The surface and tribological chemistry of carbon tetrachloride on iron

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The thermal decomposition of carbon tetrachloride on clean iron was studied in ultrahigh vacuum using molecular beam strategies, where it is found that carbon tetrachloride thermally decomposes on the surface to deposit iron and carbon with exactly identical kinetics as found at high pressures. No gas-phase products are detected and the activation energy for the reaction (14.2 ± 0.5 kcal/mol) is in good agreement with the value measured at high pressures. Little carbon is detected on the surface using Auger spectroscopy following reaction and it is found that this diffuses into the surface much faster when formed from CCl_4 than from CH_2Cl_2. This effect is ascribed to the effect of co-adsorbed chlorine on the adsorbed carbon, which is proposed to decrease the activation energy for diffusion into the bulk of the sample. This effect explains the increased tendency for carbon tetrachloride to form carbides under extreme-pressure tribological conditions.

Keywords: carbon tetrachloride, molecular beams, ultrahigh vacuum, Auger spectroscopy, reactivity, carbide formation

1. Introduction

It has been demonstrated that chlorinated hydrocarbons act as extreme-pressure (EP) additives by thermally decomposing at the hot, lubricated interface to form a film that prevents the contacting surfaces from seizing [1–7]. When methylene chloride [8,9] and chloroform [10,11] are used as the additive, this layer consists of $FeCl_2$. Carbon tetrachloride shows a remarkable activity as an extreme-pressure additive so that very low additive concentrations allow extremely high loads to be borne by the contacting surfaces [12,13]. It has been shown that this is due to an increased tendency of carbon tetrachloride to react to form, not only a layer of ferrous chloride, but also a layer of iron carbide [13]. The reactivity of methylene chloride and chloroform with iron has been investigated previously in ultrahigh vacuum using molecular beams of these chlorinated molecules [14]. These experiments confirmed that iron halides were indeed formed by the reaction of chlorinated hydrocarbons with the iron surface and that the primary gas-phase product in both cases was hydrogen. This strategy is applied to investigating the chemistry of carbon tetrachloride on iron surfaces in order to understand why they are such effective lubricant additives and also to identify the nature of the films that are formed without intervening exposure to air.

2. Experimental

Experiments were carried out using a $12''$-diameter ultrahigh vacuum chamber which was pumped by means of

an ion pump and operated at a base pressure of $\sim 1 \times 10^{-10}$ Torr following bakeout [14]. The chamber was also equipped with a single-pass, cylindrical-mirror electron energy analyzer with a co-axial electron gun for Auger analysis of the sample and a quadrupole mass analyzer for residual gas analysis, leak testing and for detecting products formed following interaction of the carbon tetrachloride beam with the iron surface. The iron foil sample was mounted to the end of a carousel-geometry sample manipulator and could be resistively heated, and the sample temperature was monitored using a chromel/alumel thermocouple spot-welded to the sample. The d.c. molecular beam was provided by a 1 mm diameter capillary that was directed at the sample while it was located in front of the ionizer of the quadrupole mass analyzer. The mass spectrometer was surrounded with a shroud with 1 cm diameter hole in the front to minimize interference from signals not arising from the sample. Molecular beam data could be collected either by continuously varying the sample temperature at a relatively low heating rate of ~ 1 K/s, while simultaneously monitoring the intensity at various masses or by maintaining the sample temperature at some value and measuring the steady-state signal intensity. As demonstrated below, both methods yielded identical results. Following film deposition, the sample could be moved directly in front of the cylindrical-mirror analyzer and an Auger spectrum collected.

The iron sample was cleaned by cycles of oxidation and ion bombardment and the surface cleanliness monitored using Auger spectroscopy. The sample was judged clean when no signals due to oxygen or carbon, the primary contaminants, could be detected. The carbon tetrachloride

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(Aldrich, 99.9%) was transferred from the bottle to a glass vial and purified by repeated freeze–pump–thaw cycles and stored in glass until use. Its purity was monitored by mass spectroscopy.

