Surface Chemistry of Methylene Chloride on Iron: A Model for Chlorinated Hydrocarbon Lubricant Additives

P. V. Kotvis,[†] L. A. Huezo, and W. T. Tysoe[*]

Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53211

A model is proposed for the chemistry of methylene chloride as a lubricant additive on an iron surface operating under conditions of "extreme pressure"; that is, when the force between the lubricated surfaces is very high. Under these conditions, material is continually removed. The large power dissipated also produces large increases in interfacial temperature and values up to ~950 K can be attained. The chlorinated hydrocarbon additive (here methylene chloride) dissolved in the lubricant thermally decomposes at the surface forming a protective layer consisting of $FeCl_2$ and carbon. The rates of growth and removal of this layer are independently measured and used to calculate the net film thickness during lubrication. Failure of the lubricant is assumed to occur when the protective ($FeCl_2$ + C) film is removed. Values of the load at failure (the seizure load) calculated under these assumptions agree well with experimentally measured results thereby confirming the validity of the assumptions of the model. These results serve to emphasize the importance of the chemistry of the additive at the metal surface in the description of extreme pressure lubrication. The relative growth rates of several volatile chlorinated hydrocarbons (e.g., CH_2Cl_2, $CHCl_3$, CCl_4) also correlate well with their activities as extreme pressure additives.

Introduction

Additives are often used in lubricating fluids that are required to operate under conditions of "extreme pressure" (EP), that is, when the forces acting on the rubbing surfaces are extremely large. These fluids are used in such manufacturing operations as ferrous metal machining, wire-drawing, and forming and generally consist of at least two components. The first is a base fluid which may be a mineral oil or, in some cases, water. The second component, which is added to this in concentrations of a few percent, significantly improves the tribological properties of the fluid, in particular under EP conditions, by decreasing the coefficient of friction and preventing seizure between the two surfaces. Such additives are often oil-soluble chlorine-, phosphorus-, or sulfur-containing organic compounds. Probably the most commonly-used of these are chlorine-containing compounds and are therefore the focus of this work. At present there is essentially no understanding of the way in which these chlorinated hydrocarbon additives function. Several theories have, however, been proposed. These include formation of "friction polymers",[1] the emission of exoelectrons,[2] and the formation of an inorganic halide film.[3] Unfortunately, despite these theories no definitive picture of the role of the chlorinated hydrocarbon additives has emerged, and there appears to be little understanding of the related chemical processes that lead to their effectiveness.[4-19] It

has been suggested that, under the extremely large loads existing between the contacting surfaces, material is removed, thereby exposing fresh or "nascent" metal to the lubricant so that the chemistry at the interface will resemble that of an uncontaminated metal (iron) surface.[20-25]

Results are presented in the following that indicate that an $FeCl_2$ film *is* deposited by the thermal decomposition at the surface of a methylene chloride additive and that this constitutes the tribologically-significant film. The film growth rate by the thermal decomposition of chlorinated hydrocarbon vapor is in the order $CCl_4 > CHCl_3 > CH_2Cl_2$ which correlates well with their effectiveness as extreme pressure additives. It is further shown that the kinetics of film growth from the thermal decomposition of a chlorinated hydrocarbon vapor (in this case methylene chloride) measured on an iron foil can be successfully used to model the extreme pressure behavior. These results demonstrate that the surface chemistry of the chlorinated hydrocarbon plays a central role in understanding lubrication under EP conditions.

Experimental Section

Several pieces of experimental apparatus were used in this work. The first, a pin and v-block apparatus (Figure 1a), was used to determine the extreme-pressure tribological behavior of the model lubricant. Secondly, a microbalance was used to measure the film growth kinetics from the thermal decomposition of chlorinated hydrocarbon vapor on an iron foil.

