

Structure and Growth Kinetics of Films Formed by the Thermal Decomposition of CCl₄ on Iron Surfaces

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Carbon tetrachloride thermally decomposes on iron in the temperature range 500–700 K to form films that consist predominantly of iron chloride. Two growth regimes are found: (1) parabolic, where the film thickness (X) varies as a function of time as $X^2 \sim t$ and where the growth rate is independent of pressure, and (2) a linear growth region ($X \sim t$), where the growth kinetics are first order in CCl₄ pressure. The kinetics are analyzed by a model which assumes that growth is controlled either by CCl₄ thermally decomposing at the growing gas–film interface or by diffusion through the film. Analysis of the experimental data gives an activation energy for diffusion of 21.5 ± 0.3 kcal/mol and an activation energy for CCl₄ decomposition of 18.3 ± 0.5 kcal/mol. In contrast to the behavior found for methylene chloride and chloroform, where small particles of carbon were identified in the film using Raman spectroscopy, no carbon particles are found in films formed from carbon tetrachloride decomposition below ~ 700 K although carbon is found in the film using X-ray photoelectron spectroscopy. XPS results also suggest that, in addition to completely thermally decomposing to yield carbon and chlorine, a small portion of the CCl₄ can react to form adsorbed CCl₂ species.

1. Introduction

Chlorinated hydrocarbons are used as additives in lubricants that operate when the loads between the contacting surfaces are extremely high, under so-called “extreme pressure” (EP) conditions.^{1–10} It has been shown that interfacial temperatures in excess of 1000 K can be attained under such conditions and that the chlorinated hydrocarbons thermally decompose on the surface to form a lubricating film.^{11–15} The film growth kinetics due to the thermal decomposition of both methylene chloride¹⁶ and chloroform¹⁷ have been measured, and these can be used to quantitatively rationalize their tribological behavior under extreme pressure conditions. In these cases, it has been demonstrated that a film is formed that consists of an iron halide (predominantly FeCl₂) which incorporates small carbon particles. Since FeCl₂ melts at ~ 950 K,¹⁸ these additives provide effective EP lubrication only up to applied loads that result in surface temperatures less

than this value.^{12–15} In contrast, when CCl₄ is used as an additive, surface temperatures are attained that significantly exceed the melting point of FeCl₂, suggesting that another, higher-melting-point interfacial material is deposited in this case.¹⁹ Mössbauer analysis of films deposited at above 1000 K reveals the formation of Fe₃C, and tribological experiments suggest that this indeed forms the antiseizure layer at high applied loads.¹⁹ At lower loads, FeCl₂ forms the antiseizure layer in a similar way as was found for methylene chloride and chloroform. However, preliminary experiments have shown that the film growth kinetics due to the thermal decomposition of CCl₄ are substantially more rapid than those due to either chloroform or methylene chloride.¹¹ The film growth kinetics from the decomposition of methylene chloride and chloroform are limited by the rate of thermal decomposition of the chlorinated hydrocarbon at the growing interface, and growth ceases after the deposition of a film of some finite thickness due to surface poisoning.^{16,17} We have therefore further investigated the kinetics and composition of films formed by the thermal decomposition of carbon tetrachloride under similar conditions. Analysis of the films using X-ray photoelectron and Raman spectroscopies reveals the formation of similar halide films by both methylene chloride and chloroform. The major differences are first that much less carbon is incorporated into films grown from CCl₄ and that XPS reveals the presence of organochlorine species on the surface. In addition, CCl₄ reacts significantly more rapidly than either methylene chloride or chloroform so that a regime is encountered where the film growth rate is limited by ion diffusion through the film, resulting in a classical parabolic growth law (where X , the film thickness, varies with time as $X^2 = At^{20-25}$). As the reactant pressure is lowered, this converts to a linear growth law ($X = At$), indicating that

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growth is now limited by thermal decomposition at the growing interface.²⁶⁻³¹

2. Experimental Section

The equipment that was used for these experiments has been described in detail elsewhere.¹²⁻¹⁵ The film growth kinetics were measured using a Cahn model 2000 microbalance by monitoring the change in mass of an iron foil in the presence of various pressures of CCl_4 as a function of time.¹³ The microbalance was enclosed in a shroud that was evacuated to $\sim 1 \times 10^{-7}$ Torr, and the sample was suspended from one arm of the balance and enclosed in a quartz tube which was inserted in a tube furnace. Temperatures were measured by means of a thermocouple placed in a well in the bottom of the quartz tube. Carbon tetrachloride was placed into a glass vial attached to the vacuum line, and the CCl_4 was purified by repeated freeze-pump-thaw cycles and was leaked into the system with the pressure being measured by means of a calibrated bellows manometer. The thickness of the iron foil was 0.1 mm, larger than that used for the CHCl_3 and CH_2Cl_2 experiments, since when thinner foils were used, growth ceased in many cases due to the complete consumption of the foil. Control experiments were carried out in which the sample was heated to 600 K in 700 Torr of hydrogen prior to measuring growth kinetics. It was found, however, that merely heating *in vacuo* rather than hydrogen yielded exactly identical growth kinetics in both cases. This behavior can be rationalized, since the native oxide layer is only ~ 40 Å thick³² whereas films grown by CCl_4 decomposition are $> 10^4$ Å thick. Note also that iron oxide is reduced at relatively low temperatures by CCl_4 .³³ Following reaction, the sample was removed from the microbalance and stored in an evacuated desiccator for subsequent Raman or XPS analysis.

