reaction mechanisms and with roughly the same kinetics on Fe. Upon heating, they decomposed on the Fe surface to deposit carbon and phosphorous and produce gas phase H_2 , CO, toluene and cresol. The amounts of carbon and phosphorous deposited onto the Fe surface by TCP (*aryl*/phosphate) decomposition were compared to those deposited by decomposition of tributylphosphate (TBP), an *alkyl*/phosphate. Thermal decomposition of all three TCP isomers deposits substantial amounts of carbon onto the Fe surface while TBP decomposition does not. We suggest that it is the lack of β -CH bonds in the methylphenoxy intermediates and the high reactivity of the tolyl intermediates generated during TCP decomposition are the primary reasons for the differences in behavior of TCP and TBP and the root cause of the differences in behavior of *aryl*/phosphates and *alkyl*/phosphates as vapor phase lubricants.

KEY WORDS: tricresylphosphate, iron, isomers, temperature-programmed desorption, Auger spectroscopy, thermal decomposition

1. Introduction

The development of high-efficiency engines operating at extremely high temperatures cannot rely on the use of traditional fluid lubrication and has required the development of new lubrication schemes compatible with operating temperatures in excess of 500°C . Vapor-phase lubrication (VPL) has been proposed as a method for the lubrication of high-temperature engine components [1–3]. VPL is a lubrication scheme in which vaporized lubricants are delivered continuously in a carrier gas to the hot sliding surfaces of engine components. The vapor-phase lubricant reacts to deposit a thin solid lubricating film on these surfaces. Typical vapor-phase lubricants are phosphorous-containing organics, including *aryl*/phosphates such as tricresylphosphate (TCP) $[(\text{CH}_3-\text{C}_6\text{H}_4\text{O})_3\text{P}=\text{O}]$ and *alkyl*/phosphates such as tributylphosphate (TBP) $[(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{O}]$ [4–6]. These phosphates are thought to decompose on reactive metal surfaces such as Fe and Cu to form polyphosphate films containing some graphitic carbon and metal elements [5]. One interesting observation is that *aryl*/phosphates are more effective than *alkyl*/phosphates for the deposition of lubricious films [7,8].

The TCP commonly used as vapor-phase lubricant is a mixture of species containing all three isomers of the cresyl group: *ortho*-, *meta*-, and *para*-. Previous studies of the thermal decomposition of different TCP isomers

on Fe have suggested that there can be differences in the surface chemistry of the different TCP isomers. An early study reported that *p*-TCP on Fe produced toluene desorption upon heating to 330°C (600 K) [9]. A more recent study showed that *m*-TCP generated primarily cresol while *o*-TCP yielded some fused aromatic compounds as well as cresol [10]. This suggests that there are some differences in the decomposition reactions of the different TCP isomers. In this work we have tried to explore the possible differences in the behavior of the different TCP isomers by studying the decomposition of the three isomers containing only *ortho*-, *meta*-, or *para*-cresyl groups. Upon heating, all TCP isomers decompose to deposit carbon and phosphorus on the Fe surface while also resulting in the evolution of H_2 , CO, toluene and cresol into the gas phase. Surprisingly, the results indicate that the three TCP isomers have a very similar decomposition chemistry on the Fe surface.

The second point of this paper is to compare the efficiency of carbon and phosphorus deposition by TCP and TBP in order to probe the origin of the superior performance of *aryl*/phosphates over *alkyl*/phosphates as vapor-phase lubricants. The results of this work show that TCP decomposition results in the deposition of substantial amounts of carbon and some phosphorus onto Fe, while TBP decomposition results in the deposition of phosphorus only. As shown in our earlier work, the origin of this difference between TCP and TBP can be attributed to the differences in the species produced by their initial decomposition on the Fe surface [11]. The butyl surface intermediate produced

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during TBP decomposition has β -CH bonds and can readily react by β -hydride elimination to produce 1-butene which desorbs from the surface without depositing carbon. By β -hydride elimination we refer to breaking of a C-H bond adjacent to the atom bound to the surface. TCP, on the other hand, produces aryloxy intermediates that do not have β -CH bonds and aryl intermediates that are highly reactive and thus undergo complete decomposition to deposit carbon and phosphorus on the surface. It has been observed that lubricating graphitic particles generated by catalytic decomposition of hydrocarbons on hot surfaces can reduce the friction between contacting surfaces [12–14]. Given this fact, the results of our investigation suggest that the reason that TCP is a better vapor-phase lubricant than TBP is simply that it can decompose by a mechanism that deposits graphitic carbon onto the surface more efficiently.