* Author to whom correspondence should be addressed.
† Benz Oil, Inc., Frank P. Farrell Laboratory, Milwaukee, WI 53209.
(1) Furey, M. J. *Wear* 1973, *26*, 369.
(2) Rabinowicz, E. *Sci. Am.* 1977, *74*, 236.
(3) Shaw, M. C. *Ann. N.Y. Acad. Sci.* 1951, *53*, 962.
(4) Dorinson, A.; Ludema, K. C. *Mechanics and Chemistry in Lubication*; Elsevier: 1985.
(5) Gregory, P. N. *J. Inst. Pet.* 1948, *34*, 670.
(6) Davey, W. *J. Inst. Pet.* 1946, *32*, 575.
(7) Studt, P. *Erdol Kohle, Erdgas, Petrochem.* 1968, *21*, 340.
(8) Mould, R. W.; Silver, H. B.; Syrett, R. J. *Wear* 1972, *2*, 269.
(9) Prutton, F. C.; Turnbull, D.; Dlouhy, G. *J. Inst. Pet.* 1946, *32*, 90.
(10) Sakurai, T.; Sato, K.; Yamamoto, Y. *Bull. Jpn. Pet. Inst.* 1965, *7*, 17.
(11) Dorinson, A. *ASLE Trans.* 1973, *16*, 22.
(12) Nakai, N.; Konda, N. *Proc. JSLE Int. Tribol. Conf.* 1985, *2*, 515.
(13) Morimoto, T.; Tomomura, K.; Kishinoue, K. *Mem. Fac. Eng., Osaka City Univ.* 1981, *22*, 19.

(14) Clason, D. L. *Lubr. Sci.* 1989, *1*, 281.
(15) Schey, J. A. *Tribology in Metalworking*; American Society for Metals: Metals Park, OH, 1983.
(16) Wolfe, K. J. B.; Kinman, M. P.; Lennerd, G. *J. Inst. Pet.* 1954, *40*, 253.
(17) Cassin, C.; Boothroyd, G. *J. Mech. Eng. Sci.* 1965, *7*, 67.
(18) Tabor, D. *J. Lubr. Technol.* 1981, *103*, 196.
(19) Shaw, M. C. *ACS Symp. Chem. Frict. Wear* 1958, *A191*.
(20) Kotvis, P. V.; Tysoe, W. T. *Appl. Surf. Sci.* 1989, *40*, 213, and references therein.
(21) Kotvis, P. V.; Huezo, L.; Millman, W. S.; Tysoe, W. T. *Wear* 1991, *147*, 401.
(22) Kotvis, P. V.; Tysoe, W. T.; James, M. N. *Wear* 1992, *153*, 305.
(23) Smentkowski, V. S.; Cheng, C. C.; Yates, J. T., Jr. *Surf. Sci.* 1989, *215*, L279.
(24) Smentkowski, V. S.; Cheng, C. C.; Yates, J. T., Jr. *Langmuir* 1990, *6*, 147.
(25) Smentkowski, V. S.; Yates, J. T., Jr. *Surf. Sci.* 1990, *232*, 102.
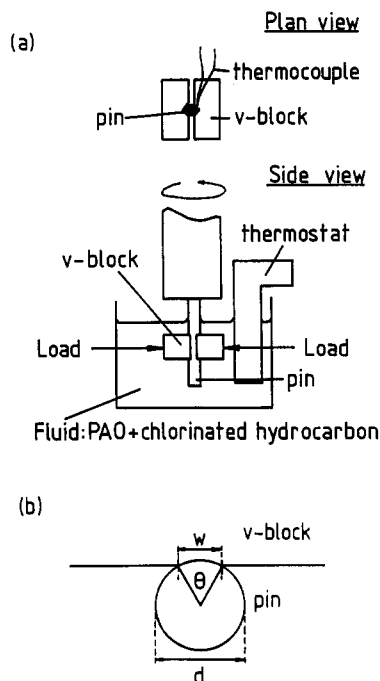
Figure 1. (a) Schematic diagram showing the pin and v-block apparatus and (b) the values used in eqs 4 and 5 for calculating removal rates.

Figure 2. Plots of seizure load versus chlorinated hydrocarbon concentration for a range of chlorinated hydrocarbons dissolved in a poly-α-olefin obtained using a pin and v-block apparatus.

