Interaction of Effusive Beams of Methylene Chloride and Chloroform with Clean Iron: Tribochemical Reactions Explored in Ultrahigh Vacuum

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The growth kinetics of films formed from the thermal decomposition of small, volatile chlorinated hydrocarbons on iron have been previously measured at relatively high pressures (a few Torr) using a microbalance. These results were used to model the tribological behavior of these molecules as extreme-pressure lubricant additives. Similar chemistry is examined on clean iron prepared in ultrahigh vacuum using a dc molecular beam created using a directional dosing source where the beam is incident on the clean sample and the gas-phase products of the reaction are detected mass spectroscopically. The temperature- and pressure-dependence of the decomposition rate of both methylene chloride and chloroform are found to agree well with the kinetics measured in the microbalance. In addition, the nature of the reactive film, which consists of $FeCl_2$ and incorporates carbon, is found to be identical in both regimes suggesting that film growth kinetics can be successfully measured in ultrahigh vacuum. Finally, the only gas-phase reaction product detected in either case was hydrogen, indicating that both reactants thermally decompose to form $FeCl_2$, deposit carbon, and evolve hydrogen.

1. Introduction

Despite the health and environmental problems of chlorinated hydrocarbons, they are still extensively used as additives to lubricants that operate under conditions of extreme pressure, generally known as extreme pressure (EP) lubricant additives.[1−6] These additives turn out to be particularly amenable for study, precisely because they operate under extreme conditions, for several reasons. First, material is removed from the rubbing surfaces under the influence of such high loads so that it is often argued that the interface exposed to the lubricant has had all of the surface contaminants removed and can be modeled by a clean surface. Second, the high applied loads lead to a high power dissipation and, therefore, high interfacial temperatures where values of ∼1000 K are not uncommon.[7] Such high reaction temperatures first imply that the chemistry at the surface should be rather simple and also that reaction rates should be quite high.

Reaction kinetics for decomposition of both methylene chloride and chloroform[8−11] have been measured using a microbalance at relatively high pressures by monitoring the change in the thickness of the film reactively deposited onto an iron foil as a function of time. These kinetics can be used as input parameters to successfully predict the tribological behavior of these additives.[12] Analysis of the films also reveals that they consist of $FeCl_2$ and incorporate small carbonaceous particles.

These lubricant additives are, therefore, proposed to operate by thermally decomposing at the hot interface to yield an $FeCl_2 + C$ film. When methylene chloride and chloroform are used as additives, this effectively acts as an antiseizure layer and lowers the interfacial friction coefficient. The lubricant is assumed to fail when the sliding conditions become so severe that the film is removed leading to metal−metal contact and welding.[12]

Previous research on the surface chemistry of organochlorine compounds on various iron surfaces has been carried out. Yates and co-workers have extensively investigated the interaction of Cl_2, CCl_4, CCl_2F_2, and C_2Cl_4 on Fe(110). They observe a zero-order $FeCl_2$ desorption process at 560 K and a second desorption process of iron chloride species at high temperatures (900 K and higher). When carbon-containing molecules are adsorbed onto Fe(110) at ∼300 K, the zero-order $FeCl_2$ desorption process is not observed.[13,14,16,17] In the work presented by Benziger and Madix on the adsorption of CH_3Cl on Fe(100), the only desorption product detected was hydrogen at 475 K.[19]

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Several questions concerning the chemistry at the interface remain to be addressed. The first is, what are the gas-phase products of the reaction? Work on methyl chloride above suggests that this should be hydrogen. Note that these questions cannot be answered by microbalance experiments, since gas-phase products are extremely difficult to detect under these circumstances. To address this question, we have elected to carry out dc molecular beam experiments in ultrahigh vacuum. This allows gas-phase products to be detected and analyzed directly using a quadrupole mass analyzer. These results can be compared with kinetic data collected in the microbalance in a number of ways. First, the activation energy for both regimes can be compared from the temperature dependence of the reaction rate in both cases. Second, the reaction rate can be measured as a function of pressure for both regimes and, finally, the composition of the resulting reactively deposited films can be compared. The agreement between the kinetic data collected in this work under ultrahigh vacuum conditions and those measured at high pressure is generally good.