Raman spectra were collected using a Spex double monochromator and the scattered photons detected using a Peltier-effect-cooled photomultiplier. Spectra were excited using 5145 Å light from an Argon ion laser which was backscattered from the film.

X-ray photoelectron spectra were collected on a VG Escalab spectrometer using $\text{Mg K}\alpha$ radiation (10 kV using 40 mA emission; total power 400 W), and the pass energy was set to yield an overall spectral resolution of 0.6 eV.

3. Results

Figure 1 displays growth kinetics (plotted as film thickness *versus* time (\square)) for a film deposited onto an iron foil by the thermal decomposition of 55 Torr of CCl_4 , as a function of reaction temperature where films several microns in thickness are formed. Shown also plotted are theoretical fits to these data (see below). Thicknesses are measured from the mass change as a function of time. This is simply converted into film thickness X , assuming that iron forms only FeCl_2 . This assumption is based on the observation that FeCl_2 is formed during tribological experiments¹¹⁻¹⁵ and is found on iron single-crystal surfaces following CCl_4 absorption in ultrahigh vacuum.³³⁻³⁶ Note that the formation of another chloride is found on $\text{Fe}(110)$ ³³ but with a much lower yield than that of FeCl_2 . This yields only approximate *absolute* values for the film thickness although the relative values are correct.¹³ Note that if these films, in fact, consisted

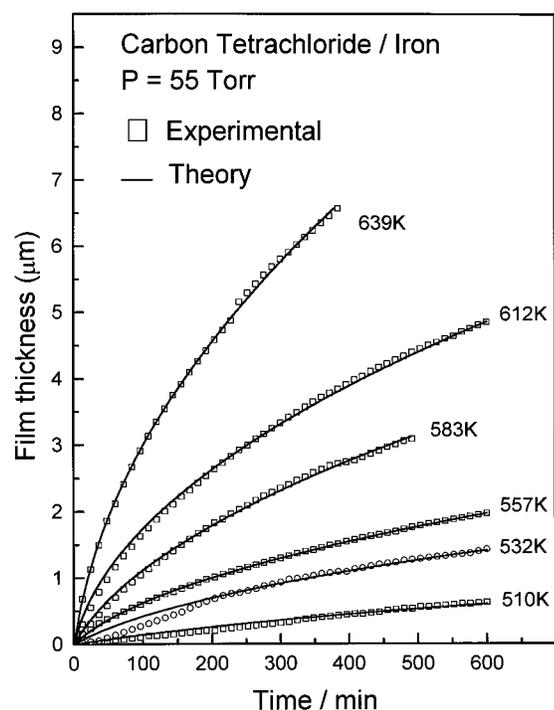


Figure 1. Plots of film thickness *versus* time (\square) for the thermal decomposition of 55 Torr of carbon tetrachloride on an iron foil measured using the microbalance as a function of sample temperature (see text). Reaction temperatures are marked adjacent to each of the curves. The solid lines on this curve represent theoretical fits to the data (see text).

of FeCl_3 , this would result in a constant relative error in the measurement of the film thickness of only 7%.

As expected, the film growth rate increases with reaction temperature. The shapes of the curves are, however, completely different from those found for films grown from both methylene chloride and chloroform, where an initial rapid growth was found in those cases but where growth ceased completely after some time.^{16,17} In the case of the carbon tetrachloride reaction, growth kinetics at high temperatures are parabolic. At lower temperatures, however, the growth rate becomes linear. The transformation between these two growth regimes will be discussed in greater detail below.

Figure 2 displays the pressure dependence of the growth kinetics, in this case, for reaction at 617 K (\square). Fits are shown to these data and will be discussed in greater detail below. Here a similar transition from parabolic to more linear growth is noted as the carbon tetrachloride pressure decreases so that, at the highest reaction pressures (> 8 Torr), the curve is essentially parabolic whereas, at the lowest pressures (1 Torr), growth is rather linear. The film growth rate increases with reactant pressure up to ~ 8 Torr but becomes essentially independent of reactant pressure above this value. That is, the reaction order varies from some positive value at low pressures and changes to a zero-order pressure dependence at higher pressures. Since pressures of ~ 2 Torr or less are relatively difficult to measure accurately using a bellows manometer, the pressure dependence of the reaction was measured using a lower reaction temperature of 540 K. The corresponding film growth kinetics are shown plotted as a function of reactant pressure in the range 10–30 Torr in Figure 3 and indicate that the growth rate increases with pressure over this range. Again fits are shown to the data (see below).