3. Results

Figure 1 displays the 118 amu signal from the iron sample at various temperatures with an incident d.c. beam of carbon tetrachloride. The data obtained by slowly ramping the sample temperature or by maintaining a sample temperature and measuring the steady-state signal are essentially identical. This confirms that the data are collected under equilibrium conditions. This mass is uniquely due to carbon tetrachloride and shows that the signal decreases negligibly below ~ 700 K but diminishes substantially in intensity with increasing temperature and indicates that carbon tetrachloride thermally decomposes at the heated iron surface. No other reaction products, in particular C_2Cl_4 (from the signals at 167, 130 and 95 amu) were found. Surface analyses of CCl_4 adsorbed on iron surface have revealed the formation of intermediate CCl_2: species [15–17]. Evidently, at these high reaction temperatures,

these undergo further thermal decomposition and do not oligomerize. The activation energy of this thermal decomposition process measured from an Arrhenius plot taken from these data (figure 2) is 14.2 ± 0.5 kcal/mol. Thicker films can also be grown on iron foils where pressures up to 30 Torr of carbon tetrachloride are used and growth is limited by either the rate at which the film grows or by reaction at the growing interface. The energetics of these processes can be measured by monitoring the rate at which the resulting film thickness varies with time at various temperatures and indicates that the activation energy for thermal decomposition is 18.3 ± 0.5 kcal/mol. This is slightly higher than the value measured from molecular beams, but is in reasonable agreement with it. In that case, the surface film was analyzed using X-ray photoelectron and Raman spectroscopies, both of which confirmed that the film consisted of $FeCl_2$ and carbon. In the case of films grown by reacting methylene chloride or chloroform, carbon was present as small particles whereas no carbonaceous particles were found in films formed from carbon tetrachloride. Figure 3(a) displays the results of an Auger analysis of a film grown from a molecular beam of carbon tetrachloride in ultrahigh vacuum at ~ 1053 K and shows large Cl (180 eV
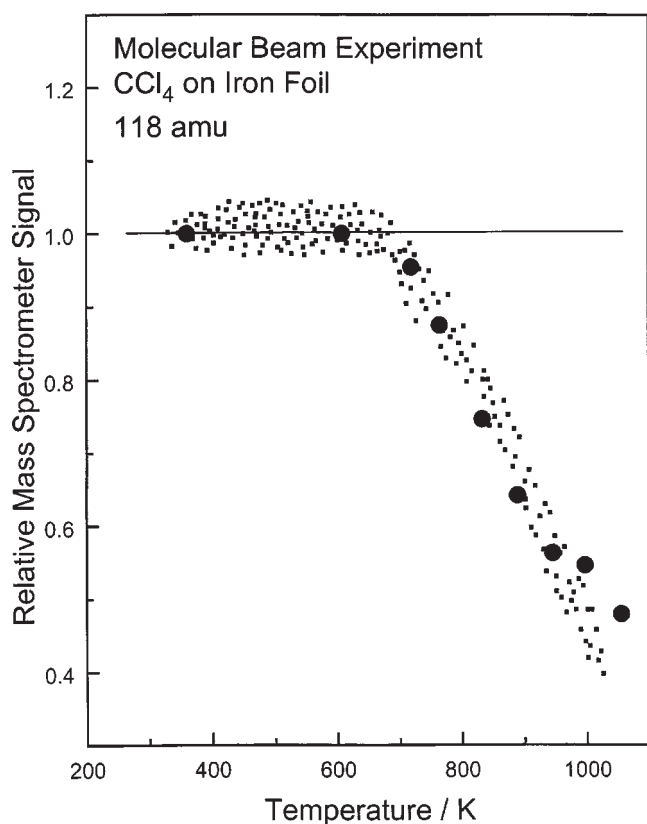