2. Experimental

All experiments were conducted in a stainless ultra-high vacuum (UHV) chamber with a base pressure of 10^{-10} Torr achieved through the use of an ion-pump and turbomolecular pump. The chamber is equipped with an Ar^+ ion sputtering gun for surface cleaning, a cylindrical mirror analyzer for Auger electron spectroscopy and a quadrupole mass spectrometer for detection of desorbing species during temperature programmed reaction spectrometry (TPRS). The mass spectrometer has a mass range of 1–200 amu and is capable of monitoring up to five masses simultaneously as a function of time during TPRS experiments. A high mass evaporative doser was used to adsorb low vapor pressure compounds such as TCP and TBP onto the Fe surface. The polycrystalline Fe sample was mounted to a UHV manipulator that allowed cooling with liquid nitrogen and resistive heating through a temperature range of 160–1200 K.

The Fe (99.9+%) disk was obtained from the Goodfellow Corporation and was cleaned by cycles of Ar^+ ion sputtering and annealing to 800 K. This cleaning process produced a surface that showed carbon contamination of $29 \pm 1\%$. The relative carbon concentration was determined based on the Auger peak-to-peak height of the Fe peak at 651 eV and scaled by the Auger elemental sensitivities (0.21 for Fe and 0.19 for C at a beam voltage of 3 keV, [15]). Although this surface is not truly clean it was highly reproducible. Since we are trying to study a process that occurs on surfaces of engine components that would normally be contaminated with carbon we believed such a surface is sufficient for this work.

In order to introduce *o*- and *m*-TCP into the vacuum chamber, they were heated to 410 K in the glass vial of the high mass doser and the dosing tube was moved into

the chamber to locate the end of the tube 5 mm from the Fe surface. Since *p*-TCP was in solid form, it was necessary to heat it to 430 K in order to melt it and achieve a high enough vapor pressure to introduce the molecule into the chamber. The TBP adsorption process was similar to that of TCP except that TBP was not heated during dosing. All three isomers of TCP [$(\text{CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}=\text{O}$, 97%] and TBP [$(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{O}$, 99%] were purchased from Fisher Scientific. One-third of the initial samples of TCP and TBP were evaporated from the sample vials for purification purposes prior to introducing the vapor into the chamber. The purity of TCP and TBP was checked by mass spectrometry.

3. Results and discussion

3.1. Surface chemistry of TCP isomers on Fe

The possible differences in the surface chemistry of TCP isomers on Fe have been investigated by studying their thermal decomposition patterns. In all three cases, the observed products during TCP decomposition were H_2 , CO_2 , $\text{CH}_3\text{C}_6\text{H}_5$ (toluene) and $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ (cresol). Figures 1, 2, and 3 respectively show the TPR spectra of *o*-TCP, *m*-TCP, and *p*-TCP adsorbed on Fe.