A typical Raman spectrum of a film deposited by the thermal decomposition of 55 Torr of CCl_4 at a temperature

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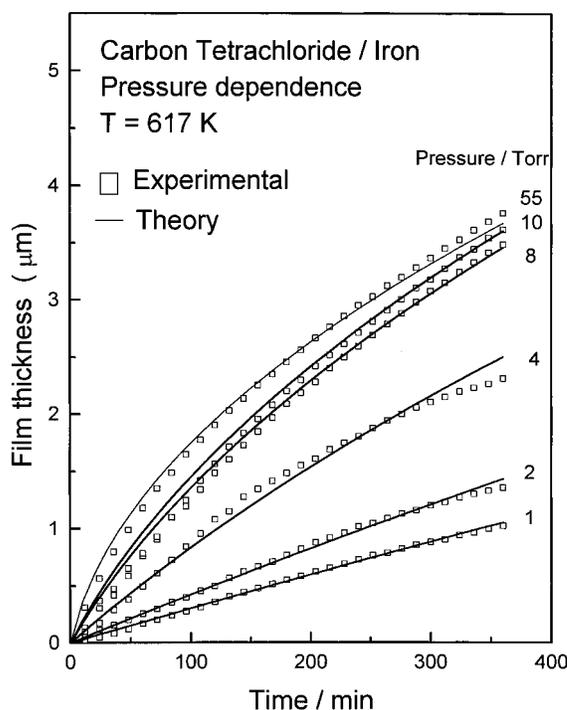


Figure 2. Plots of film thickness *versus* time for the thermal decomposition of carbon tetrachloride on an iron foil at 617 K measured using the microbalance as a function of reactant pressure (\square). The solid lines on this curve represent theoretical fits to the data (see text).

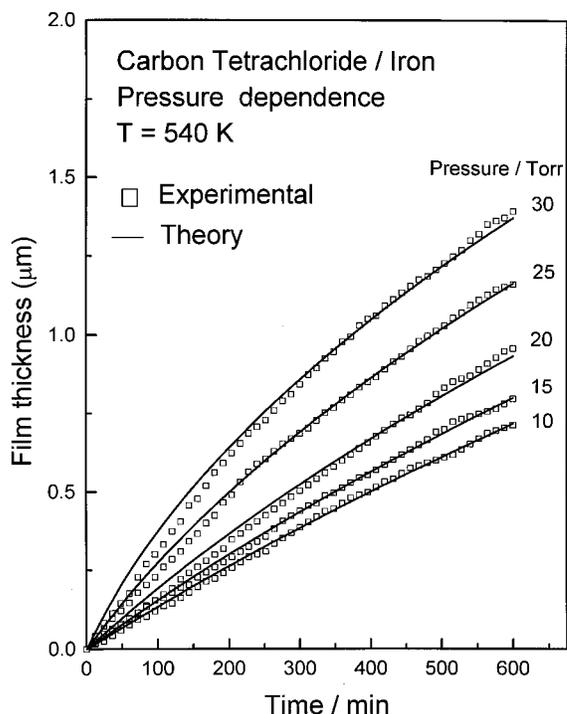


Figure 3. Plots of film thickness *versus* time for the thermal decomposition of carbon tetrachloride on an iron foil at 540 K measured using the microbalance as a function of reactant pressure (\square). The solid lines on this curve represent theoretical fits to the data (see text).

of 532 K is displayed in Figure 4. Shown for comparison is the Raman spectrum for a film deposited under similar conditions (15 Torr, 508 K) using CH_2Cl_2 . Both spectra show low-frequency modes (below 400 cm^{-1}) due to the lattice vibrations of an iron halide.^{37,38} Apparent in the spectrum of the film formed by methylene chloride decomposition are features at 1600 ± 10 and 1350 ± 10

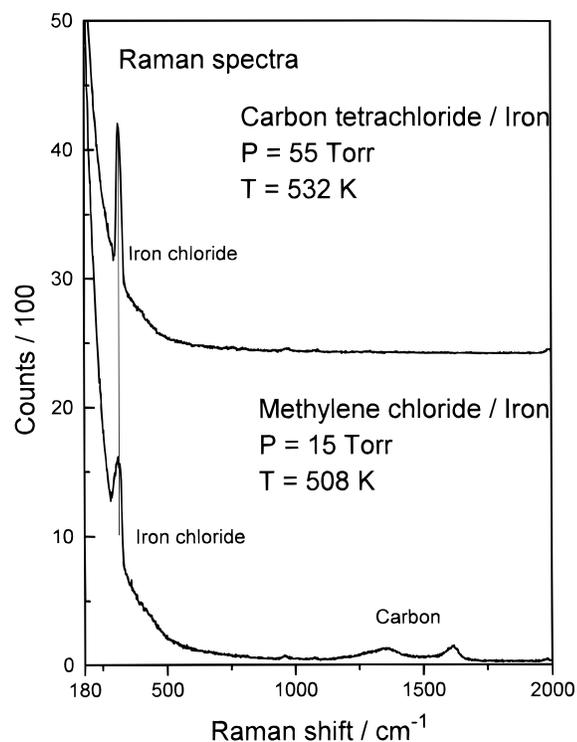


Figure 4. Raman spectra of films grown on an iron foil by the thermal decomposition of 55 Torr of CCl_4 at 532 K. Shown for comparison is the corresponding spectrum of films formed by the thermal decomposition of methylene chloride (15 Torr, 508 K).

cm^{-1} due to the presence of small carbonaceous particles which are incorporated into the film.^{39–41} These have been observed previously and are called g and d features respectively.^{16,39–41} This spectrum has been extensively studied, and it has been shown that the peak intensity ratio (of the 1600 and 1350 cm^{-1} modes, respectively) can be related to the diameter of the small carbonaceous particles.^{39–41} Analysis of the spectrum in Figure 4 suggests that the particles are approximately $50 \pm 20\text{ \AA}$ in diameter. These features are completely absent in the spectrum of the film grown from carbon tetrachloride, indicating the absence of small carbonaceous particles in the film in this case. Identical spectra (not shown) were obtained for films formed from CCl_4 at all reaction temperatures except the highest (712 K), where the presence of a small number of carbon particles was detected where the amount of carbon was about 20% of that found for films grown from methylene chloride.