Figure 1. Plot of 118 amu (CCl_4) intensity *versus* sample temperature for carbon tetrachloride impinging on a clean iron surface collected by continually ramping the sample at ~ 1 K/s and continually monitoring the 118 amu signal (■) or by maintaining a sample temperature and measuring the equilibrium signal (●). The horizontal line shows the 118 amu signal measured for no surface reaction.
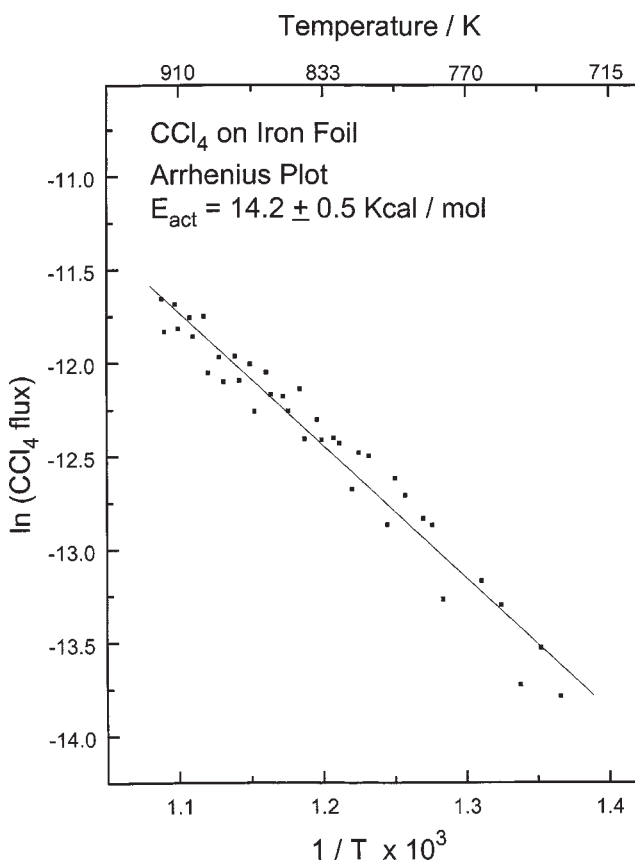

Figure 2. Arrhenius plot of ln(CCl_4 reaction rate) *versus* $1/T$, where T is the sample temperature from the molecular beam data shown in figure 1 from data collected by continually varying the sample temperature (■). The flux is measured from the decrease in the CCl_4 signal (in figure 1) multiplied by $\sqrt{T}$. The activation energy for the surface reaction from the slope of these curves is 14.2 ± 0.5 kcal/mol.
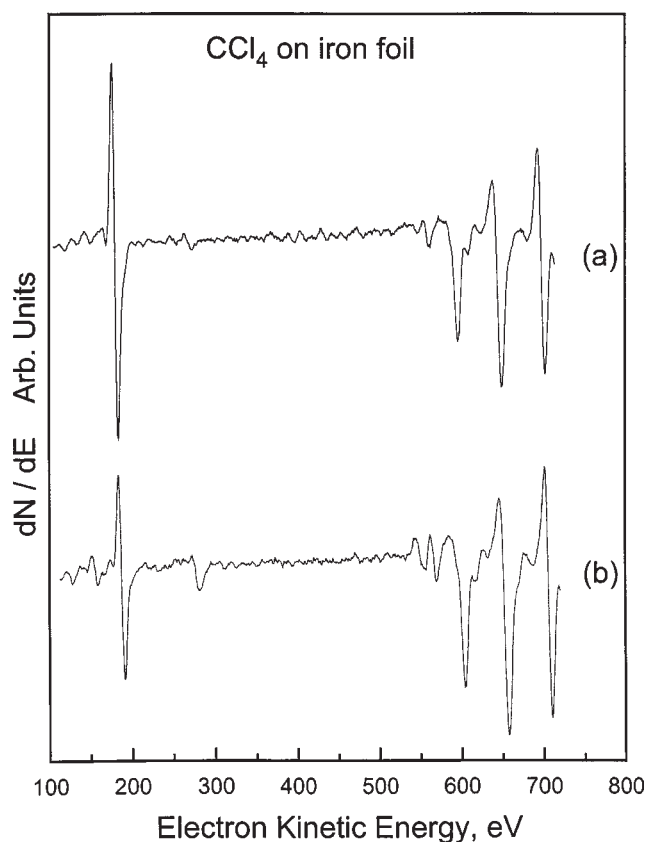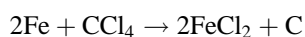
Figure 3. Auger spectra (a) collected following reaction at ~ 1053 K and (b) after annealing the sample at 1100 K *in vacuo* for 10 s.