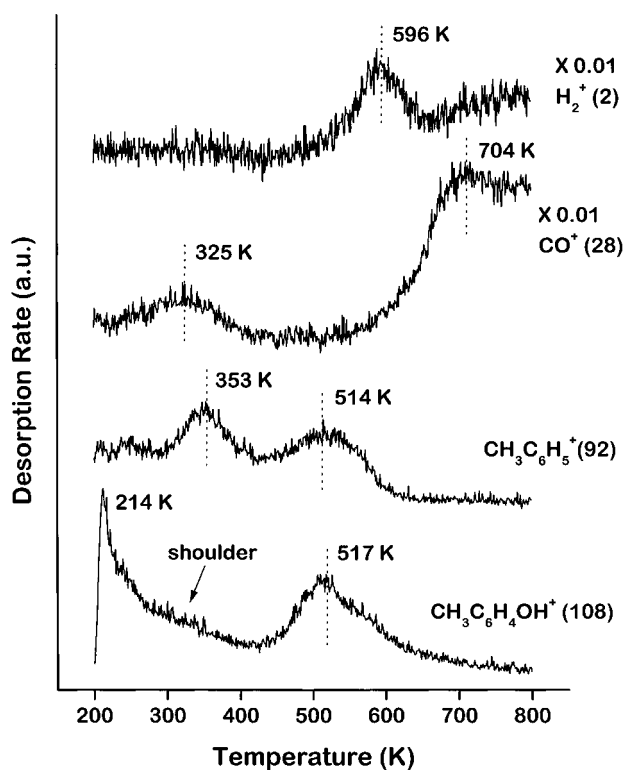


Figure 1. TPRS spectra of *o*-TCP obtained following adsorption of the Fe surface at 200 K. Deposition at this temperature resulted in the saturation of the monolayer without multilayer adsorption. The spectra was generated by monitoring the fragments with $m/q = 2$ (H_2^+), 28 (CO^+), 92 ($\text{CH}_3\text{C}_6\text{H}_5^+$), and 108 ($\text{CH}_3\text{C}_6\text{H}_4\text{OH}^+$). The heating rate was 2 K/s.

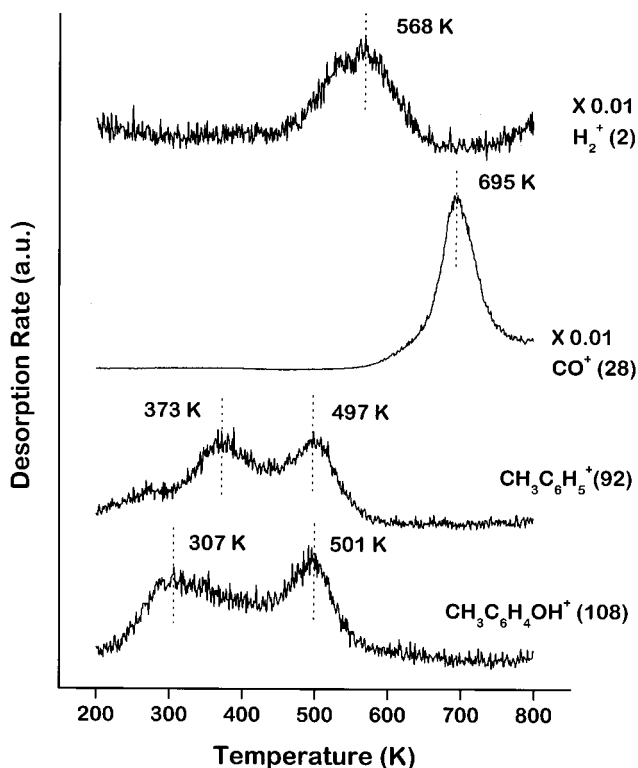


Figure 2. TPR spectra of *m*-TCP obtained following adsorption on the Fe surface at 200 K. The spectra were generated by monitoring the fragments with $m/q = 2, 28, 92,$ and 108 . The heating rate was 2 K/s.

