

A molecular-beam study of the tribological chemistry of carbon tetrachloride on oxygen-covered iron

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Dc molecular-beam methods are used to examine the reactivity of carbon tetrachloride with oxide films grown on iron in ultrahigh vacuum. The incident CCl_4 beam flux is sufficiently low that the nature of the surface oxide is dictated by the annealing temperature allowing the reactivity of Fe_2O_3 , Fe_3O_4 and FeO films to be examined. Carbon tetrachloride reacts rapidly with Fe_2O_3 and reaction with Fe_3O_4 commences at ~ 620 K to evolve CO. The activation energy for this process is 20.6 ± 1.0 kcal/mol. CCl_4 reacts with FeO above ~ 790 K, also to evolve CO, and the activation energy for this reaction is 5.7 ± 0.4 kcal/mol. X-ray photoelectron spectroscopy shows the formation of a halide after reaction at 900 K. These results are in accord with film-growth kinetics measured using a microbalance at high pressures, where it was found that it was not necessary to remove the oxide layer prior to reaction. This contrasts with the behavior of sulfur-containing molecules, where the oxide layer had to be removed before a film would grow. This effect may contribute to the additive synergies commonly found in extreme-pressure lubricant additives where one of the roles of the chloride may be to reduce the oxide layer.

KEY WORDS: molecular beams; Auger spectroscopy; X-ray photoelectron spectroscopy; carbon tetrachloride; oxidized iron; tribological chemistry

1. Introduction

A general model has been developed for the operation of extreme-pressure (EP) lubricant additives, which proposes that they thermally decompose at the hot interface (where temperatures of the order of 1000 K can be attained) to reactively form a lubricating film [1–14]. Since this film is continually worn from the surface under the high loads encountered during extreme-pressure lubrication, the resulting thickness of the interfacial lubricating film arises from a balance between the rate of its reactive formation and tribological removal. It has been shown that films formed from methylene chloride and chloroform on iron consist of FeCl_2 and incorporate small (~ 50 Å diameter), carbonaceous particles [8,9]. In contrast, when carbon tetrachloride is used as an additive, iron carbide is formed, leading to a much more effective additive [13,14]. It was also found in measuring the film-growth kinetics of model extreme-pressure additives using a microbalance, that it was necessary to carefully remove the oxide layer for films to form at a reasonable rate when using sulfur-containing additives. In contrast, chlorinated hydrocarbons grew even on surfaces containing a native oxide layer where

the growth kinetics were not substantially affected by previously reducing the oxide layer to the metal [9,15]. It has been found that extreme-pressure additives often work better in combination than alone [16–18]. There may be several origins for this effect, but clearly one possible role for chlorine-containing additives is to remove the oxide layer, thereby allowing the other additive to react. We have used molecular-beam methods to explore the possible reduction of oxides on iron by a model chlorinated hydrocarbon additive, in this case, carbon tetrachloride. We have shown previously that the decomposition kinetics of chlorinated hydrocarbons measured using molecular beams mimic those found using higher pressures [14]. The advantage of this strategy is that the gas-phase products can be monitored in the ultrahigh vacuum environment used for the molecular-beam experiments, and the nature of the resulting film can also be measured. It was found, using these strategies, that chlorinated hydrocarbons thermally decompose to form a halide film and evolve hydrogen. In addition, the oxidation and thermal reduction on iron has been extensively investigated in ultrahigh vacuum using Auger spectroscopy [19], where both the lineshapes of the iron Auger feature at ~ 43 and 51.5 eV kinetic energy, as well as the ratios of the intensity of the oxygen Auger feature at ~ 510 eV kinetic energy to that of the iron Auger feature at 703 eV, vary with the nature of the oxide. This allows both the reaction chemistry and the state of the oxide to be simultaneously monitored rather conveniently in ultrahigh vacuum.

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2. Experimental

The experiments were carried out in a stainless-steel, ultrahigh vacuum chamber operating at base pressures of 1×10^{-10} Torr following bakeout, which has been described in detail elsewhere [14]. The sample was mounted on a carousel geometry manipulator and the iron foil sample could be resistively heated to 1200 K, where the temperature was monitored by means of a chromel–alumel thermocouple spot-welded to the back of the foil.