Figure 5 displays X-ray photoelectron spectra of the films formed by carbon tetrachloride thermal decomposition on an iron foil with Fe 2p peaks evident at 710.8 ± 0.2 and $724.6 \pm 0.2\text{ eV}$; these binding energies correspond to Fe(II) or Fe(III) in the surface region of the film.⁴² A typical Cl 2p spectrum is also displayed in Figure 5 and shows a feature at $198.1 \pm 0.2\text{ eV}$ BE with a shoulder at

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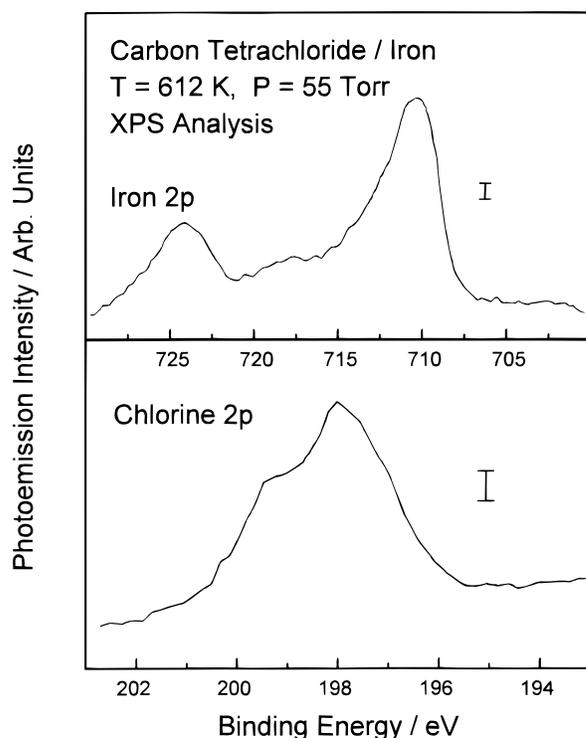


Figure 5. Cl 2p and Fe 2p X-ray photoelectron spectra of films grown on an iron foil by the thermal decomposition of 55 Torr of CCl_4 at 612 K. The vertical line adjacent to each spectrum corresponds to a count rate of 1 KHz.

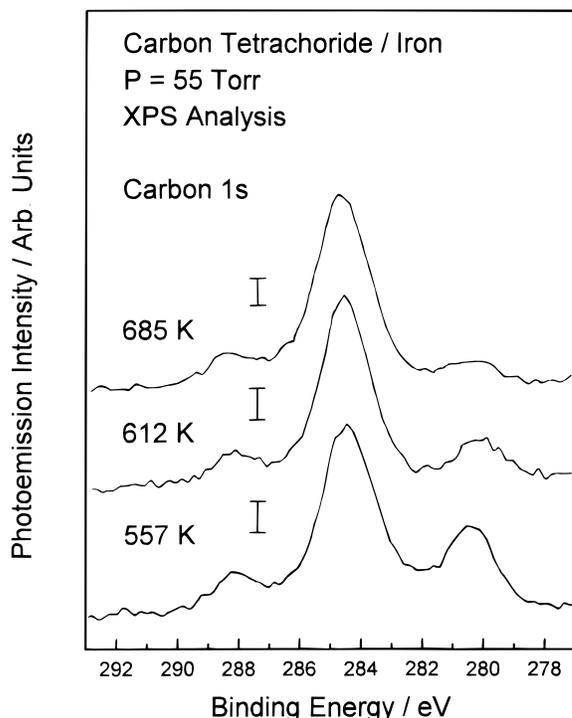


Figure 6. C 1s X-ray photoelectron spectra of films grown on an iron foil by the thermal decomposition of CCl_4 taken using 55 Torr at various temperatures. Reaction temperatures are marked adjacent to their corresponding spectra. The vertical line adjacent to each spectrum corresponds to a count rate of 1 KHz.

199.5 ± 0.2 eV corresponding to the spin-orbit-coupling split doublet of the chlorine 2p peak.^{43,44}

Typical C 1s spectra are displayed in Figure 6 for various deposition temperatures and do reveal the presence of carbon in the film. The C(1s)/Fe(2p) intensity ratio for

film growth at 612 K is 0.4×0.1 . Using standard X-ray photoelectron sensitivity factors⁴³ (0.25 for carbon and 2.0 for iron 2p_{3/2}), this yields an approximate C/Fe ratio for the film of 3 ± 2 . Spectra of films taken at other temperatures are essentially identical. However, the Raman data presented above indicate that it is not present as particles. These spectra have a relatively complex structure with a main peak centered at 284.6 ± 0.5 eV binding energy assigned to graphitic or polymeric carbon.^{42,44} Note that the spectra are normalized to the intensity of this feature with respect to the baseline at between 290 and 292 eV binding energy. Additional smaller features are evident at 288.1 ± 0.2 and 280.5 ± 0.2 eV binding energies, both of which decrease slightly in relative intensity with increasing deposition temperature. Note that the corresponding C 1s spectra of films deposited by the thermal decomposition of chloroform exhibit only a single C 1s peak at 284.6 eV.¹⁶

