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Understanding the tribological chemistry of chlorine-, sulfur- and phosphorus-containing additives[☆]

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Abstract

It is demonstrated that the surface chemistry of simple-model extreme-pressure lubricant additives, measured in ultrahigh vacuum, corresponds to that measured at higher pressures, where film growth rates are monitored using a microbalance. This chemistry and reaction kinetics are used to explain the extreme-pressure lubrication behavior by successfully modeling the measured seizure load vs. additive concentration curves. It is also demonstrated, by growing ferrous chloride films on iron substrates in ultrahigh vacuum, that these have the same friction coefficients as those found for model extreme-pressure lubricants. It is found that a monolayer of a solid boundary lubricant film is sufficient to lower the interfacial friction coefficient to its minimum value. These results demonstrate that the chemistry measured under conditions of thermodynamic equilibrium at some temperature can be successfully applied to the formation of a boundary film, in the extreme-pressure regime.

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1. Introduction

The goal of understanding boundary-layer lubrication, in which lubricant components (additives) decompose to form an anti-wear or anti-seizure film, is extremely challenging for a number of reasons. First, since reaction occurs at a moving solid–solid interface, it is extremely difficult to monitor this interface in situ and information concerning the surface chemical processes that lead to tribofilms must be inferred from post-mortem analyses or modeling. Second, even the apparently smoothest contacting surfaces are rough at some length scale. This leads to large localized energy dissipations as the asperities of the rough surfaces pass over each other. This is often described by a “flash temperature” to characterize the energy density during this process [1]. However, since these processes are unlikely to be in thermodynamic equilibrium, it is, in

general, difficult to relate chemistry occurring at the tribological interface at such “flash temperatures” to potentially analogous thermal chemistry. Third, the surfaces in most macroscopic tribological experiments are rather ill defined since they are covered by oxides and other contaminants and, further, since the structure of these surfaces is likely to be altered by the rubbing action itself, this makes any effort to relate the surface chemistry at the tribological interface to that occurring on model systems extremely difficult.

These problems may be mitigated in the extreme-pressure regime for the following reasons. First, under extreme-pressure conditions, the asperity–asperity contacts occur sufficiently rapidly that a stochastic average over such rapidly occurring “flash temperatures” may once again lead to a meaningful thermodynamic definition of temperature. This, of course, does not solve the problem of measuring such (potentially very high) temperatures at the buried interface, but it is likely that such a temperature may correspond reasonably to a correct thermodynamic definition of temperature. Second, wear rates are generally high under extreme-pressure conditions so that any surface

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contaminants will be rapidly worn away, and the high interfacial temperatures might also serve to anneal out surface defects. Finally, the additives used for extreme-pressure applications, generally chlorine-, sulfur- and phosphorus-containing molecules, are relatively simple and lend themselves to a detailed exploration of their surface chemistry [2,3].

In order to explore whether the surface chemistry occurring thermally is indeed applicable to the tribological interface, the chemistry of model extreme-pressure additives is first investigated in detail in ultrahigh vacuum. This chemistry is then related to that found in tribological experiments by measuring the seizure load when using a model lubricant with a commercial pin and v-block apparatus. It is shown in the following that the chemistry measured in ultrahigh vacuum is directly applicable to that found during extreme-pressure lubrication. From a practical point of view, this allows a link to be made directly between the thermal reaction and the tribological chemistry of the additive; they appear to be identical under extreme-pressure conditions. It should be emphasized that this may not necessarily be true under less severe boundary conditions, but does provide a starting point for investigating less severe boundary lubrication regimes. It is thus possible, in the case of extreme-pressure lubrication, to predict the nature of the film that is formed from a particular additive chemistry. That link having been made, preliminary data are presented to investigate the film properties that are required to provide low friction by measuring the properties of well-characterized tribological films grown in ultrahigh vacuum.

2. Experimental

Surface chemistry experiments were carried out in stainless-steel, ultrahigh-vacuum chambers operating at base pressures of 5×10^{-10} Torr following bakeout [4]. The tribology chamber is equipped with an ultrahigh-vacuum-compatible tribometer, which simultaneously measures normal forces, lateral forces and the contact resistance between a moving tribotip and a stationary metal foil substrate. All tribological measurements were made using a single pass on a freshly prepared surface and the tribopin was heated by electron bombardment in vacuo prior to each experiment to clean it. The chamber also contained a single-pass, cylindrical-mirror analyzer for Auger analysis of the surface, a quartz crystal microbalance for measuring the thickness of the evaporated films, an argon ion bombardment source for sample cleaning, and an evaporation source for deposition of inorganic materials [5]. The clean metal foil samples were mounted onto a steel plate (1.0 mm thick) to provide a rigid base for the tribological measurements. The samples could be resistively heated and cleaned using ion bombardment to remove any impurities (primarily carbon, chlorine and sulfur) and the sample cleanliness was monitored using Auger spectroscopy. All experiments were carried out for atomically clean surfaces.

The tribopin (12.7 mm diameter) was made from tungsten carbide containing some cobalt binder. This was cleaned by electron-beam heating via a retractable filament that could be placed in front of the pin. An Auger analysis of the pin following this treatment was in accord with the bulk structure. Measurement of the pin topology using AFM showed that it was substantially rougher than the iron substrate with an approximately Gaussian height distribution having a width at half height of ~ 2000 Å [4].