2. Experimental Section

Experiments were carried out in a stainless steel, ultrahigh vacuum chamber that has been described in detail elsewhere.[20] However, in brief, it consists of a 12 in. diameter chamber that operates at $\sim 5 \times 10^{-11}$ Torr following bakeout and which is pumped by a combination of ion and sublimation pumps. The iron foil (Aesar, 99.999%) is mounted to the end of a carousel geometry manipulator and can be heated to ~ 1200 K for sample cleaning. The iron sample is never heated above its phase transition temperature (1200 K). The chamber is equipped with a cylindrical mirror analyzer that is used for Auger analysis of the sample and a shielded quadrupole mass spectrometer which is used for residual gas analysis and monitoring products evolved in chemical reaction with the surface. No current was detected at the sample when the sample was placed in front of the shrouded mass spectrometer so that electron-beam effects in the chemistry can be excluded. Auger spectra were obtained using typical acquisition conditions (a 3-kV electron beam current of 1×10^{-6} for 10 min). The sample was never exposed to higher currents to avoid beam damage.

The chlorinated hydrocarbon molecular beam is generated by leaking the reactant via a variable leak valve through a 1 mm internal diameter capillary that is incident at $\sim 70°$ to the normal onto the iron foil sample, while the sample is simultaneously located in front of and in line of sight of the ionizer of a quadrupole mass spectrometer. The quadrupole mass spectrometer can rapidly scan several masses (five are generally selected) with a residence time per mass of 5 ms. These data can be collected into memory located in the control electronics of the Dycor quadrupole mass analyzer and subsequently downloaded via an RS232 connection to a personal computer. The computer can simultaneously monitor the sample temperature via a digital-to-analog convertor. The input of the digital-to-analog convertor is optoisolated from the thermocouple temperature sensor to avoid ground loops. The computer then converts mass intensity and temperature versus time data into mass intensity versus temperature plots. Alternatively, the intensity at a series of selected masses can be monitored while the sample temperature is kept constant, so that the product flux can be monitored under isothermal conditions. Since material is continually being deposited onto the surface, this leads to the possibility that the surface or growth kinetics may change during the course of the reaction. This was checked by comparing signal intensities at various temperatures while both increasing and decreasing the temperature and checking for consistency between both sets of data. To further establish if any further changes were taking place, the signals at intermediate temperatures were monitored periodically.

The beam flux is monitored from the background pressure. While this has not been accurately calibrated, measurement of

uptake kinetics in a King and Well's[21] type experiment suggests that pressure enhancement is a factor of ~ 500. This implies that the effective reactant pressure at the sample is ~ 500 times higher than the background ambient pressure. Note that pressures quoted on the data are background pressures measured by the ionization gauge but are uncorrected for ionization gauge sensitivity factors. The sample temperature was monitored by means of a chromel–alumel thermocouple spot welded directly to the foil. The foil was cleaned using a combination of heating in 5×10^{-8} Torr of oxygen at 900 K for 5 min and then annealing to ~ 1000 K and argon ion bombardment (2 kV, 1×10^{-4} A/m²) using 4×10^{-6} Torr of argon for 10 min.[14] The foil was judged clean when no other Auger signals except those due to iron at 598, 651, and 703 eV kinetic energy[22] were detected.

The methylene chloride and chloroform (Aldrich, 99.9%) were transferred from the bottle to glass ampules where they were attached to the vacuum system's gas-handling line and purified by repeated freeze–pump–thaw cycles. Cleanliness was monitored by leaking samples into the ultrahigh vacuum chamber and observing the mass spectrum which agreed well with standard spectra.

3. Results

The thermal decomposition of methylene chloride on an atomically clean iron foil was examined using a continuous effusive beam of methylene chloride. The gas-phase products formed by the reaction are monitored using a quadrupole mass analyzer and the surface analyzed using Auger spectroscopy. Note that films formed by methylene chloride decomposition in a microbalance at higher pressures ($\sim$Torr) consist of ferrous chloride and incorporate small (~ 50 Å diameter) carbonaceous particles.[12] The only gas-phase product found under any reaction conditions in ultrahigh vacuum is hydrogen. Thus, only other masses apart from 2 amu that could be assigned to methylene chloride itself were detected. This suggests that the surface chemistry can be characterized by the equation

$$Fe + CH_2Cl_2 \rightarrow FeCl_2 + C + H_2 \qquad (1)$$
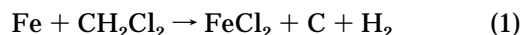
It should be noted that these products conform with those thermodynamically predicted.[12,23] It should be emphasized that no hydrocarbon products are detected, except that a small amount of CO is found to desorb from the sample supports at high temperatures (1000 K and higher). Similar results were obtained by Benziger and Madix on the adsorption and reaction of CH_3Cl on Fe-(100).[19]