4. Discussion

Raman spectroscopy (Figure 4), which samples the whole of the film, indicates that an iron chloride film is deposited onto an iron foil by the thermal decomposition of carbon tetrachloride. This result is confirmed by the XPS data of Figure 5, which exhibit an Fe 2p_{3/2} feature at 710.8 ± 0.2 eV BE corresponding to the presence of Fe(II) or Fe(III)⁴² and a Cl 2p_{3/2} peak at 198.1 ± 0.2 eV BE which is due to Cl^- .^{43,44} In contrast to the behavior for reaction with methylene chloride and chloroform,^{16,17} no evidence for carbonaceous particles was found in the Raman spectra of these films except at the very highest reaction temperatures (Figure 4). However, the XPS data of Figure 6 indicate the presence of carbon in the surface region. The nature of these peaks will be discussed in greater detail below.

The growth kinetics for 55 Torr of carbon tetrachloride are displayed in Figure 1 as a function of temperature. Reaction at sufficiently high temperature (above ~ 580 K) appears to be parabolic, where the film thickness (X) varies as a function of time as X^2 .²⁰⁻²⁵ At lower temperatures, the reaction kinetics become more linear; here the film thickness (X) varies as a function of time as X . A similar trend is found as a function of CCl_4 pressure (Figures 2 and 3), where the reaction kinetics are parabolic at high pressures but revert to a linear growth dependence as the pressure is decreased.

It is clear therefore that, at sufficiently high reaction temperatures and pressures, film growth kinetics are parabolic. This situation has been described in terms of growth via ion diffusion through the film and of this diffusion being assisted by the electric field that is present because of the contact potential difference between the film and the substrate.²⁰⁻²⁵ The nature of the species diffusing through the chloride film, whether it is the chloride or the iron ions, is not known from our experiments, but this will not affect the final results of the analysis described below. Following Mott and Cabrera,²⁰ the diffusion flux (j_d) of ions through the film is given by

$$j_d = -2D_i(dn/dx) \quad (1)$$

where D_i is the ion diffusion coefficient through the film and dn/dx the corresponding concentration gradient. Since this gradient is uniform,²⁰ for a surface concentration of n_0 and a film thickness X , this simply yields

$$j_d = -2D_i n_0 / X \quad (2)$$

The compositional variation of a film grown by the thermal decomposition of chloroform has been measured by Auger

depth profiling and exhibits the linear concentration variation predicted by this model.¹⁷ Since j_d is proportional to the growth rate, this equation can be directly integrated to yield a parabolic growth law.²⁰ This theory implicitly assumes that the thermal decomposition rate of reactants at the interface is sufficiently large that the resulting growth kinetics are limited exclusively by transport through the film. However, kinetics measured at sufficiently low pressures and temperatures in this work (Figures 1–3) are linear, indicating that, under suitable conditions, this criterion is not always fulfilled. It is assumed therefore that carbon tetrachloride can react at the surface to form precursors to the formation of a film. The possible nature of the reactions at the surface will be discussed in greater detail below. A similar transition from linear to parabolic growth associated with either reaction- or diffusion-limited rates has been found for iron oxidation by mixtures of CO and CO₂.^{26–31} The nature of the surface reaction precursors arising from CCl₄ decomposition will be discussed in detail below. In this case, the reaction flux is taken to be⁴⁵

$$j_r = k_r P_r^n (1 - \Theta) \quad (3)$$

where k_r is a reaction rate constant, P_r is the reactant (in this case, CCl₄) pressure, and n is the order of the decomposition reaction. Θ is taken to be the coverage of decomposition products and assumes Langmuir adsorption kinetics and takes account of the fact that reaction will be inhibited by the presence of decomposition products on the surface. Note that Θ , the coverage, and n_0 , the concentration at the surface, are related. If the volume of film formed by the decomposition of a CCl₄ molecule is taken to be Ω and a monolayer of the film taken to have thickness l , where $\Omega = \beta$, then $\Theta = n_0/l$. It is assumed that the coverage Θ can adjust sufficiently rapidly as growth proceeds that equilibrium conditions are established.⁴⁵ In this case, $j_d = j_r$, so that combining eqs 1 and 2 yields

$$2D_i \Theta / X = k_r P_r^n (1 - \Theta) \quad (4)$$

and

$$j_d = -2D_i \Theta / X \quad (5)$$

The film growth rate dX/dt is related to the flux of ions through the films via $j_d = \Omega(dX/dt)$, and combining this with eqs 4 and 5 yields

$$\Omega(dX/dt) = (2D_i l \alpha / (1 + \alpha X)) \quad (6)$$

where $\alpha = k_r P_r^n / 2D_i l$. This can be solved straightforwardly to yield

$$X^2 + B(P_r, T)X - A(T)t = 0 \quad (7)$$

where $B = 4D_i l / (k_r P_r^n)$ and $A = 4D_i l / \Omega$. Thus, B is a function of reactant pressure and temperature whereas A is a function of temperature only.