3. Results and discussion

3.1. Surface chemistry of lubricant additives measured in ultrahigh vacuum

The reactive properties of simple chlorinated hydrocarbons were measured using molecular beam methods in ultrahigh vacuum [6–9]. This experiment was carried out by placing a capillary dosing source in front of a clean iron sample to allow a beam of the reactant to impinge onto the surface. The reflected flux was monitored as a function of sample temperature using a quadrupole mass spectrometer in order to measure reaction activation energies and gas-phase products. The resulting surfaces were also analyzed using Auger or X-ray photoelectron spectroscopy. Typical results for the reaction of methylene chloride with clean

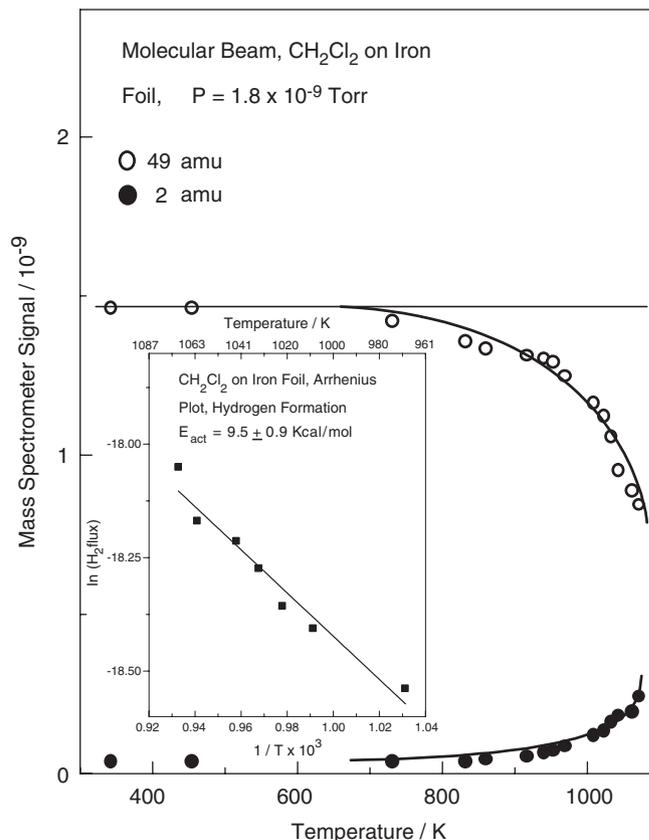


Fig. 1. Plot of the reflected 49 (methylene chloride) and 2 (hydrogen) amu signals for a beam of methylene chloride incident onto a clean iron surface in ultrahigh vacuum. The inset is an Arrhenius plot taken from these data.

iron are shown in Fig. 1. The decrease in 49 amu signal (due to methylene chloride) with temperature indicates reaction with the surface, and the concomitant increase in 2 amu (hydrogen) signal indicates that only hydrogen gas is formed. Similar results for other chlorinated hydrocarbons showed that CH_2Cl_2 , CHCl_3 and CCl_4 completely thermally decomposed at the surface to deposit carbon, form FeCl_2 and evolve hydrogen (except for CCl_4). An Arrhenius plot taken from the CH_2Cl_2 data is shown as an inset and reveals that the reaction activation energy is 9.5 ± 0.9 kcal/mol [6].

Model sulfur-containing additives, dimethyl and diethyl disulfide, were examined using a similar strategy where reaction proceeds by the initial formation of methyl and ethyl thiolate species, respectively, and the results are displayed in Fig. 2 [9]. The methyl thiolate species decompose to yield gas-phase methane and deposit sulfur and carbon on the surface, while the ethyl thiolate primarily undergoes β -hydride elimination to evolve ethylene, so that the surface chemistry is initiated in either case by sulfur–sulfur bond cleavage. A depth profile of the resulting films (Fig. 2(c)) shows that, following reaction on clean iron at >1000 K, the sulfur (in the form of ferrous sulfide) is located predominantly at the surface, while the carbon diffuses rapidly into the bulk of the sample. In this case, the Auger line shape demonstrates that the carbon is carbidic [9].

The surface chemistry of more complex lubricant additives, such as phosphate or phosphite esters, was examined on an Fe_3O_4 surface using temperature-programmed desorption (TPD) and surface spectroscopies [10,11]. The TPD experiment consists of adsorbing the reactant onto the surface at low temperatures and heating the sample such that its temperature varies linearly with time. The resulting gas-phase reaction products are monitored mass spectroscopically, enabling the surface reaction pathways to be identified in detail. Typical desorption traces are shown in Fig. 3, where molecular tributyl phosphate desorbs at ~ 450 K (Fig. 3(a)). These data can be analyzed to estimate the heat of adsorption of tributyl phosphate on the oxide surface [12], yielding a value of ~ 120 kJ/mol. The major desorption products, however, are butanal (Fig. 3(b)) and 1-butanol (Fig. 3(c)), which desorb at ~ 600 K. These species arise due to scission of the P–O bond, thereby forming surface butoxy species. A portion of these decomposes by a β -hydride elimination reaction, yielding butanal (Fig. 3(b)), where the hydrogen reacts with remaining butoxy species to yield 1-butanol (Fig. 3(c)). This indicates that alkoxy overlayers are extremely thermally stable on the oxide surface. The surface chemistry of tributyl phosphate on an Fe_3O_4 surface is summarized in Fig. 4. Analysis of the nature of the surface following reaction also reveals that the phosphorus diffuses rapidly into the oxide, while the carbon is located preferentially at the surface (Fig. 3(d)). This is in complete contrast to the behavior found on metal surfaces, where carbon diffuses rapidly into the iron, while

the chlorine or sulfur is preferentially located at the surface (see Fig. 2(c)).