The data of Figure 1 confirm the reaction proposed in eq 1. This plots the hydrogen (2 amu) and methylene chloride (49 amu) signals as a function of sample temperature. As noted in the Experimental Section, these data were collected by monitoring the ion signals at various masses at a constant sample temperature and so are due to reaction on the film formed on the iron surface rather than on clean iron. The signal intensities in Figure 1 are corrected for their respective mass spectrometer ionizer sensitivities and therefore represent the methylene chloride and hydrogen pressure directly. These calibrations were obtained either by leaking hydrogen or methylene chloride into the vacuum chamber and measuring the 2 and 49 amu signals, respectively, at fixed background pressures. The background pressures were also corrected for ionization gauge sensitivities. Note that the decrease in methylene chloride signal is mirrored by a corresponding increase in hydrogen pressure. However, the amount

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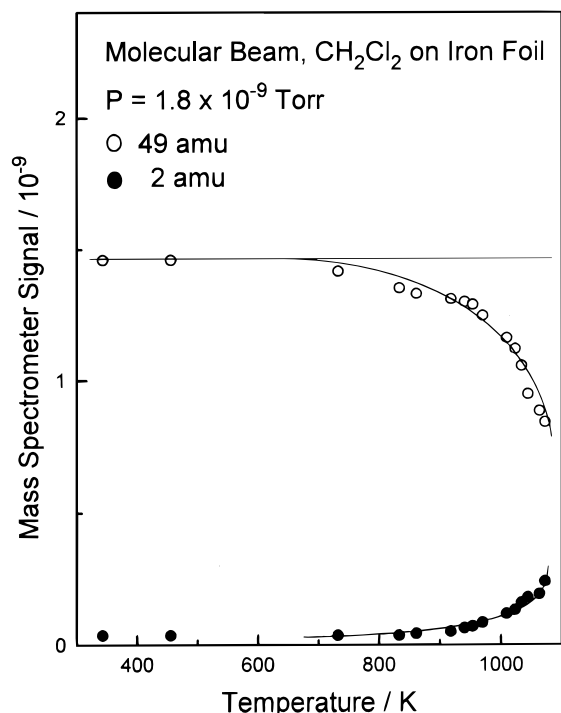
Figure 1. Plot of methylene chloride and hydrogen fluxes as a function of sample temperature for a dc effusive beam of methylene chloride ($p = 1.8 \times 10^{-9}$ Torr) incident on an initially clean iron foil.

by which the 49 amu signal decreases does not exactly match the increase in 2 amu signal as is predicted by eq 1. This likely reflects errors in ion gauge sensitivity factors for hydrogen and methylene chloride.

These temperature data can be plotted in Arrhenius form by calculating a rate (flux) by multiplying the mass spectrometer signal by $\sqrt{T}$ to take account of the velocity variation of desorbing species as a function of sample temperature. The resulting plots are shown in Figure 2 and Figure 3 for hydrogen formation and methylene chloride consumption. The slopes yield activation energies of 9.5 ± 0.9 and 9.8 ± 0.9 kcal/mol, respectively.

The reaction rate can be measured from the 2 amu signal as a function of the incident beam pressure. The results are plotted in Figure 4 for methylene chloride incident on an iron foil heated to 943 K where the pressure represents the methylene chloride pressure monitored by the ion gauge. The effective pressure of the beam incident on the sample surface is $\sim$500 times larger than this value. There appears to be two different regimes, one below a pressure of $\sim 8.4 \times 10^{-9}$ Torr of methylene chloride where the slope is 0.50 ± 0.02 and indicates a half-order (dissociative) adsorption process. Above this pressure, the slope is 0.78 ± 0.03.