In the limiting case that P_r , the CCl₄ pressure, is large, eq 7 simplifies to yield $X^2 = At = (4D_i l / \Omega)t$. This result is identical to that from Mott–Cabrera theory²⁰ and predicts a growth regime in which the film thickness varies parabolically with time and which also predicts a zero-order pressure dependence for the growth kinetics (Figure 2), as found experimentally. The constant in the growth kinetics is given by $4D_i l / \Omega$, where l and Ω are geometrical

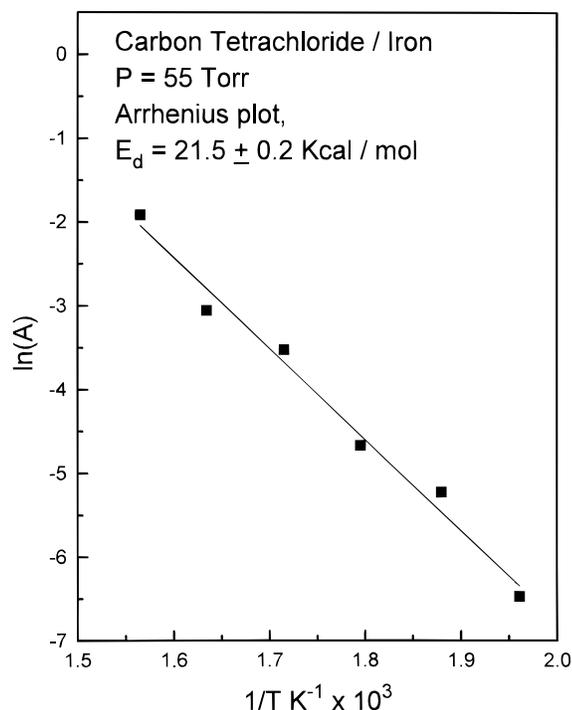


Figure 7. Arrhenius plot of $\ln(A)$ versus $1/T$ taken from the data shown in Figure 1. Measurement of the slope of the line yields an activation energy of 21.5 ± 0.2 kcal/mol.

constants and therefore not temperature dependent. D_i , the diffusion coefficient through the film, does however depend on temperature.

The term $B(P_r, T)$ becomes more important at lower pressures (assuming that n is positive), and in the limit that $P_r \rightarrow 0$, eq 7 reduces to $X = (A/B)t = (k_r P_r^n / \Omega)t$. Now growth depends only on the rate of reaction at the surface, yielding linear growth kinetics with a pressure-dependent rate. Equation 7 therefore reproduces the general features of the kinetic results. In order to establish whether the theory reproduces the experimental results quantitatively, eq 7 is fit to the experimental data in Figure 1 for the temperature dependence of the growth kinetics using a commercial nonlinear least squares program. Fits are shown as solid lines on the data, and clearly the agreement between experiment and theory is good. An Arrhenius plot for the constant $A(T)$ used for fitting the data, corresponding to the parabolic portion of the curve, is shown in Figure 7 and yields a good straight line. The temperature dependence of the constant $B(P_r, T)$, for the linear portion of the curve, is shown in Figure 8 and again yields a good straight line. According to the formulae given in eq 7, these depend on the activation energies for diffusion and thermal decomposition at the interface, since $B = 4D_i l / (k_r P_r^n)$ and $A = 4D_i l / \Omega$. Assuming that D_i is given by $D_i = D_i^0 \exp(-E_d/RT)$, the constant A is given by $A = (4D_i^0 l / \Omega) \exp(-E_d/RT)$ so that the Arrhenius plot in Figure 7 yields E_d directly as 21.5 ± 0.3 kcal/mol. Also assuming that the reaction rate constant k_i is given by $k_i = k_i^0 \exp(-E_k/RT)$, then the constant $B = 4D_i^0 l / (k_i^0 P_r^n) \exp(-(E_d - E_k)/RT)$ and the slope of the Arrhenius plot in Figure 8 corresponds to $(E_d - E_k) = 3.2 \pm 0.3$ kcal/mol. Since $E_d = 21.5 \pm 0.3$ kcal/mol, $E_k = 18.3 \pm 0.5$ kcal/mol and corresponds to the activation energy for thermal decomposition of CCl₄ at the growing iron chloride surface.

Equation 7 is also fit to the pressure-dependent film growth kinetics shown in Figures 2 and 3. In this case, the constant A is taken from the fit to the data in Figure 1 for the temperature dependence so that each of the curves is fit using only one adjustable parameter using the

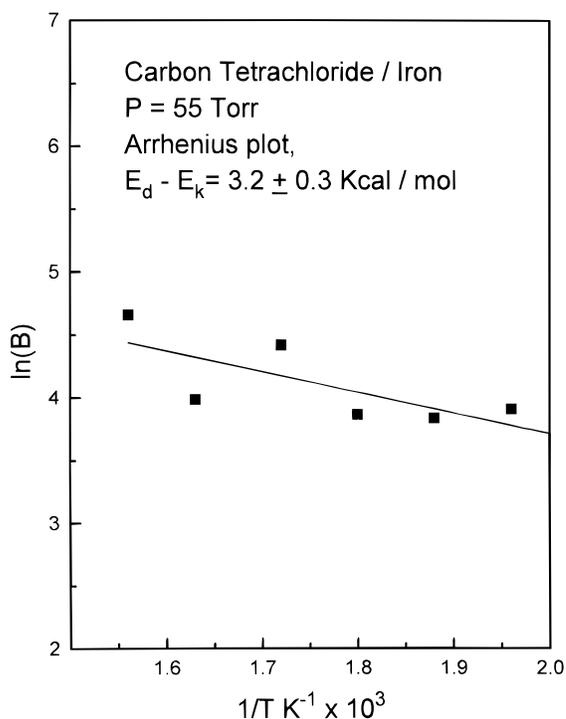


Figure 8. Arrhenius plot of $\ln(B)$ versus $1/T$ taken from the data shown in Figure 1. Measurement of the slope of the line yields an activation energy of 3.2 ± 0.3 kcal/mol.