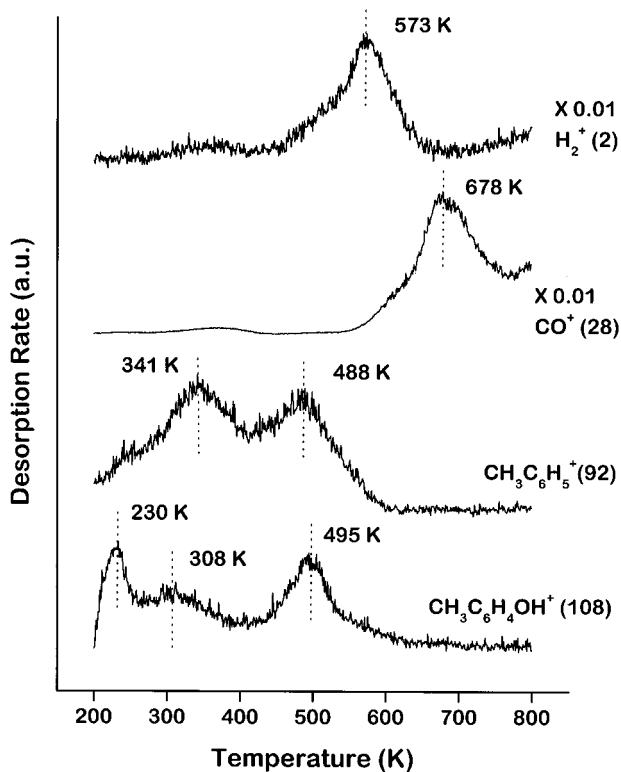


Figure 3. TPR spectra of *p*-TCP obtained following adsorption on the Fe surface at 200 K. The spectra were generated by monitoring the fragments with $m/q = 2, 28, 92,$ and 108 . The heating rate was 2 K/s.

All three isomers were adsorbed on Fe at 200 K to give a monolayer saturation coverage on the Fe surface. Monolayer saturation coverage was defined as the coverage above which the multilayer desorption peak starts to appear in the TPR spectra. Following adsorption the Fe surface was heated to 800 K. During heating the desorbing products were monitored using the mass spectrometer. The spectra shown in figure 1 were produced by monitoring the signal at mass-to-charge ratios of $m/q = 2$ (H_2^+), 28 (CO^+), 92 ($\text{CH}_3\text{C}_6\text{H}_5^+$) and 108 ($\text{CH}_3\text{C}_6\text{H}_4\text{OH}^+$). All three sets of TPR spectra have similar shapes and desorption peak temperatures suggesting that all three isomers of TCP have similar decomposition mechanisms and decomposition kinetics.

The first decomposition product to examine is cresol, which is observed by monitoring the signal at $m/q = 108$. There are three distinct features in the signal at $m/q = 108$. The peaks at 214 K for *o*-TCP and 230 K for *p*-TCP reveal molecular desorption of TCP because these peaks grow indefinitely with increasing TCP exposure. The features at ~ 300 K indicate the formation of methylphenoxy groups [$\text{CH}_3\text{-C}_6\text{H}_4\text{O-}$] through P-O bond scission at temperatures below ~ 300 K followed by hydrogenation and desorption as cresol. In our earlier work, we have concluded that *m*-TCP initially generates methylphenoxy groups on Fe by showing that the TPR spectra of *m*-TCP were similar to those of adsorbed *m*-cresol and significantly different from those of 3-iodotoluene. This conclusion makes the reasonable assumption that *m*-cresol produces methylphenoxy by deprotonation on the Fe surface while 3-iodotoluene generates tolyl groups [$\text{CH}_3\text{-C}_6\text{H}_4\text{-}$] through C-I bond cleavage on Fe [11]. Further examination of the TPR spectra in figures 1, 2, and 3 reveals that cresol also desorbs in the temperature range 500–520 K for all three isomers of TCP. Previous reaction studies have shown that *o*-TCP and *m*-TCP produced cresol through reaction on Fe [10]. Those observations of cresol production are consistent with our observations of cresol desorption during TCP decomposition.

TCP decomposition on the Fe surface results in toluene desorption in two different temperature ranges. Toluene desorption occurs in both low-temperature (350–370 K) and high-temperature (490–520 K) regimes. Toluene desorption is suggestive of the formation of tolyl groups on Fe as a result of C-O bond scission in the methylphenoxy groups generated below ~ 300 K. These tolyl groups must then be hydrogenated to produce toluene. The details of the origins of two toluene desorption features are unclear at this point; however, they must be rate limited by two different processes. As mentioned earlier, a previous study using XPS proposed that thermal decomposition of *p*-TCP produces toluene at temperatures below 600 K [9]. This is consistent with our observation of toluene desorption at ~ 350 K and ~ 500 K.