Molecular-beam data were collected by continually impinging a beam of reactant onto the sample while it was heated at a constant rate of ~ 3.5 K/s. Desorbing species were detected using a Hiden HAL 301/3F quadrupole mass spectrometer located in line of sight of the sample, where five masses can be monitored sequentially during the same desorption sweep. The chamber also contained a double-pass, cylindrical-mirror analyzer (CMA) for Auger and X-ray photoelectron spectroscopic analyses of the sample following reaction. X-ray photoelectron spectra (XPS) were collected using a Mg $K\alpha$ X-ray source with the double-pass CMA operating at a pass energy of 100 eV.

The sample was cleaned using a standard procedure [20] which consisted of bombarding with argon ions (3 keV, $1 \mu\text{A}/\text{cm}^2$) at 300 K and then annealing to 1000 K *in vacuo* to remove any remaining surface species. The cleanliness of the sample was monitored by means of Auger spectroscopy and the sample was judged clean when no signals not due to the iron substrate could be detected. The state of the oxide layer was monitored using Auger spectroscopy where the literature results, both lineshapes and relative intensities, were reproduced [19].

In the case of molecular-beam experiments, the carbon tetrachloride (Aldrich, 99%) was transferred to glass vials and attached to the gas-handling line of the vacuum system and further purified by repeated freeze–pump–thaw cycles and its cleanliness monitored mass spectroscopically. Normal oxygen (99% purity) and isotopically labeled oxygen ($^{18}\text{O}_2$, Cambridge Isotope Laboratories, 98 at%) were used as received.

3. Results

Shown in figure 1 is the result of a dc molecular-beam experiment in which a constant flux of carbon tetrachloride is incident onto a clean iron foil. The reflected carbon tetrachloride signal (47 amu) is continually monitored by means of a mass spectrometer, where the initial signal at a sample temperature of 300 K monitors the flux totally reflected from the surface. As the sample temperature is raised, the reflected flux decreases due to reaction of carbon tetrachloride with the surface so that the decrease in flux corresponds to the rate of reaction with the surface. No reaction products were detected, indicating that the CCl_4 thermally decomposes at the surface to form a halide film and deposit carbon, and these results are in good agreement with previous measurements [21]. In particular, the

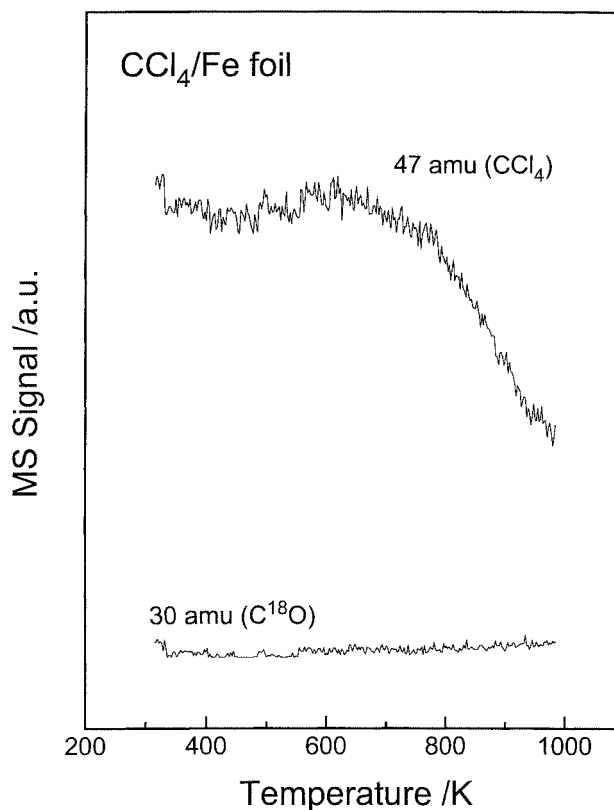


Figure 1. Plot of reflected flux at 47 amu (CCl_4) versus sample temperature for the reaction of a molecular beam of CCl_4 with a clean iron foil.

decrease in signal can be used to measure the activation energy for the reaction, and yields a value of 17.6 ± 0.8 kcal/mol, in good agreement with previous results [21] and also for the activation energy for film growth at higher pressures made using a microbalance [12].