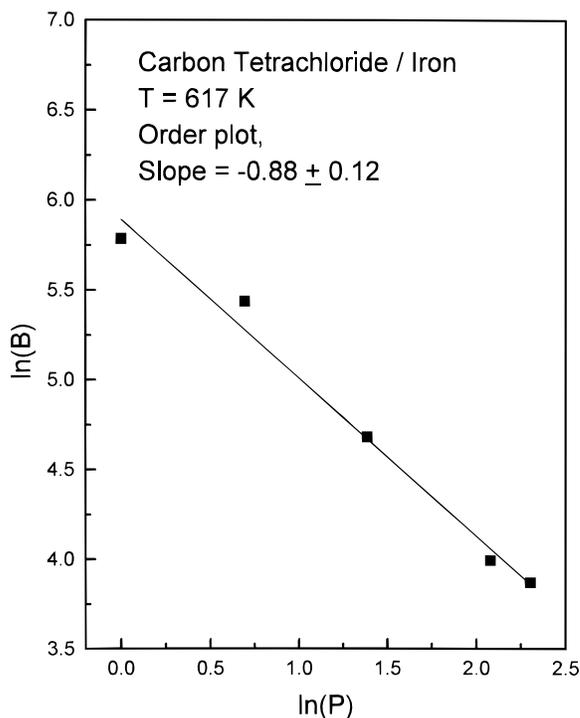


Figure 9. Plot of $\ln(B)$ versus $\ln(P)$, where P is CCl_4 pressure, illustrating the pressure dependence of the linear growth kinetics for reaction at 617 K.

nonlinear least-squares method described above. The resulting fits are also plotted onto the data in Figures 2 and 3, and again the agreement between experiment and theory is good. The resulting pressure dependence of the constant B is shown in Figure 9 for reaction at 617 K, where $\ln(B)$ is plotted versus $\ln(P)$, where P is the CCl_4 pressure. The slope of this curve is -0.88 ± 0.12 . Since $B = 4D_i/(k_r P_i^n)$, this indicates that $n \sim 1$ and that the thermal decomposition of CCl_4 at the growing iron chloride interface is first order in carbon tetrachloride pressure

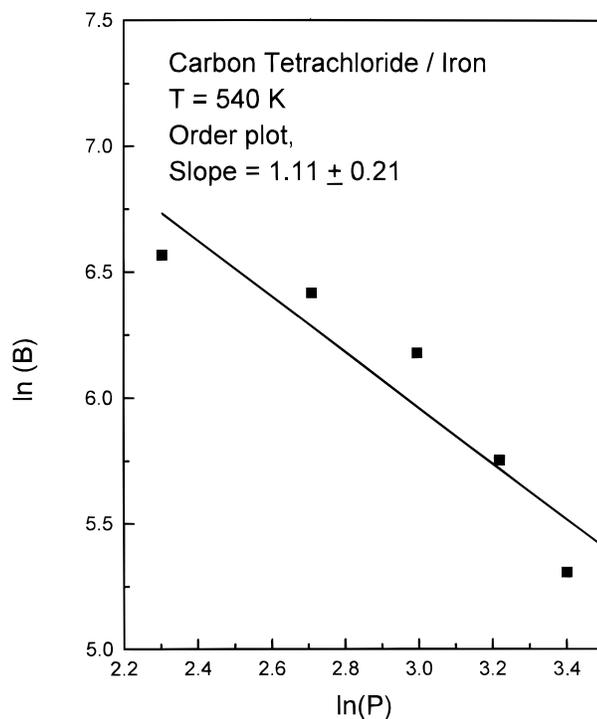


Figure 10. Plot of $\ln(B)$ versus $\ln(P)$, where P is CCl_4 pressure, illustrating the pressure dependence of the linear growth kinetics for reaction at 540 K.

for this reaction temperature. As noted above, pressures of ~ 1 Torr are difficult to measure using a bellows manometer, and a similar plot of $\ln(B)$ versus $\ln(P)$ for reaction at 540 K is shown in Figure 10. The slope of this curve is -1.11 ± 0.21 , again giving $n = 1$, indicating first-order decomposition of CCl_4 at the surface.