3.2. Reactions of model additives at higher pressures: relationship to tribological properties

Since the chemistry in the previous section was explored under ultrahigh-vacuum conditions to allow the reaction intermediates and pathways to be followed in detail, it is first necessary to investigate whether similar reactions occur at higher pressures. This is illustrated in the following using methylene chloride as an example. In this case, the rate of film growth by reaction between iron and methylene chloride is investigated using a microbalance, which continually measures the change in mass of an iron foil [13–17]. As a film is formed on the surface, the mass of the foil changes, where the mass change is directly proportional to the thickness of the film. Since the apparatus can be pressurized to several Torr of reactant, this allows film growth kinetics to be monitored at higher pressures than in ultrahigh vacuum. These experiments reveal that films are formed on the surface and that the initial activation energy for film growth is ~ 10 kcal/mol, identical to that found in ultrahigh vacuum (see Fig. 1). The nature of the resulting film can be analyzed using various techniques, which reveal the formation of ferrous chloride, as found in ultrahigh vacuum. Raman spectroscopy [17] provides additional information on the nature of the carbon that is incorporated into the ferrous chloride film and shows that it is present as small (~ 50 Å diameter) particles. Some carbon also diffuses into the iron.

Next, the tribological properties of a model lubricant, consisting of the additive dissolved in a poly α -olefin selected to have physical properties similar to those of commercial base oils, were measured. These were investigated using a pin and v-block apparatus where both the seizure load and friction coefficient were monitored. The friction coefficient remained constant at ~ 0.08 until seizure. As expected, the seizure load increased with additive concentration and reached a plateau after the addition of ~ 1.5 wt% of chlorine from methylene chloride (Fig. 5, ●). A similar behavior was found for chloroform, whereas carbon tetrachloride showed extremely good anti-seizure behavior and showed no sign of reaching a plateau [18,19].

Since the reactive formation of ferrous chloride was found from the surface analysis experiments described above, it was postulated that a low-friction ferrous chloride film acted to prevent seizure, and the reasonable assumption was made that seizure would occur when a condition had been reached at which this film was removed, leading to metal–metal contact. It was further assumed that the net film thickness during a tribological experiment arose from a balance between the rate of reactive film formation with methylene chloride, and the rate at which the film was worn from the surface. Thus, the thickness of the ferrous chloride film varies during the experiments, but is proposed

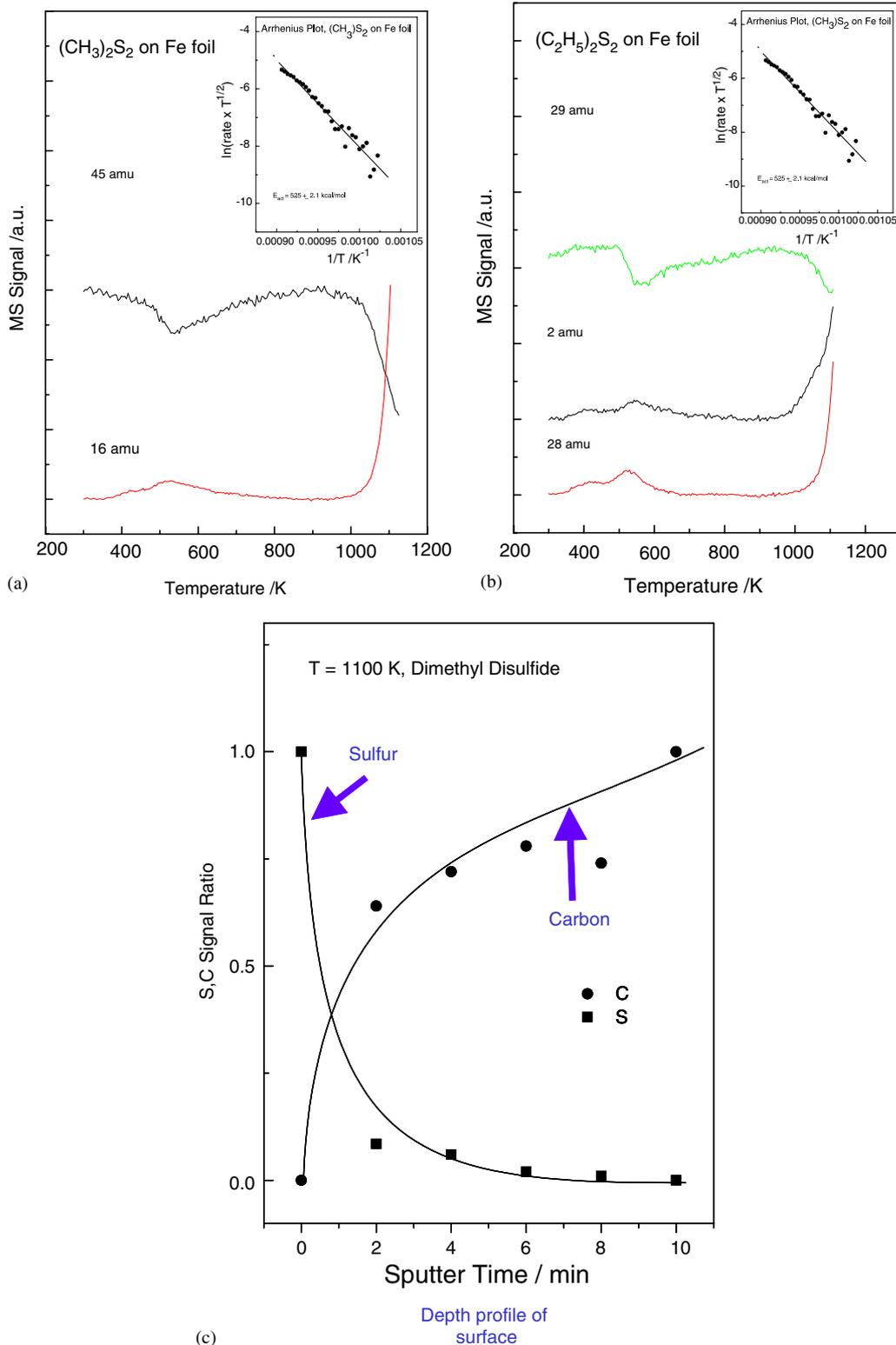


Fig. 2. Molecular beam data for (a) dimethyl disulfide and (b) diethyl disulfide reacting with clean iron. (c) The resulting depth profile measured by removing material using argon ion bombardment.