The complete decomposition of the hydrocarbon fragments generated during TCP decomposition results in the desorption of hydrogen. H_2 evolves in the temperature range 570–600 K. The simple recombination of hydrogen atoms on Fe surfaces is known to occur in the temperature range 300–500 K [16–19]. Thus, the high-temperature desorption of the H_2 observed during TCP decomposition must be rate limited by the scission of C–H bonds in C_xH_y fragments that are produced during the decomposition of methylphenoxy or tolyl groups. This complete decomposition also results in the deposition of carbon and oxygen atoms which then recombine to form CO. CO desorption occurs in the temperature range 680–710 K. These peak temperatures are similar to the CO desorption temperatures (700–900 K) observed during carbon and oxygen atom recombination on other Fe surfaces [18–21]. The difference in the peak temperatures might result from the use of Fe polycrystalline or the presence of phosphorus on the surface as a result of TCP decomposition. The CO desorption peak at 325 K in the spectra for *o*-TCP decomposition is probably due to CO adsorbed molecularly from the background vacuum. It has been reported that the CO desorbs from the Fe(111) surface at temperatures in the range 300 K and 400 K depending upon CO coverage [20,21]. The increase of H_2 and CO desorption rates observed in figures 1, 2, and 3 at temperatures > 770 K is due to the desorption of H_2 and CO from the heated manipulator.

The TPRS results suggest that all TCP isomers produce methylphenoxy and tolyl groups on Fe during decomposition. These groups either desorb via hydrogenation as cresol or toluene or further decompose upon heating resulting in H_2 and CO desorption and carbon and phosphorus deposition onto the surface. As will be shown below, the major fraction of TCP completely decomposes to deposit carbon and phosphorus on the Fe surface.

3.2. Carbon and phosphorus deposition onto Fe from TCP and TBP

In order to examine changes in surface composition as a result of the TCP decomposition, Auger spectra of the Fe surface were taken after the TPRS of TCP. In order to compare the efficiencies of carbon and phosphorous deposition by *aryl*/phosphate and *alkyl*/phosphate decomposition the spectra obtained after TCP decomposition were compared with those obtained after TBP decomposition. Figure 4a shows an Auger spectrum of the Fe surface prior to TCP adsorption and reveals the presence of residual carbon that could not be cleaned from the foil surface. The set of small peaks in the range of 250 to 270 eV at the shoulder of the carbon peak are characteristic of carbidic carbon [22]. This Fe surface was highly reproducible and was used as the