The surface of the samples can be analyzed using Auger spectroscopy after reaction and without any intervening exposure to air. Note that the electron-stimulated desorption cross section of halides, and in particular chlorides, is rather high,[24] so care was taken to minimize the electron dose. The ESD effect was gauged by tuning the Auger spectrometer to the Cl LMM Auger peak (181 eV kinetic energy) and the rapidly moving the sample to intercept the electron beam. A decrease of chlorine signal was noted as a function of time, presumably due to ESD, but the decrease was always $<20\%$ of the original signal during the time required to collect an Auger scan. This effect is
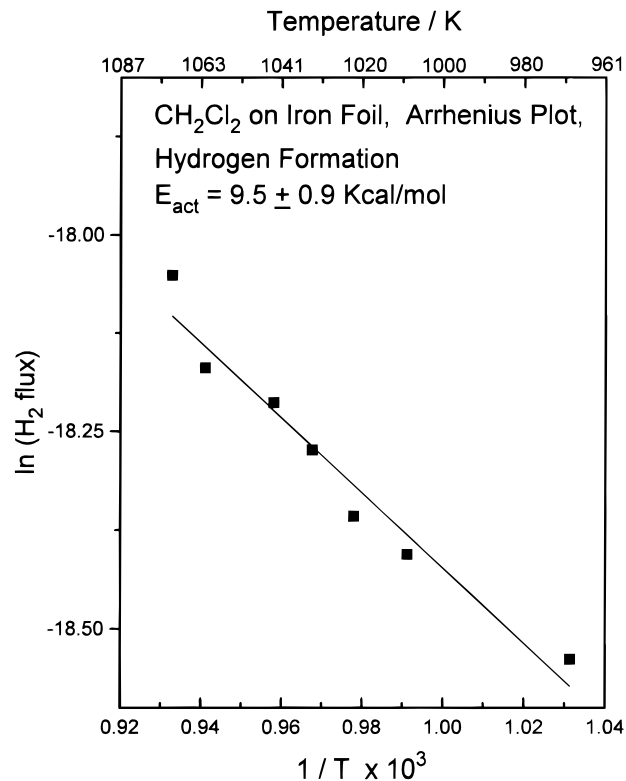
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Figure 2. Arrhenius plot of ln(rate of hydrogen formation) versus $1/T$ for the reaction of methylene chloride with iron taken from the data of Figure 1.

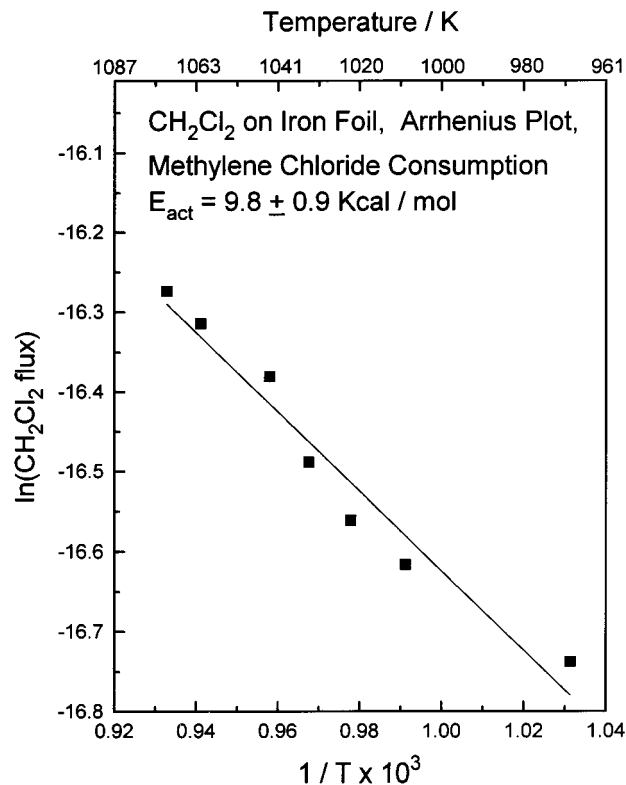**Figure 3.** Arrhenius plot of ln(rate of consumption) versus $1/T$ for the reaction of methylene chloride with iron taken from the data on Figure 1.