The oxides formed by reaction between iron and oxygen in ultrahigh vacuum have been extensively investigated [19]. Shown in figure 2 are the results for the thermal reduction of an oxide layer formed on an iron foil by exposing it to ~ 50 L of O_2 at 300 K. This initially leads to the formation of Fe_2O_3 , where the ratio of the peak-to-peak intensity of the oxygen Auger signal at 510 eV to that of the iron at 703 eV, designated $\text{O}^{510}/\text{Fe}^{703}$, is 1.5 ± 0.1 (\bullet) [19]. The Auger lineshapes at ~ 43 and 51.5 eV kinetic energy (not shown) are also in good agreement with those assigned to Fe_2O_3 . As the sample is heated *in vacuo* to above ~ 490 K, the relative oxygen Auger intensity decreases. This has been proposed to be due to the formation of Fe_3O_4 [19] and the Auger lineshape found in this case also agrees well with previous results. Fe_3O_4 persists up to a temperature of ~ 790 K, where an additional slower thermal reduction rate is noted above that temperature. $\text{O}^{510}/\text{Fe}^{703}$ ratios of ~ 0.8 and lower indicate the formation of FeO and, once again, the Auger lineshape confirms the presence of this oxide. The presence of the different oxides is indicated in figure 2 by horizontal lines. In order to examine the reactivity of each of these oxides with CCl_4 , a relatively low incident flux was selected so that the oxide film would not be too

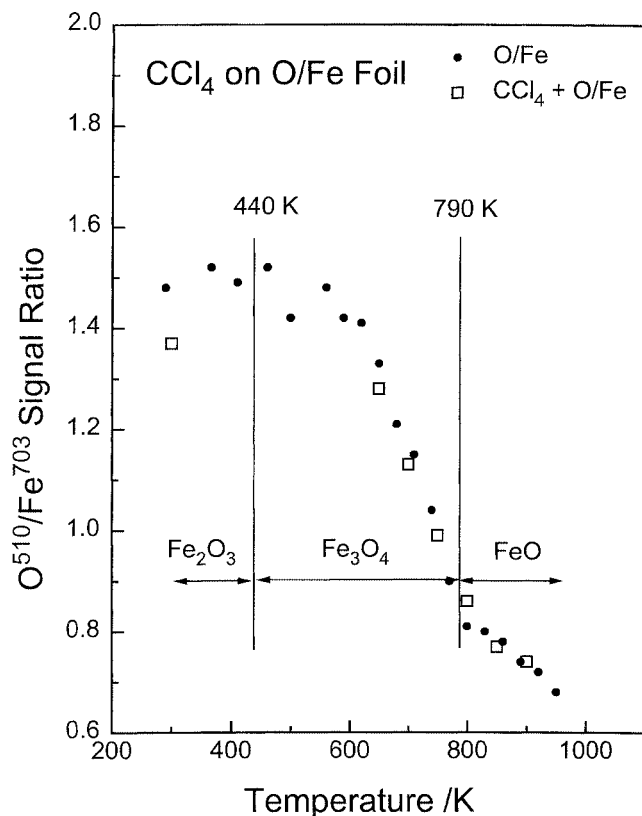


Figure 2. Plot of O Auger signal (510 eV kinetic energy) ratioed to the iron Auger signal (703 eV kinetic energy) plotted for oxidized iron plotted versus sample temperature: (●) formed by annealing in ultrahigh vacuum and (□) formed by heating in the presence of a beam of CCl_4 .

rapidly reduced by the carbon tetrachloride, while at the same time allowing reaction products to be detected. The background pressure with the beam on under these conditions was $\sim 1 \times 10^{-9}$ Torr. A molecular-beam experiment was carried out using a heating rate of ~ 3.5 K/s and the reaction stopped periodically to allow an Auger spectrum of the surface to be collected. Reaction was allowed to proceed once again at a heating rate of ~ 3.5 K/s and the state of the oxide monitored at several temperatures. The resulting values of $\text{O}^{510}/\text{Fe}^{703}$ are also plotted in figure 2 (□). These ratios as a function of sample temperature are in good agreement with those found by thermally annealing the surface (●), indicating that the CCl_4 dose during the experiment was sufficiently small that it did not cause substantial additional reduction of the surface. The only exception is for reaction at ~ 300 K where the value of $\text{O}^{510}/\text{Fe}^{703}$ is reduced from ~ 1.5 to ~ 1.38 indicating that Fe_2O_3 may have been reduced to Fe_3O_4 under these conditions.