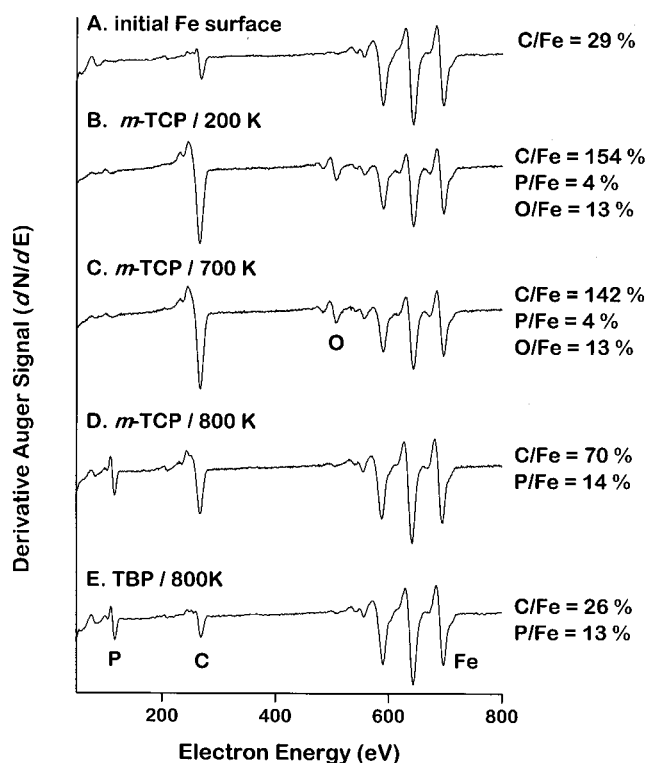


Figure 4. Auger spectra of the Fe surface (a) before *m*-TCP adsorption, (b) after *m*-TCP adsorption at 200 K, (c) after heating to 700 K, (d) after heating to 800 K, and (e) after TBP adsorption at 160 K and heating to 800 K. Spectrum (a) shows the initial contamination level of the Fe surface with carbon. Spectra (b) and (c) have no significant differences in surface composition reflecting no significant loss of TCP decomposition products from the surface during heating from 200 to 700 K. Spectrum (d) shows the final amounts of carbon (273 eV) and phosphorus (120 eV) on Fe after *m*-TCP decomposition and heating to 800 K. The absence of an oxygen peak indicates that almost all the oxygen atoms of *m*-TCP are removed from the surface by recombination with carbon and desorption as CO at ~ 700 K. Spectrum (e) shows that TBP thermal decomposition results in phosphorus deposition but virtually no deposition of carbon. The oxygen atoms from TBP and a small portion of the carbon initially present as contamination are removed from the surface by carbon and oxygen recombination and desorption as CO.

initial surface for this work. The Auger spectrum in figure 4b was obtained after adsorbing *m*-TCP at 200 K. Figure 4c and d show Auger spectra of the Fe surfaces after heating to 700 and 800 K respectively to induce decomposition. The composition of the surface does not change significantly as a result of heating from 200 to 700 K. This indicates that although there is desorption of toluene and cresol in this temperature range this is only due to the decomposition of a small fraction of the total amount of adsorbed TCP. After heating to 800 K there is a substantial decrease in the coverages of adsorbed carbon and oxygen. This indicates that the primary mechanism for loss of carbon and oxygen is CO desorption by recombination at a temperature over 700 K. This observation is consistent with the appearance of the CO desorption peaks at ~ 700 K in the TPR

spectra shown in figures 1, 2, and 3. Examining the initial surface and that produced by heating adsorbed TCP to 800 K it is clear that coverage of carbon on Fe increased from 29 to 70% as a result of *m*-TCP decomposition. The Auger spectra obtained following the decomposition of *o*-TCP and *p*-TCP revealed the deposition of similar amounts of carbon and phosphorus onto the Fe surface. This significant increase in the amount of adsorbed carbon indicates that the major fraction of the adsorbed TCP completely decomposed to deposit carbon and phosphorus on the Fe surface. It should be noted that the state of the carbon is graphitic since the small carbidic carbon peaks from 250 to 270 eV are gone. The complete removal of surface oxygen atoms and partial loss of surface carbon atoms can be explained by toluene, cresol and CO desorption observed in TPR spectra. This result shows that all three isomers have the ability to deposit carbon onto the Fe surface. It also suggests that the ratio of TCP isomers present in the mixtures used for vapor-phase lubrication applications might not affect their performance since all three isomers apparently have the same reaction mechanism on Fe. Thus, the amount of toxic *o*-TCP isomer in the TCP mixture can be minimized in vapor-phase lubrication applications without compromising performance.

The Auger spectra (figure 4e) taken following the decomposition of TBP on the Fe surface are significantly different from those obtained following the

decomposition of *m*-TCP. The concentration of adsorbed phosphorus relative to Fe is 13% following TBP decomposition. This is close to the 14% phosphorus coverage observed following *m*-TCP decomposition. The obvious distinction between the surfaces following TBP and *m*-TCP decomposition is that in the case of TBP decomposition there is no increase in the amount of adsorbed carbon on the Fe surface. Figure 5 shows the TPR spectra of a saturation coverage of TBP adsorbed on the Fe surface at 160 K. There is a H₂ desorption peak at 555 K and a broad desorption feature for 1-butene in the temperature range from 240 to 740 K. This result suggests that TBP, the *alkyl*/phosphate vapor-phase lubricant, decomposes via C–O bond cleavage to produce butyl groups [CH₃CH₂CH₂CH₂-] on the surface. These then decompose via β -hydride elimination to desorb as 1-butene [CH₃CH₂CH=CH₂] and H₂ without appreciable carbon deposition onto the surface.