included in the error estimates of the Auger intensities. Analyses of the spectra yield a Cl(180)/Fe(700) intensity ratio of 2.3 ± 0.6, where intensities are measured as peak-to-peak intensities of the first derivative. The relatively large error in this case derived from uncertainties as-
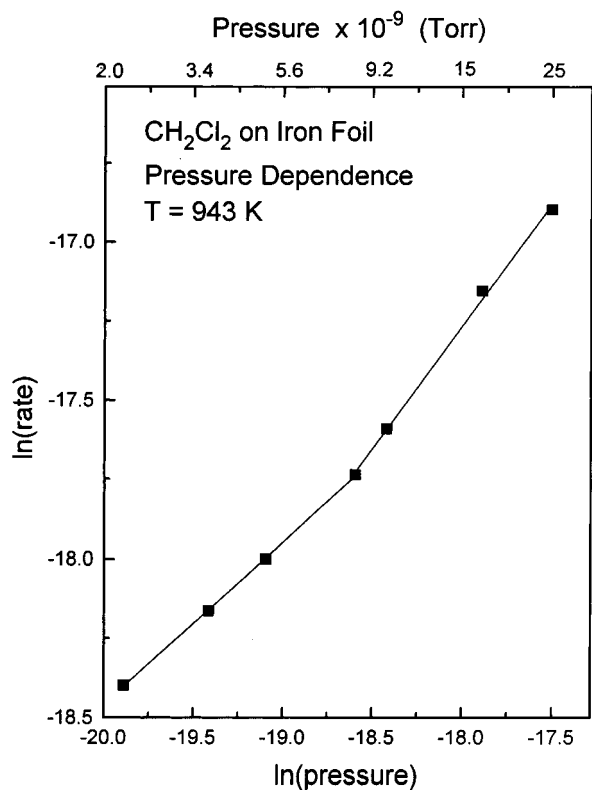
Figure 4. Plot of ln(rate of hydrogen formation) versus ln-(pressure) where pressure is the chamber pressure due to methylene chloride leaked into the chamber via the effusive beam source and incident on an initially clear ion foil heated to 940 K.

sociated with the ESD effects alluded to above. The amount of carbon monitored at the resulting $C(273)/Cl$-(180) ratio was 0.18 ± 0.01.

The corresponding results for chloroform incident on the iron surface are displayed in Figures 5, 6, 7, 8, and 9. Again, the only reaction product evolving from the surface under any reaction condition was hydrogen, suggesting that the chloroform chemistry is characterized by the equation

$$3Fe + 2CHCl_3 \rightarrow 3FeCl_2 + 2C + H_2 \qquad (2)$$

The temperature-dependent data of Figure 5 have again been corrected for relative mass spectrometer sensitivities where eq 2 predicts the formation of 1 mol of hydrogen for each 2 mol of chloroform consumed. Clearly the experimental ratio is ~1:1, again reflecting the errors in measuring these quantities. Nevertheless, there is a clear decrease in chloroform signal which correlates well with a corresponding increase in hydrogen signal. The hydrogen flux is plotted versus $1/T$ in Figure 6 and yields an activation energy of 7.2 ± 0.5 kcal/mol. The corresponding Arrhenius plot using the chloroform consumption rate (Figure 7) yields an activation energy of 8.3 ± 0.9 kcal/mol. The hydrogen signal plotted as a function of chloroform pressure is plotted in logarithmic form in Figure 8 and reveals two different regimes above and below ~6 × 10^{-9} Torr (corresponding to a beam pressure of ~3 × 10^{-6} Torr). Below this pressure, the reaction order is 0.64 ± 0.04 and again implies a dissociative rate-limiting step and the rate is close to first order (0.98 ± 0.02) above this pressure.