to decrease to zero when seizure occurred. In order to properly implement such a model, it was necessary to be able to measure the temperature at the interface between the pin and the v-block. In order to carry out this

measurement, the wear rates of known materials were measured as a function of applied load [20]. As expected, it was found that the wear rate was linear with applied load for low loads, but increased drastically at somewhat higher

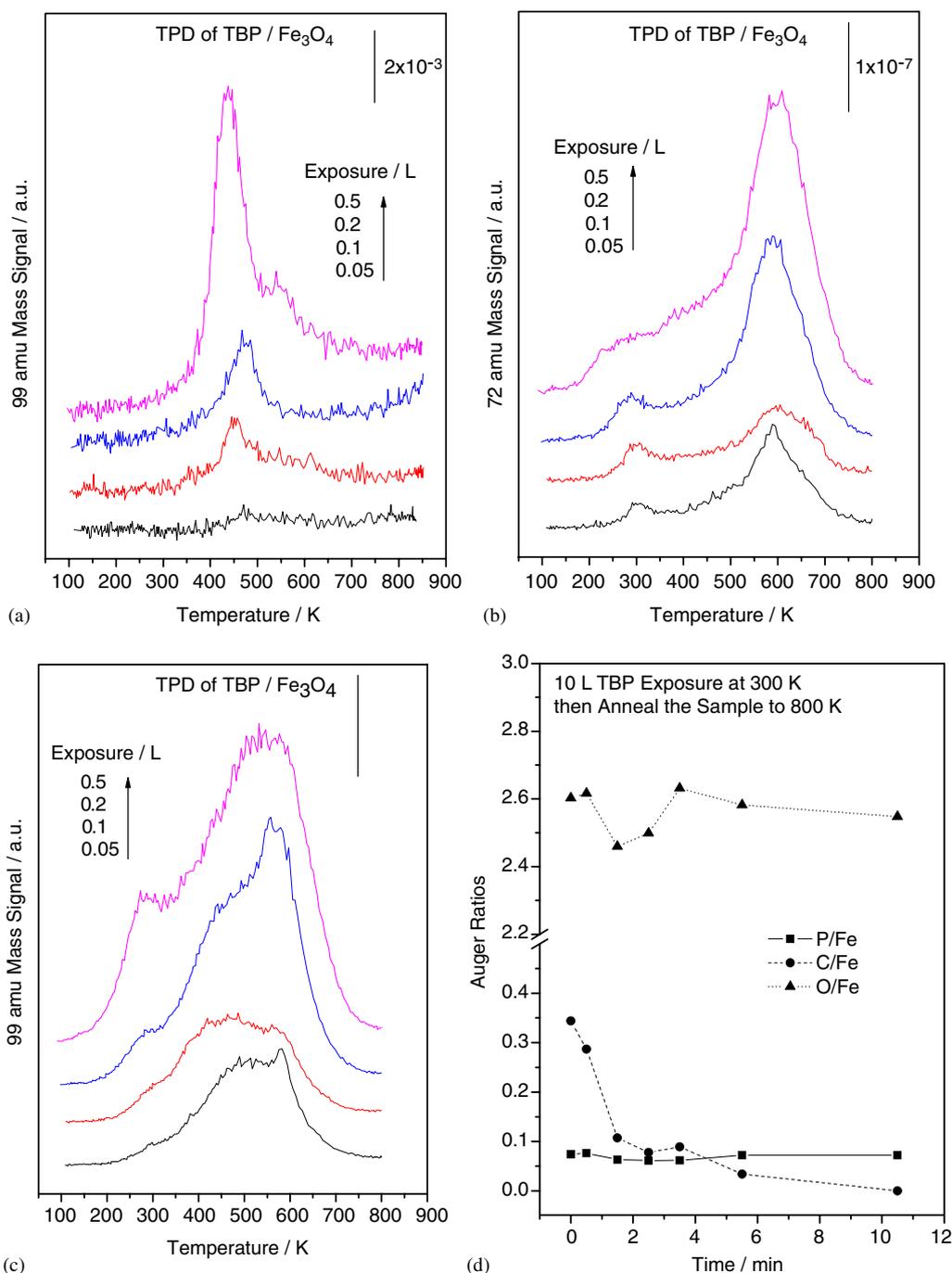


Fig. 3. TPD spectra collected following various exposures of tributyl phosphate on an Fe_3O_4 surface monitoring (a) 99 amu (tributyl phosphate), (b) 72 amu (butanal) and (c) 31 amu (1-butanol). (d) The resulting depth profile measured by removing material using argon ion bombardment. Tributyl phosphate exposures are marked on each figure.