From the viewpoint of trying to understand VPL, these results provide insight into the origin of the differences in the performance of *alkyl* and *aryl* phosphates as vapor-phase lubricants. The *alkyl* phosphates decompose via alkyl groups that readily undergo β -hydride elimination and desorb as olefins, thus removing carbon from the surface. In contrast, the *aryl* phosphates generate aryloxy groups by P–O bond scission and aryl groups by further C–O bond scission. Aryloxy groups

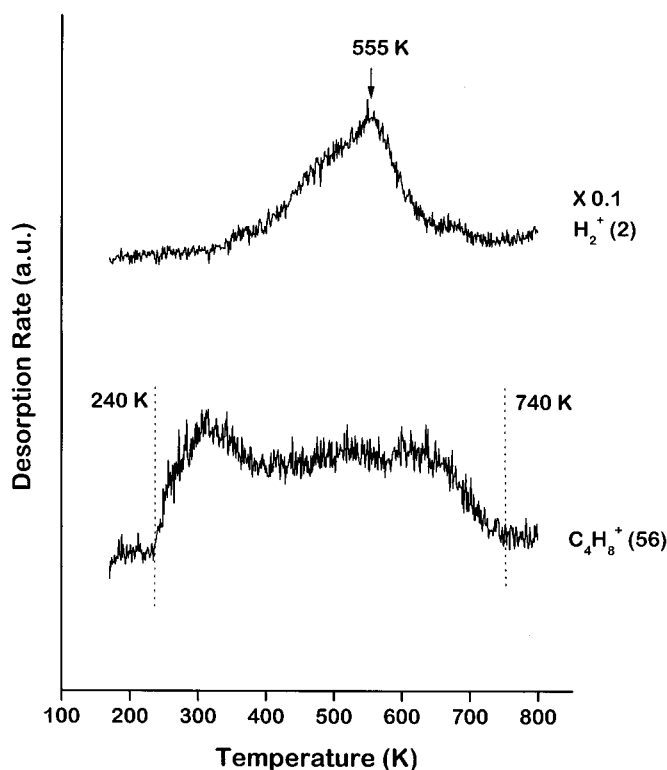


Figure 5. TPR spectra of a saturation coverage of TBP adsorbed on the Fe surface at 160 K. The desorption products were H₂ ($m/q = 2$) and 1-butene ($m/q = 56$, C₄H₈⁺). The heating rate was 2 K/s.

cannot undergo β -hydride elimination to desorb from the surface because they do not have β -CH bonds. Aryl groups can undergo β -hydride elimination to form intermediates such as benzyne (C_6H_4) but these intermediates are highly reactive and will not desorb from the surface. As a result, both aryloxy and aryl groups decompose to deposit carbon onto the Fe surface. Thus, the absence of β -CH bonds in the aryloxy groups and the high reactivity of the aryl groups formed during arylphosphate decomposition lead to high rates of carbon deposition and may be the root cause of differences in performance of *alkyl*phosphates and *aryl*phosphates as vapor-phase lubricants.

4. Conclusions

The surface chemistry of three isomers of TCP on the Fe surface was studied in order to probe possible differences in their decomposition chemistry and their performance as vapor-phase lubricants. All three TCP isomers (*o*-TCP, *m*-TCP, and *p*-TCP) appear to decompose via the same reaction mechanism and with similar kinetics on Fe. Initially they generate methylphenoxy groups by P–O bond cleavage. These groups are either hydrogenated to desorb as cresol or break the C–O bond to generate tolyl groups which either desorb as toluene (through hydrogenation) or completely decompose to deposit carbon and phosphorus onto the surface with the evolution of CO and H₂. In addition, the carbon deposition yield from TCP (*aryl*phosphate) decomposition was compared to that of TBP (*alkyl*phosphate). These results have shown that TCP decomposition results in the deposition of significant amounts of carbon onto the surface while the decomposition of TBP results in little or no carbon deposition onto the Fe surface. The lack of β -CH bonds in the methylphenoxy groups and the high reactivity of tolyl groups generated during TCP thermal decomposition

lead to a complete decomposition of TCP resulting in substantial carbon deposition onto the surface.

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