The results of a surface analysis are displayed in Figure 9, again revealing the presence of iron, chlorine, and
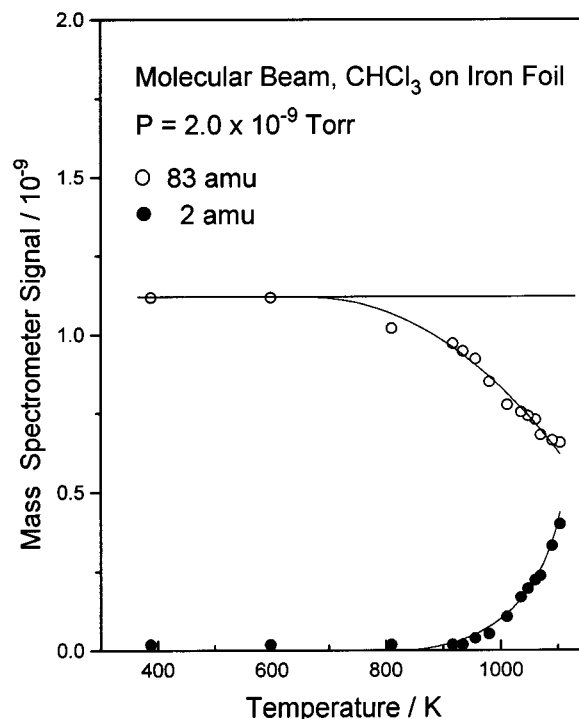
Figure 5. Plot of chloroform and hydrogen fluxes as a function of sample temperature for a dc effusive beam of chloroform ($p = 2.0 \times 10^{-9}$ Torr) incident on an initially clean iron foil.
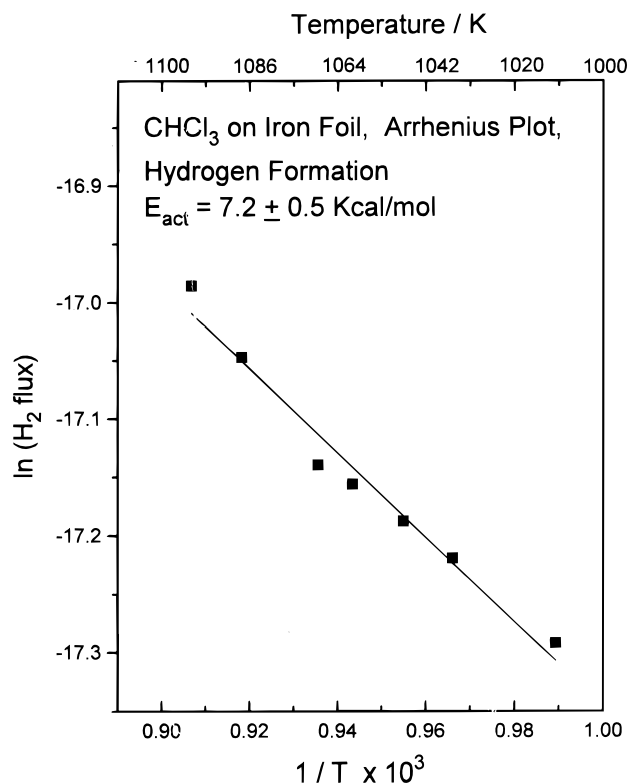
Figure 6. Arrhenius plot of ln(rate of hydrogen formation) versus $1/T$ for the reaction of chloroform with iron taken from the data of Figure 5.

carbon. The $Cl(180)/Fe(700)$ intensity ratio is 2.1 ± 0.6 and the $C(273)/Cl(180)$ ratio is 0.13 ± 0.01, slightly less than that for methylene chloride. A typical C KLL peak profile is also displayed as an inset in Figure 9 and reveals a mean peak at 276 eV kinetic energy with relatively large satellites at lower kinetic energy.
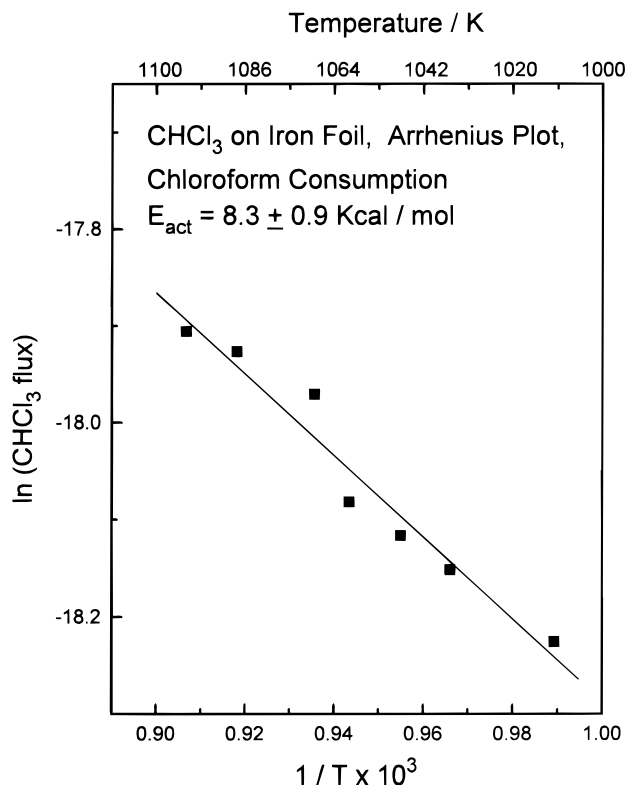
Figure 7. Arrhenius plot of ln(rate of consumption) versus $1/T$ for chloroform with iron taken from Figure 5.
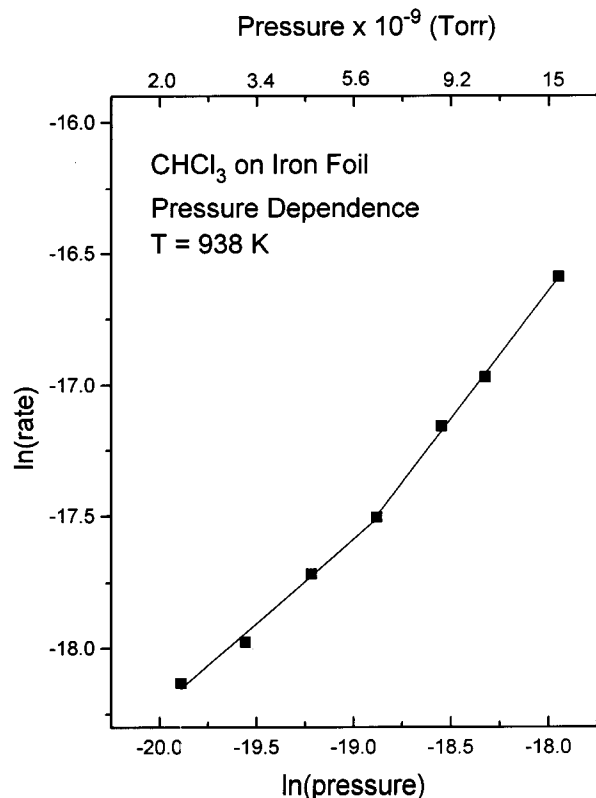