loads, eventually reaching extremely large values. Such asymptotes in the wear rate were associated with the material at the interface reaching its melting point, thereby forming a liquid layer that is removed extremely rapidly [21]. A calibration curve of interfacial temperature could then be obtained by using a range of materials with different melting points. This calibration, combined with the kinetic data for the rate of film growth, allowed the thickness of the film during pin and v-block experiments to

be calculated. As proposed above, the load at which the film thickness became zero was taken to be the seizure load. The resulting calculated values of seizure load are plotted as a solid line on the data of Fig. 5 and are in excellent agreement with the experimentally measured values (●). This indicates that, at least under extreme-pressure conditions, the rates of surface chemical reactions measured under ultrahigh vacuum, or at higher pressures using a microbalance, are very similar to those occurring under

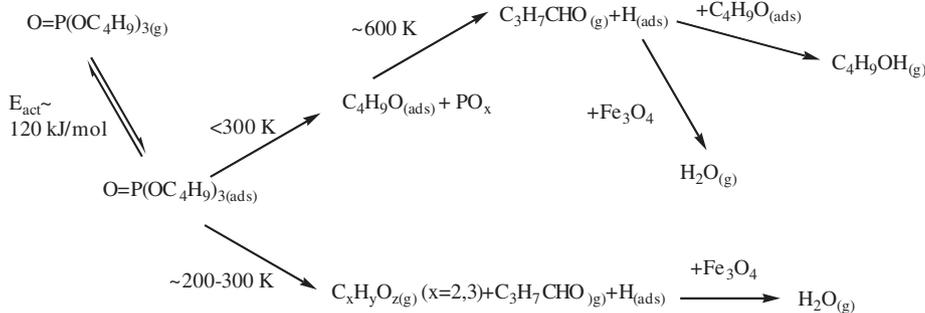


Fig. 4. Proposed reaction pathway for tributyl phosphate on Fe_3O_4 .

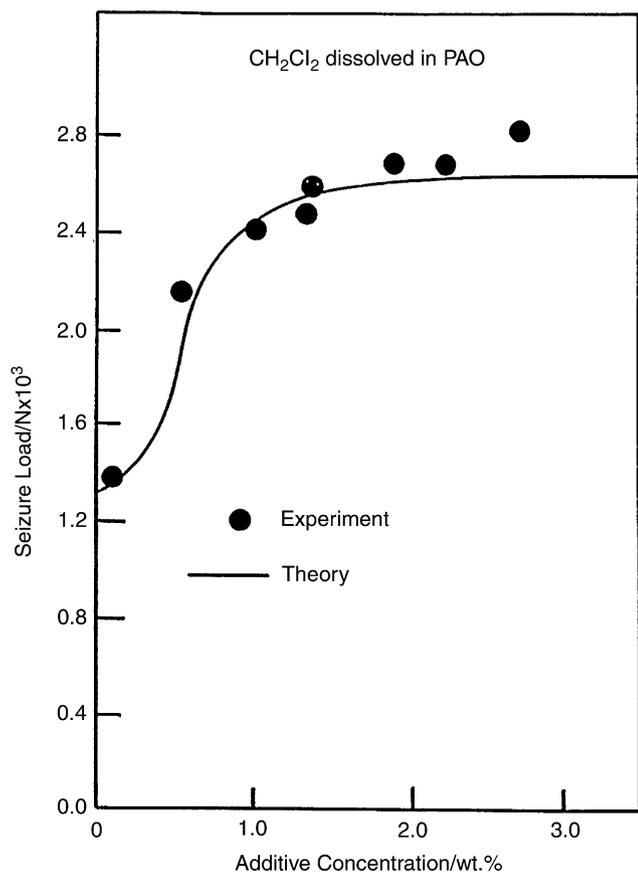


Fig. 5. Experimental values of seizure load vs. additive concentration (●) for methylene chloride dissolved in PAO. The solid line is a theoretical fit to these data (see text).

tribological conditions in the pin and v-block apparatus. It should be emphasized that this correspondence need not necessarily be true under all boundary lubrication conditions for the reasons delineated above.

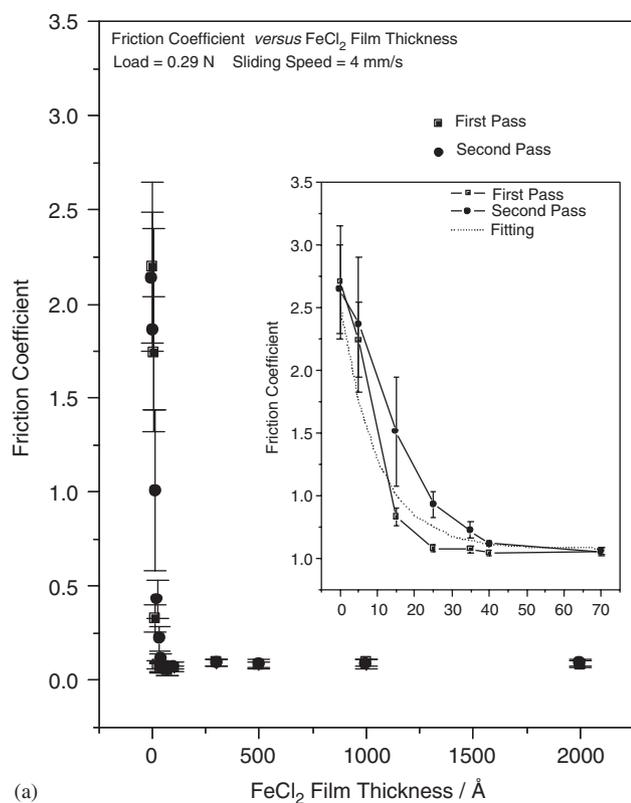
An explanation for the presence of the plateau in the plot of seizure load vs. additive concentration noted in Fig. 5 arises naturally from this model. As the additive concentration increases, the rate of film formation increases, initially leading to higher seizure loads. However, at higher concentrations, a point is reached where the interface

temperature reaches the melting point of the film material. In the case of methylene chloride (Fig. 5), the interfacial temperature at $\sim 2.6\text{ kN}$ is $\sim 960\text{ K}$, approximately the melting point of ferrous chloride. Thus, the wear rate of the film becomes exceedingly high, such that forming it more quickly by the addition of more chlorinated hydrocarbon has no beneficial effect.