The corresponding molecular-beam results are displayed in figure 3. In this case, the oxide layer was formed using $^{18}\text{O}_2$ to avoid interference from any background CO. A decrease in the 47 amu signal is noted due to the reaction of CCl_4 with the surface, although the rate of reaction is clearly lower than on clean iron (figure 1). The removal of CCl_4 from the beam is exactly mirrored by an

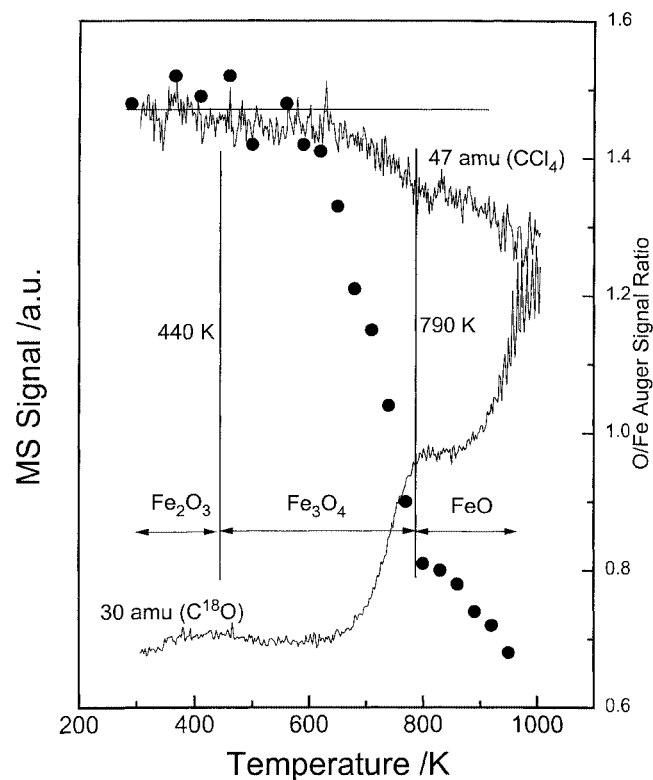


Figure 3. Plot of the reflected fluxes at 47 amu (CCl_4) and at 30 amu (C^{18}O) versus sample temperature for a molecular beam of CCl_4 incident onto an iron foil oxidized using $^{18}\text{O}_2$. Shown for comparison are the O/Fe Auger signal ratios (●) taken from figure 2. The various oxides present on the surface are indicated by horizontal lines.

increase in the 30 amu signal (C^{18}O). No other reaction products are detected. Plotted for comparison are the values of $\text{O}^{510}/\text{Fe}^{703}$ as a function of sample temperature (●) reproduced from figure 2. The oxide present on the surface in each temperature range is again indicated as a horizontal line. An additional small CO peak is noted at between 350 and 550 K, which may be associated with an initial reduction of Fe_2O_3 , as found in the data of figure 2.

A Cl 2p X-ray photoelectron spectrum of an oxidized surface after reaction at ~ 900 K with CCl_4 is displayed in figure 4. Data were collected for 100 s with a pass energy of 100 V. This yields a feature at 198.6 eV binding energy. Note that the resolution of the spectrometer was not high enough to resolve the spin-orbit coupling split components of this line.

4. Discussion

The data of figure 3 show that carbon tetrachloride reacts with oxidized iron to evolve carbon monoxide into the gas phase. The formation of C^{18}O from a surface oxidized with $^{18}\text{O}_2$ confirms that the CO arises from reaction with the surface. Furthermore, the carbon tetrachloride flux was sufficiently low that the nature of the oxide present on the surface is primarily dictated by the sample temperature (figure 2), which allows the reactivity of each of the oxides to

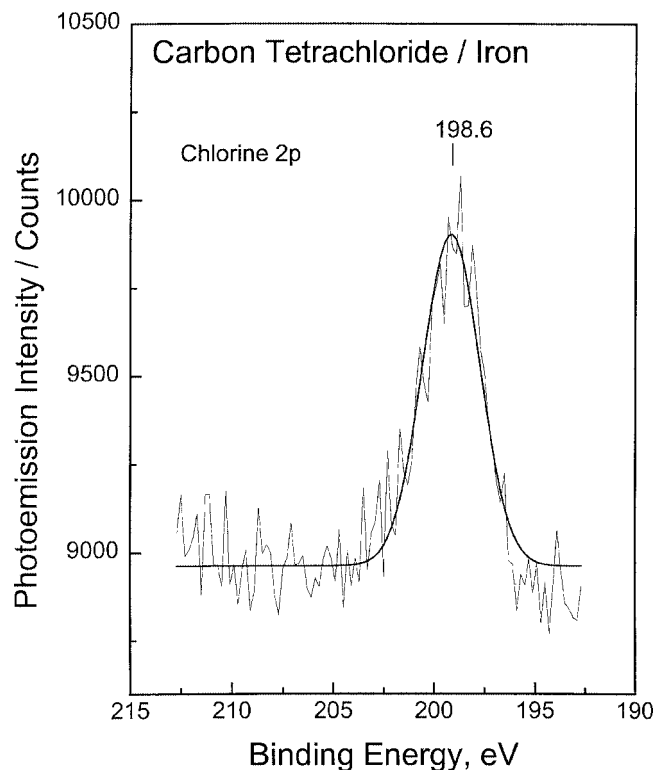


Figure 4. Cl 2p X-ray photoelectron spectrum after reaction of CCl_4 with an oxidized iron foil at 900 K.