Figure 4. Histogram showing the relative reactivity of CCl_4, $CHCl_3$ and CH_2Cl_2 with a clean iron foil at 900 K using molecular beams.

kinetic energy (KE)) and Fe (590, 650 and 710 eV KE) signals corresponding to the growth of a layer of $FeCl_2$. In addition, a small carbon peak is evident at ~ 273 eV KE in figure 3(a). The sample is heated briefly to 1110 K *in vacuo* to remove much of the $FeCl_2$ and the resulting spectrum is displayed in figure 3(b). The chlorine signal (180 eV KE) has significantly diminished in intensity consistent with the desorption of $FeCl_2$ from the surface and the carbon signal (273 eV KE) has relatively increased in intensity since this remains on the surface when the sample is heated. These results indicate that carbon tetrachloride thermally decomposes at the heated iron surface to deposit a ferrous chloride film as:

$$2Fe + CCl_4 \rightarrow 2FeCl_2 + C$$

The amount of carbon is relatively small. As will be shown below, this is due to a portion of the carbon diffusing into the bulk of the sample [15,18–20].

It has been demonstrated that carbon tetrachloride is a much more effective extreme-pressure additive than either chloroform or methylene chloride. This is partly due to the fact that carbon tetrachloride is more reactive than either of the other two additives, and it also shows a greater tendency to react with the iron surface to form iron carbide. The histograms plotted in figure 4 display the relative reactivities of each of the three model additives with clean iron foils at 900 K in ultrahigh vacuum measured
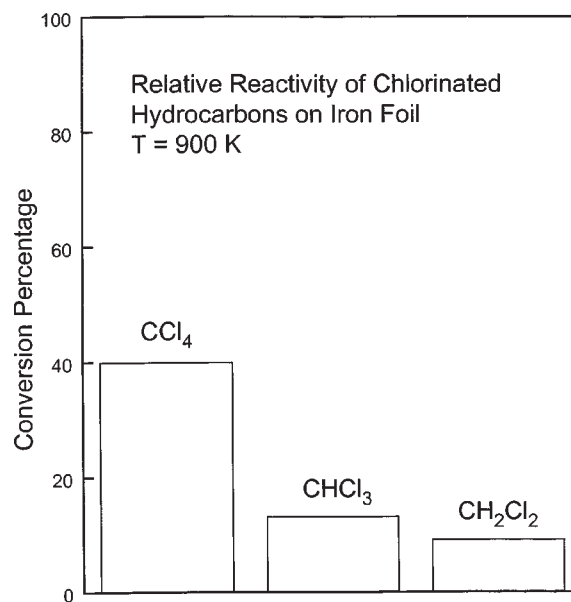
using molecular beams. Clearly the reactivity varies in the order $CCl_4 > CHCl_3 > CH_2Cl_2$, an order that exactly reflects that found by measuring relative film growth rates using the microbalance [21] and mirrors their relative efficacies as extreme-pressure additives. Finally, since carbide formation requires the diffusion of carbon from the surface into the bulk of the sample, the rate of this process was measured in the following way. First, a carbon plus chlorine overlayer was prepared by saturating a clean iron sample with either carbon tetrachloride or methylene chloride at 300 K. The sample was then annealed to various temperatures, allowed to cool to room temperature and the ratio of carbon to iron monitored using Auger spectroscopy. Negligible amounts of carbon-containing species were found to desorb from the surface so that loss of carbon is due to transport into the bulk of the iron. The results are displayed in figure 5, which plots the Auger intensity ratio (C/Fe) for methylene chloride and carbon tetrachloride as a function of annealing temperature. The initial amount of carbon on the surface is larger for methylene chloride than for carbon tetrachloride, merely reflecting the stoichiometry of the precursor molecules. As the sample is heated, the amount of carbon on the surfaces decreases due to diffusion into the bulk of the sample. However, the carbon deposited from CCl_4 diffuses much more rapidly than that from methylene chloride. This indicates that the carbon diffusion rate into the bulk increases when there is a larger amount of co-adsorbed chorine. This indicates why carbides form more easily from carbon tetrachloride than from methylene chloride; the co-adsorbed chlorine facilitates surface-to-bulk transport of the carbon. A similar effect has been noted due to the presence of oxygen [21].
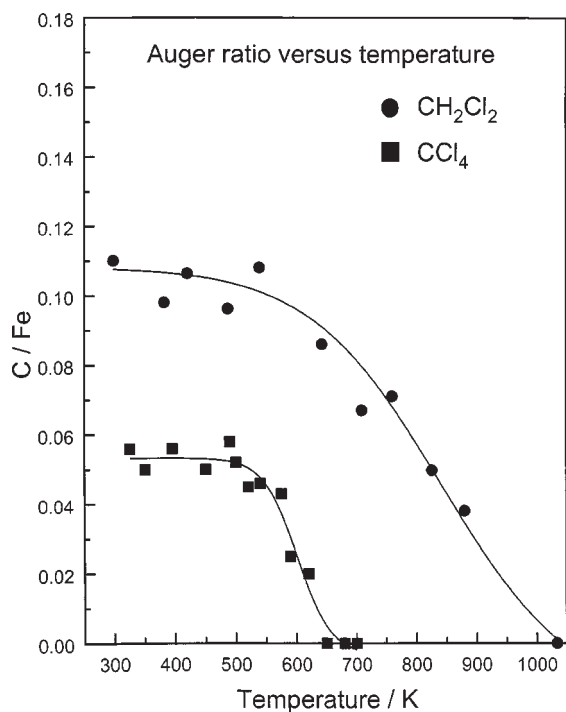
Figure 5. Plot of the C/Fe peak-to-peak ratio in the Auger spectra collected following saturation of a clean iron surface with methylene chloride (●) or carbon tetrachloride (■) as a function of annealing temperature.