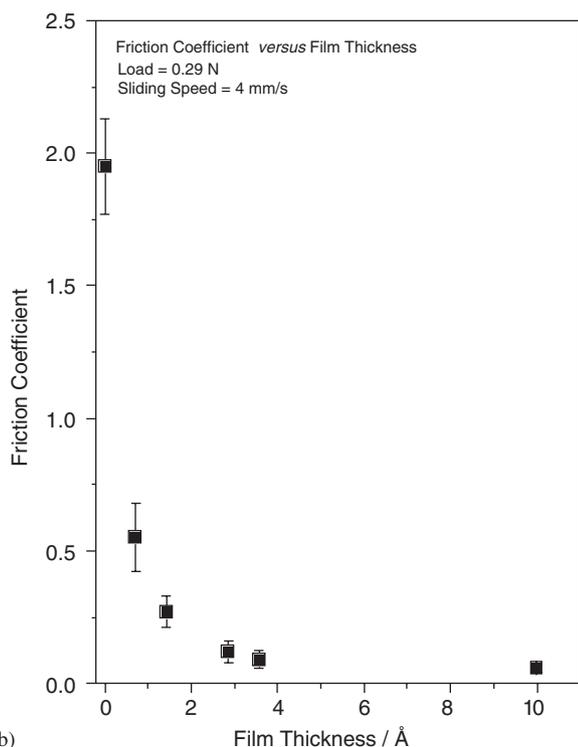
3.3. Measurement of tribological properties of lubricant films in ultrahigh vacuum

The results presented above indicate that the chemistry measured in ultrahigh vacuum, and at higher pressures in the microbalance, can be used to understand the tribological behavior in the extreme-pressure regime. Experiments were then carried out, first, to measure the tribological properties of ferrous chloride films formed in an ultrahigh vacuum and, second, to understand what film thicknesses are required to form a friction-reducing, anti-seizure film [22]. Note that the fact that the model outlined above assumes that the film thickness becomes zero before seizure occurs implies that a very thin film of material should be effective at reducing friction.

In order to address the first question, ferrous chloride was evaporated onto clean iron in ultrahigh vacuum to provide a clean, well-characterized film. The friction coefficient was measured as a function of FeCl_2 film thickness, where the thickness of the film was measured using a quartz crystal microbalance. The resulting plot of friction coefficient vs. film thickness is displayed in Fig. 6(a). This decreases from the clean-surface value of ~ 2 to a minimum of ~ 0.08 after approximately 30 \AA of FeCl_2 has been evaporated onto the surface. The friction value measured in ultrahigh vacuum is in excellent agreement with that measured in the pin and v-block apparatus (see above), confirming that FeCl_2 films have indeed been formed in the pin and v-block experiment. A similar experiment was carried out by forming the film by reaction with carbon tetrachloride in a reaction cell attached to the ultrahigh-vacuum tribometer. In this case, the film thickness was estimated from the film growth kinetics for carbon tetrachloride, measured using a microbalance, and the resulting plot of friction coefficient



(a)



(b)

Fig. 6. Plot of friction coefficient vs. film thickness for FeCl_2 on an iron surface where the film was (a) evaporated in ultrahigh vacuum or (b) grown on an iron foil by reaction with carbon tetrachloride vapor. The insets are expanded regions for thin films.

vs. film thickness is displayed in Fig. 6(b) [23,24]. This reveals a similar decrease in friction coefficient as found for the evaporated film to a similar limiting value of ~ 0.08 .

Notable in this case, however, is that this value is reached when a film of only $\sim 4 \text{ \AA}$ thick has grown on the surface. This effect will be discussed in greater detail below. Nevertheless, these data further indicate that a lubricious ferrous chloride film is formed on the surface by reaction with carbon tetrachloride.

In order to understand the frictional properties of inorganic films in greater detail, experiments were also carried out using alkali halides, since these are relatively simple and so can be fully characterized, and are sufficiently unreactive that they will not be reduced by the substrate [4,25]. Shown in Fig. 7(a) are a series of X-ray photoelectron spectra (XPS) of a KCl film as a function of thickness, revealing that the iron substrate remains metallic, while the potassium chloride is present as a stoichiometric halide. The X-ray diffraction data in Fig. 7(b) show that the film is crystalline and preferentially oriented with the KCl (100) plane parallel to the iron surface. The film thickness, measured directly using the microbalance, is shown in Fig. 7(c) and indicates that the KCl evaporation source provides a constant flux. In addition, the XPS data in Fig. 7(a) can be used to estimate the film thickness from the electron escape depth, assuming that the film is uniform. This clearly significantly underestimates the film thickness, implying that the film is not uniform and that second and subsequent layers start growing before the first layer has saturated. This suggestion is confirmed by annealing the sample to $\sim 550 \text{ K}$ and finding that the XPS signal of the KCl layer increases, indicating that the halide now wets the surface (data not shown). In addition, TPD spectra at lower coverages reveal that the first layer is more strongly bound to the surface than subsequent layers, in accord with the observation that heating the surface to 550 K wets the surface [25].