Figure 8. Plot of ln(rate of hydrogen formation) versus ln(pressure) where pressure is the chamber pressure due to chloroform leaked into the chamber via the effusive beam source and incident onto an initially clean iron foil heated to 940 K.

4. Discussion

A decrease of the hydrocarbon signal and an increase of the hydrogen signal are observed between 800 and 1100
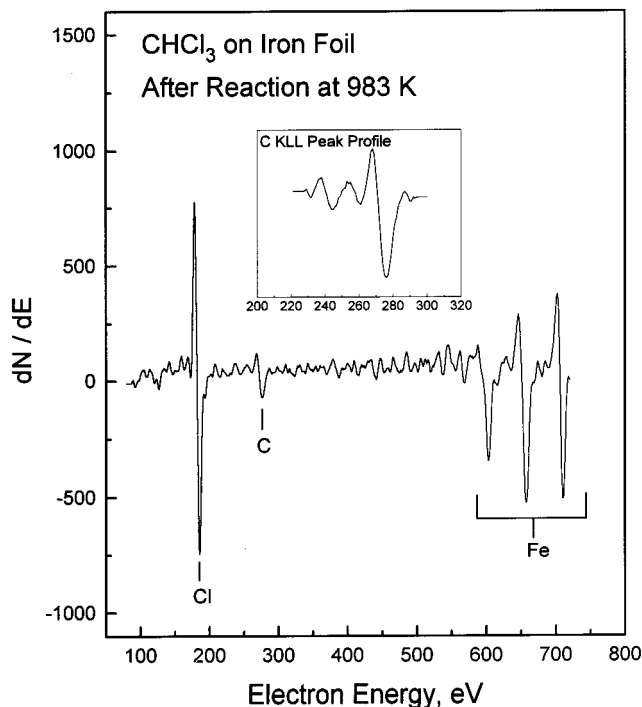

Figure 9. Typical Auger spectrum of an iron foil after reaction with chloroform at 983 K. Shown as an inset is the profile of the carbon KLL peak.

K (Figures 1 and 5). This suggests that both methylene chloride and chloroform completely thermally decompose on an initially clean iron surface to deposit a film consisting of iron chloride and carbon and evolve hydrogen into the gas phase. The measured products and the temperature range over which the chlorinated hydrocarbon signal decreases and the hydrogen signal increases in the data of Figures 1 and 5 suggest that both methylene chloride and chloroform completely thermally decompose on a initially clean iron surface to deposit a film consisting of iron chloride and carbon and to evolve hydrogen into the gas phase. The Cl/Fe Auger ratio for both films (Figure 9) after reaction with chlorinated hydrocarbons is 2.2 ± 0.6. Using the corresponding Auger sensitivity ratios[22] implies a Cl:Fe stoichiometry of 1.8 ± 0.5 corresponding to the formation of $FeCl_2$. Carbon is incorporated into the film, and careful measurement of the C KLL Auger line shape (Figure 9) indicates the presence of carbidic carbon.[25,26] The C:Cl Auger ratio is 0.18 ± 0.01 for methylene chloride and 0.13 ± 0.01 for chloroform. Note that, according to eqs 1 and 2, thermal decomposition of chloroform should only deposit 67% of the amount of carbon as methylene chloride and 67% of 0.18 is 0.12, in good agreement with the measured value of 0.13 measured above. The 1:1 stoichiometric ratio between $FeCl_2$ and C predicted by eq 1 should yield a C/Cl Auger ratio of 0.34,[22] a value much larger than that found experimentally. However, Raman analyses of films grown in a microbalance reveal the presence of small (~50 Å) carbon particles[10,11] which would yield a smaller carbon Auger signal. Note that the Auger line shape shows that the carbon is present as a carbide in accord with this model. It should also be mentioned that these are the thermodynamically predicted products over this temperature range.[12,23]