4. Discussion

Molecular beams of carbon tetrachloride thermally decompose on atomically clean iron in ultrahigh vacuum to deposit a film consisting of $FeCl_2$ which incorporates carbon. Data obtained under steady-state conditions or by ramping the sample at 1 K/s (figure 1) are identical, indicating that carbon tetrachloride decomposition is measured under equilibrium conditions in the molecular beam experiment. The decomposition rate increases with foil temperature (figure 1) and the activation energy for decomposition of the carbon tetrachloride at the growing ($FeCl_2$) interface is 14.2 ± 0.5 kcal/mol and is in fair agreement with the corresponding value measured for film growth in a microbalance. The reactivity of carbon tetrachloride is greater than either methylene chloride or chloroform (figure 4), which may partially account for carbon tetrachloride's exceptional efficacy as an extreme-pressure additive. In addition, however, carbides form much more rapidly when CCl_4 is used as an additive than from other chlorinated hydrocarbons. The data presented in figure 5 suggest a possible reason for this effect since the transport of carbon from the surface of iron into the bulk is facilitated by the addition of chlorine to the surface. Since both carbon and chlorine bond to the surface by accepting electrons from the iron substrate, the heat of adsorption of carbon on the surface is weakened by the addition of chlorine. Similar effects have been found with co-adsorbed oxygen [21]. Lowering the heat of adsorption of carbon may correspondingly lower the activation energy for diffusion into the bulk, leading to the result displayed in figure 5 and an increased tendency of more highly chlorinated hydrocarbons to form carbides.

5. Conclusions

The film growth chemistry of carbon tetrachloride measured at high pressures ($\sim$ Torr) and that found when CCl_4 is used as an extreme-pressure additive are reproduced using molecular beams interacting with atomically clean iron surfaces in ultrahigh vacuum, where the formation of a layer of $FeCl_2$ + carbon is found. The reactivity of carbon tetrachloride is found to be greater than that of either methylene chloride or chloroform, which may partially account for its exceptional effectiveness as an EP additive. Moreover, the additional chlorine present in CCl_4 facilitates the diffusion of carbon into the bulk of the sample, increasing the tendency of carbon tetrachloride to form carbides when used as an additive and therefore to be able to sustain very high loads.

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