We first address the question of the film thickness that is required to reduce the friction of the iron surface. The variation in friction coefficient of a KCl film deposited onto iron as a function of film thickness (measured using the microbalance) is displayed in Fig. 8(a), and reveals that the friction coefficient is substantially reduced by the presence of the halide film from ~ 2 for the clean surface to a minimum of ~ 0.26 when the film is present. The reduction occurs after a total of $\sim 40 \text{ \AA}$ of KCl has been deposited, and this film thickness also coincides with an increase in the contact resistance between the tribopin and the substrate [4,25]. Clearly, only a thin halide film is required to reduce friction to a constant minimum value.

As noted above, however, second and subsequent layers of the halide film grow before the first monolayer is complete. This suggests that the decrease in friction coefficient may correspond to the completion of the first monolayer of the halide on the surface. In order to test this proposal, the amount of bare iron on the surface was measured by adsorbing deuterium, which preferentially adsorbs onto the metal but not onto the halide film [25]. The amount of deuterium was monitored using TPD. Shown in Fig. 8(b) is a comparison of the first-layer KCl

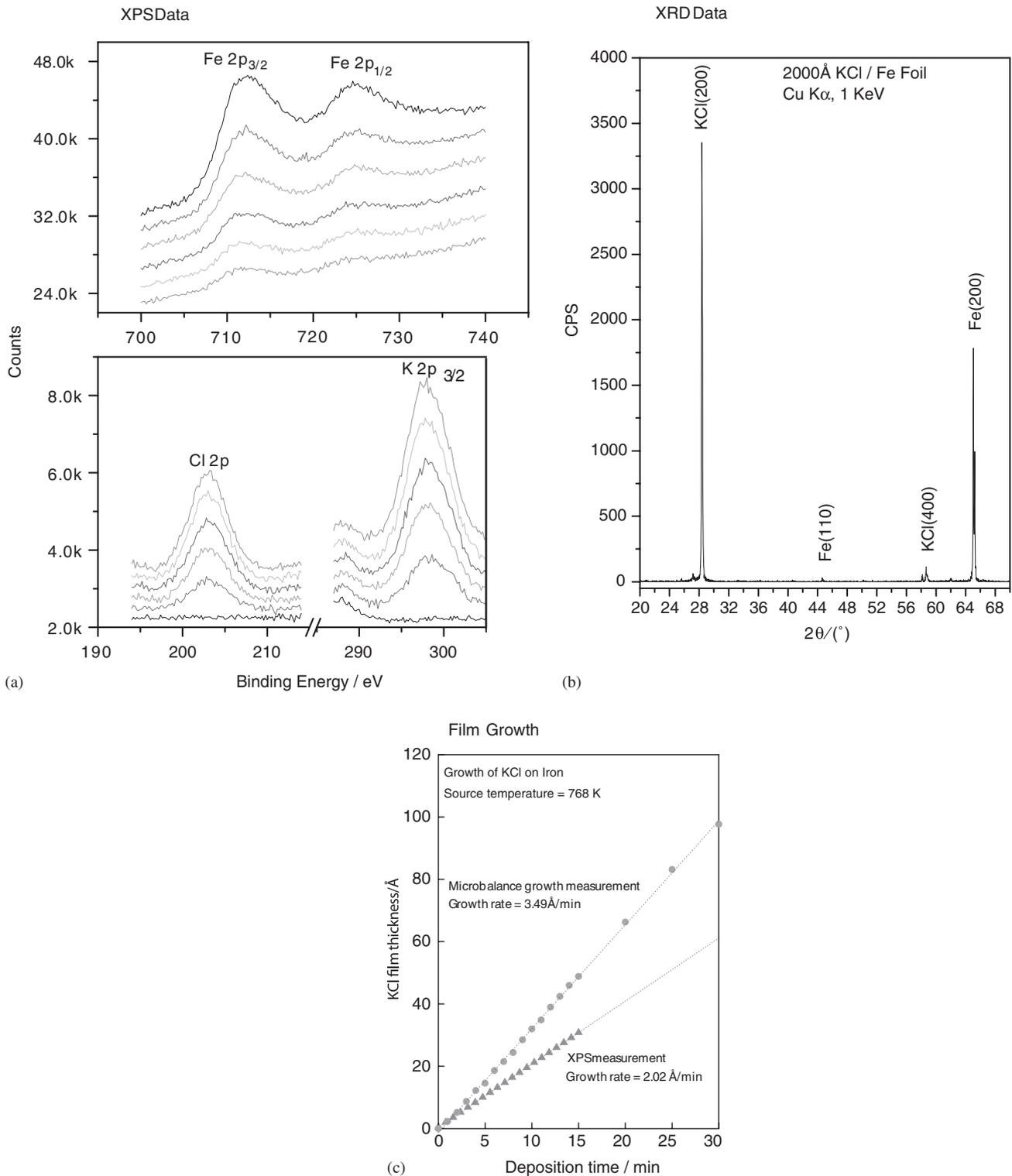
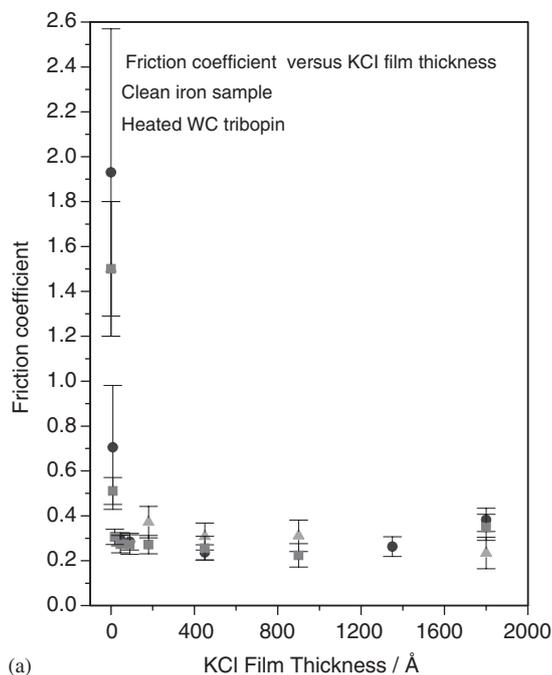