It should be emphasized that the same hydrogen flux is detected at a particular temperature and beam pressure

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independent of other parameters, for example, time, structure, or order in which experiments were carried out. In addition, the surface is oxidized rather rapidly and that the molecular beam surface chemistry proceeds, not on clean iron, but on the halide surface. The thickness of this layer is presumably changing during the course of the experiment, although this does not appear to affect the decomposition kinetics. In the microbalance experiment, a regime is attained when film growth ceases.[8-11] Film thicknesses under these conditions are approximately micrometers thick and are never attained under the ultrahigh vacuum conditions used here. The question still remains whether kinetics measured in ultrahigh vacuum mimic the initial growth rates at high pressure. Film growth kinetics have been used to quantitatively predict the extreme-pressure lubricant properties of methylene chloride as an EP additive.[12] This will be addressed below.

The initial growth rate activation energies have been measured for both methylene chloride and chloroform at high pressures.[8-11] The corresponding values measured using effusive molecular beam strategies agree very well for methylene chloride so that values of 9.5 ± 0.9 kcal/mol for the hydrogen formation and 9.8 ± 0.9 kcal/mol for the CH_2Cl_2 consumption are measured in ultrahigh vacuum compared with a microbalance value of 9.7 ± 0.9 kcal/mol. In the case of chloroform decomposition, the corresponding values in ultrahigh vacuum are 7.2 ± 0.5 kcal/mol for the hydrogen formation and 8.3 ± 0.9 kcal/mol for the $CHCl_3$ consumption. The microbalance value is 9.5 ± 1.3 kcal/mol, where now the agreement is less good. There is, however, a drastic change in activation energy for the initial growth rate for films grown from chloroform in the microbalance above and below 600 K where the value above $\sim$600 K is 9.5 ± 1.3 kcal/mol in relatively good agreement with the molecular beam results obtained here. The value at temperatures below 600 K appears to be much higher. Note that molecular beam data were collected above this temperature (Figures 5 and 6) since the product formation rate is too slow below this temperature to be measured accurately. The activation energy for initial high-pressure growth below 600 K is much larger, and it has been suggested that this transition is due to diffusion of carbon into the bulk of the sample.[27] Note that this has been shown to take place rapidly at this temperature.[28]

The growth rates due to methylene chloride decomposition measured in ultrahigh vacuum depend on the incident beam pressure (Figure 4). For pressures below 8.4×10^{-9} Torr these results show a half-order dependence and above this pressure the order is $\sim$0.8. Clearly the microbalance experiments were carried out above this pressure where the reaction order for CH_2Cl_2 is $\sim$1 so that the agreement is reasonable. Similarly, chloroform decomposes according to half-order kinetics below a pressure of 6×10^{-9} Torr, and the order above this pressure is 0.97. The corresponding order for the initial rate measured for chloroform in the microbalance is 0.88 ± 0.09, a value in good agreement with the molecular beam value. The half-order kinetics measured at low pressure suggest a dissociative mechanism under these reaction conditions whereas the rate-limiting step appears to convert to a first-order process at higher pressures. Clearly, for chlorinated hydrocarbon in the microbalance or when present as additives to lubricants, the latter, first-order kinetics regime will predominate.

5. Conclusions

The growth kinetics and the nature of the resulting surface formed in ultrahigh vacuum on an atomically clean iron surface mimic results found using the microbalance made higher pressures rather well. The microbalance kinetics have been used to model the chemistry involved in extreme pressure lubrication which suggests that such ultrahigh vacuum molecular beam experiments can also be used to mimic this chemistry. Measurement of gas-phase products and the nature of the surface indicates that both chlorinated hydrocarbons thermally decompose under EP conditions to deposit a film consisting of $FeCl_2$ and carbon and to evolve hydrogen into the gas phase.

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