be monitored in a single experiment. Note, however, that there is some initial reduction of Fe_2O_3 to Fe_3O_4 induced by carbon tetrachloride at low temperatures (figure 2). The molecular-beam data of figure 3 show the onset of significant CO formation and removal of CCl_4 from the beam at a reaction temperature of ~ 620 K due to the reaction of CCl_4 with Fe_3O_4 . The activation energy for this process can be obtained from an Arrhenius plot, which is shown in figure 5. This shows two clear regions where the initial reaction with Fe_2O_3 between 620 and 790 K (figure 3) proceeds with an activation energy of 20.6 ± 1.0 kcal/mol. CCl_4 reacts slightly more slowly with FeO above ~ 790 K. The activation energy for this process is 5.7 ± 0.4 kcal/mol. The X-ray photoelectron spectrum of the Cl 2p region following reaction at ~ 900 K (figure 4) shows a peak with a binding energy of 198.6 eV which corresponds to the formation of a chloride [22], suggesting that the iron is oxidized by the chlorine.

These results demonstrate that iron oxides are reduced by carbon tetrachloride, forming gas-phase CO, where the activation energy for this process depends on the oxide being reduced. These results are in accord with film-growth kinetics measured using a microbalance which showed that the oxide layer on the surface did not have to be removed to collect reproducible data. According to the results presented above, this is achieved by a reaction with the chlorinated hydrocarbon to evolve carbon monoxide. This contrasts with the behavior of sulfur-containing molecules where the oxide layer had to be removed before reaction could occur. This suggests that one of the roles of chlorine in mixed

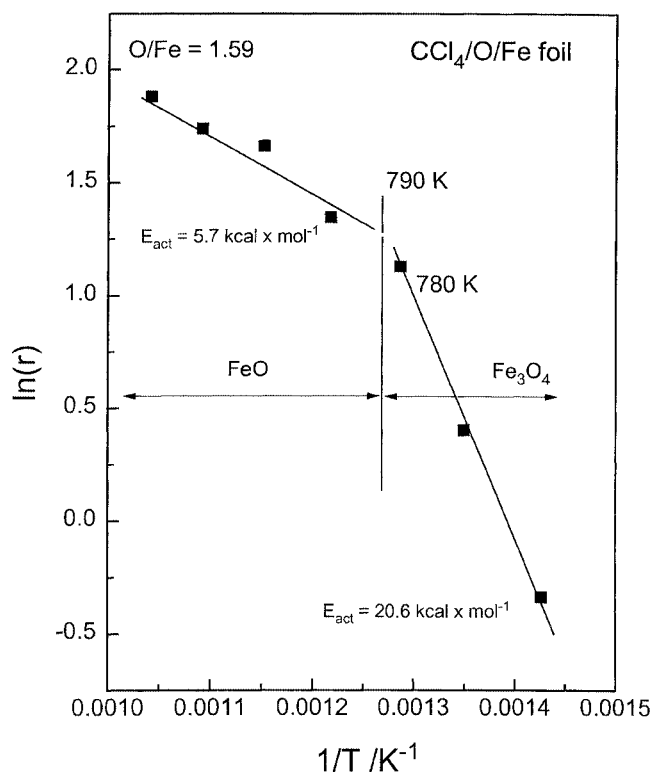


Figure 5. Arrhenius plot for the reaction of CCl_4 with an oxidized iron foil taken from the data of figure 3.

additive systems may be in the removal of the oxide layer, allowing other (for example, sulfur-containing) additives to react with the surface.

5. Conclusions

Reactions of molecular beams of carbon tetrachloride with oxidized iron in ultrahigh vacuum shows that carbon tetrachloride reacts with oxides of iron (Fe_2O_3 , Fe_3O_4 , FeO) while evolving CO into the gas phase. The activation energies for these reactions depend on the nature of the oxide being reduced and result in the formation of a halide layer at ~ 900 K. This ability of halide extreme-pressure additives to reduce the surface oxide layer may be a contributing factor in experimentally found additive synergies.

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