A significant amount of work has been carried out to examine the chemistry of chlorine and chlorinated hydrocarbons on atomically clean iron in ultrahigh vacuum. In common with most halogens on transition metal surfaces,⁴⁶⁻⁴⁹ chlorine adsorbs dissociatively, forming a chemisorbed overlayer which, at higher exposures, can lead to oxidation to form a halide.⁴⁹ Early studies of carbon tetrachloride adsorption on iron suggested that it completely thermally decomposed, yielding carbon and chlorine, the carbon diffusing into the bulk of the sample after heating to ~ 500 K.⁵⁰ More recent studies have shown the surface chemistry to be more complex.³⁴⁻³⁶ The major reaction pathway was also found in this case to be dissociative adsorption, forming atomic carbon and chlorine and the growth of FeCl_2 . A small proportion of CCl_2 species are also formed preferentially at defects on iron.^{35,36}

The composition of the much thicker films formed in this case is in accord with this chemistry, since the Raman spectrum displayed in Figure 4 for film growth at 532 K shows low-frequency modes (below 400 cm^{-1}) due to the lattice vibrations of an iron halide.^{37,38} Similar modes are observed for reaction of CH_2Cl_2 (Figure 4), and this result is in accord with the photoelectron spectral data of Figure 5. A striking difference between the spectrum for methylene chloride and that obtained for CCl_4 is the complete absence of modes due to the presence of carbonaceous particles in the Raman spectrum of the film although C 1s X-ray photoelectron data indicate the presence of

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carbonaceous deposits in the surface region of the film (C 1s peak at 284.6 ± 0.2 eV BE^{43,44}). This indicates that carbon is present in the film but does not agglomerate to form particles large enough to be detected by Raman spectroscopy. This effect may merely reflect the lower C/Cl stoichiometry in CCl_4 than that in either CHCl_3 or CH_2Cl_2 .

Note also that the C 1s photoelectron spectrum displays an additional peak at 288.1 ± 0.2 eV. A C–Cl group shifts the C 1s binding energy to ~ 286.0 eV, and CCl_4 moves it to ~ 292.2 eV,⁴⁴ resulting in a chemical shift of approximately 1.8 ± 0.1 eV/chlorine. It has also been suggested previously, from a systematic study of chlorinated hydrocarbons, that a chlorine attached to a carbon atom gives a C 1s chemical shift of ~ 1.5 eV/Cl^{51,52} so that the peak centered at 288.1 ± 0.2 eV binding energy (Figure 6) is consistent with the presence of CCl_2 species on the surface. Note that plasmon features have been associated with carbonaceous species but are generally shifted 6–7 eV from the main C 1s feature.⁴⁴ As noted above, a precedent for this chemistry exists, since the formation and desorption of stable CCl_2 species has been found for CCl_4 on clean iron surfaces.^{35,36} This suggests that a portion of the carbon tetrachloride may decompose at the surface of the growing iron halide film to yield CCl_2 species, giving rise to the 288.1 ± 0.2 eV peak. Note that the intensity of this peak is substantially smaller than that of the 284.6 eV feature, suggesting that the majority of the carbon tetrachloride completely decomposes to yield carbon and chlorine. Since X-ray photoelectron spectroscopy probes only the outermost layers of the film, the presence of this species can only be confirmed in this region. In contrast, Raman spectroscopy is not surface sensitive and samples the whole film. There is no evidence in the spectra shown in Figure 4 for C–Cl stretching modes that would appear at between 710 and 790 cm^{-1} , suggesting that any CCl_2 species are confined to the surface region.¹⁸ The atomic chlorine is presumably responsible for oxidizing the iron to form the chloride.

The exact nature of the species giving rise to the feature centered at 280.5 ± 0.2 eV is unknown. Such a lower binding energy state suggests the formation of a carbide. However, the formation of Fe_5C_3 has been observed at

~ 283.2 eV⁵³ and would be evident as a shoulder on the main 284.6 eV feature.

Note, in addition, in contrast to the behavior found for both CH_2Cl_2 and CHCl_3 , there is no evidence for the linear reaction rate saturating due to surface poisoning, as was found in both those cases.^{16,17} The fact that film growth is limited by diffusion through the film rather than surface reaction indicates that films grow much more rapidly from CCl_4 than other chlorinated hydrocarbons, and direct comparisons of the growth rates for each of these compounds confirms this. The nature of the film found following CCl_4 reaction (an iron chloride + C) is identical to those formed from both methylene chloride and chloroform under similar conditions. This result is in accord with tribological measurements which show that indeed an iron halide initially forms the antiseizure film at low applied loads (and therefore interfacial temperatures).^{11–15} The origin of the higher resistance to seizure when carbon tetrachloride is used as an additive lies in the fact that it can form an iron carbide as the applied load (and interfacial temperature) increases.¹⁹ The tendency of carbon tetrachloride to form a carbide film more easily than the other additives may be related to the faster film growth rates found from the reaction of CCl_4 than those for the other chlorinated hydrocarbons.

5. Conclusions

Films consisting of iron chloride with some carbon present are formed by the thermal decomposition of CCl_4 on iron. The growth rate is parabolic at high pressures and displays a zero-order pressure dependence, and an analysis of the growth kinetics using classical Mott–Cabrera theory shows that the activation energy for ion diffusion through the film is 21.5 ± 0.3 kcal/mol. The activation energy for thermal decomposition of the CCl_4 at the growing interface is about 18.3 kcal/mol. The growth rate becomes decomposition rate limited at lower pressures, and the rate of thermal decomposition at the growing interface is measured to be first order in CCl_4 pressure. Possible CCl_2 species are identified at the growing interface due to CCl_4 decomposition.

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