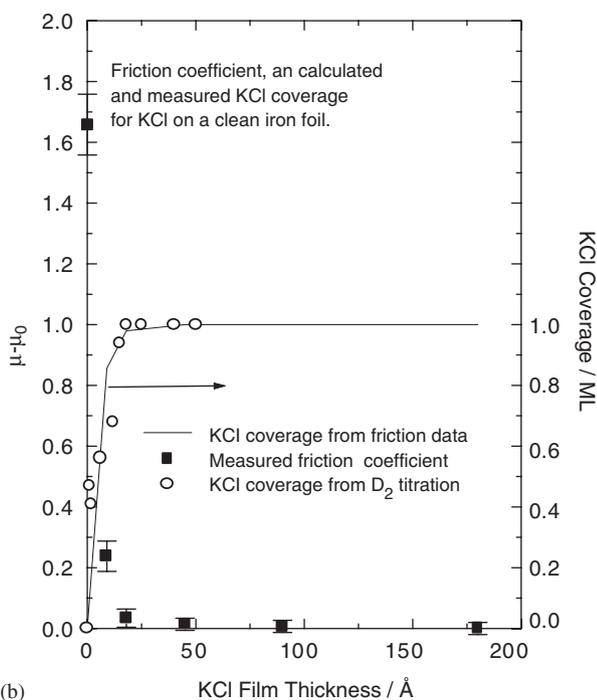
Fig. 7. Characterization of potassium chloride evaporated onto an iron foil showing (a) Fe 2p, Cl 2p and K 2p XPS, (b) X-ray diffraction data and (c) the film thickness measured as a function of time either using the quartz crystal microbalance or from XPS.

coverage measured directly from the deuterium titration experiment (\circ), compared with the coverage predicted to occur if the friction reduction were indeed due to only the first layer of the halide (solid line). These data are in

excellent agreement, indicating that the proposal that the reduction in friction is due to just the first layer of the halide is correct. This suggestion can be further tested by heating a halide film thinner than ~ 40 Å. According to the



(a)



(b)

Fig. 8. (a) Plot of friction coefficient vs. film thickness for KCl evaporated in ultrahigh vacuum onto a clean iron foil, (b) comparison of the predicted first-layer coverage as a function of film thickness, assuming that the friction reduction is proportional to the first-layer KCl coverage (solid line) compared to the first-layer KCl coverage measured from deuterium titration experiments.

above results, the halide should wet the surface, resulting in a larger first-layer coverage, and consequently a lower friction coefficient. This is indeed found to be the case [25].

These results help to explain the frictional data for FeCl_2 (Fig. 6). In the case in which ferrous chloride is evaporated

onto the surface (Fig. 6(a)), second and subsequent layers grow prior to completion of the first layer, resulting in the first layer being completely covered when the total film thickness is $\sim 30 \text{ \AA}$, resulting in the minimum friction coefficient being attained at that film thickness. In the case in which ferrous chloride is deposited reactively (Fig. 6(b)), the halide is formed by reaction with the iron so that the first layer is preferentially covered by the halide, suggesting that only about 5 \AA of the halide is required to reduce the friction coefficient to 0.08.

It is also found that the friction coefficient increases once again as the film becomes thicker [22]. This effect is ascribed to an increased contact area between the film and the rough tribotip, and the behavior is well described by a modified Greenwood–Williamson model. A third regime is found when the film becomes even thicker than the interfacial roughness, where the surfaces are completely separated by the film.

The observation that a monolayer of the halide effectively reduces friction suggests that the shear plane lies either between the tungsten carbide tribotip and the film, or between the film and the substrate. If shear were to occur between the film and static substrate, the film would move with the pin and therefore be rapidly removed from the surface, resulting in an increase in friction coefficient for multiple passes. In fact, the friction coefficient remains constant over a relatively large number of scans over the same region, indicating that shear occurs between the film and the pin.

4. Conclusions

It is shown that, in the extreme-pressure regime, the surface chemistry of simple-model extreme-pressure lubricant additives, measured in some detail in ultrahigh vacuum, corresponds to that measured at higher pressures, where film growth rates are monitored using a microbalance. In turn, these data can be used to rationalize the extreme-pressure lubrication behavior by successfully reproducing the measured seizure load vs. additive concentration curves. It is also demonstrated, by growing ferrous chloride films on iron substrates in ultrahigh vacuum, that these have the same friction coefficients as those found for model, chlorine-containing extreme-pressure lubricants. Finally, it is demonstrated that a monolayer of a solid-boundary lubricant film is sufficient to lower the interfacial friction coefficient to its minimum value. These results demonstrate that the chemistry measured under conditions of thermodynamic equilibrium at some temperature can be successfully applied to the formation of a boundary film, in the extreme-pressure regime. The challenge for the future will be to establish how to make this connection under milder conditions for which the nature of the surface is less well defined and the energy dissipation processes at the surface may lead to non-Boltzmann energy distributions.

Acknowledgments

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