Pin and V-Block Apparatus. This apparatus has been described in detail elsewhere.[21,22] Briefly, it turns a pin that is clamped between two v-shaped blocks, which together are immersed in the model lubricant (Figure 1a). Both the pin and the v-blocks are made of steel and the pin rotates at 290 revolutions per minute and the pin diameter is 6.35 mm. The load applied to the v-blocks can be varied between 0 and 8500 N, and the torque required to maintain the pin at a constant rotational velocity can also be monitored. In a typical experiment, the apparatus is initially run for a period of time using a low applied load of 1180 N for 300 s (a "run-in" period) to ensure that any surface contaminants and the initial roughness are removed and that bare metal interacts with the fluid. Although the chlorinated hydrocarbons act as effective additivies in the absence of a run-in period (since seizure load increases are measured), less reproducible values of seizure load are measured than without a run-in period. Following the run-in period, the applied load is increased linearly with time. The corresponding torque also increases linearly with load[22] up to seizure of the two surfaces, at which point the torque increases suddenly. The load at which this occurs is taken as the seizure load.

The model base fluid used for these experiments consists of a poly-α-olefin (PAO, $C_{30}H_{62}$, Chevron Chemical, 99.9%). The chlorinated hydrocarbons (98 wt % minimum, Aldrich Chemical) were dissolved in this fluid to synthesize the model lubricant. Care was taken to completely exclude all oxygen and water and, under experimental conditions, the concentration of oxygen was below the detection limit of electron paramagnetic resonance spectroscopy and so was less than 50 ppb. Karl Fischer coulometric titration indicated that the dissolved water concentration was approximately 9 ppm before and after the experiment and came from trace contaminants in the additive itself. Finally, the fluid temperature was held constant throughout the experiment to ±1 K using a recirculating temperature controller.

Microbalance Experiments. The kinetics of film formation by the thermal decomposition of volatile chlorinated hydrocarbons (predominantly methylene chloride) were measured by means of a Cahn Model 2000 microbalance.[21] The microbalance is enclosed in a glass shroud and connected to a vacuum line pumped by a liquid-nitrogen-trapped, mercury different pump which operated at a base pressure of 5 × 10⁻⁷ Torr. Pressure was monitored by means of a cold-cathode gauge attached directly to the vacuum line which could be isolated from the line when the chlorinated hydrocarbon vapor was present. Higher pressures
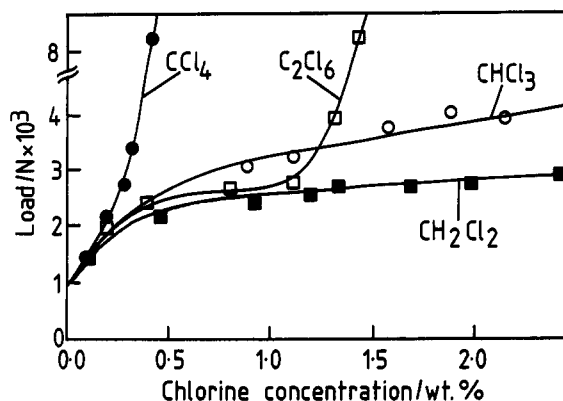
were measured using a bellows manometer which was calibrated directly using a mercury column. The volatile chlorinated hydrocarbon vapor is introduced from a glass ampule attached directly to the vacuum line and the liquid is purified using several freeze/thaw cycles prior to use.

Film growth rates are measured by monitoring the change in mass per unit area Δm of an iron foil as a function of time. The 0.025-mm-thick iron foil (Johnson Matthey, 99.999%) is suspended from one arm of the microbalance and balanced using a counterweight on the other arm. The sample is enclosed in a quartz tube which is inserted into a furnace. The temperature is monitored using a chromel/alumel thermocouple that is inserted into a well in the bottom of the tube and is approximately 5 cm from the sample. The sample temperature is controlled to ± 1 K and the mass change of the sample monitored continuously and plotted as a function of time. The mass change is approximately converted to film thickness t (assuming that the film is uniform and consists entirely of $FeCl_2$) using the formula

$$t = \Delta m/(\rho[1 - (M(\text{Fe})/M(\text{FeCl}_2))]) \quad (1)$$

where Δm is the mass change of the foil per unit area, ρ is the density of $FeCl_2$, and $M(\text{Fe})$ and $M(\text{FeCl}_2)$ denote the molar masses of iron and ferrous chloride, respectively. The area of the foil sample is calculated directly from its dimensions. Note that analysis of the film indicates that it also contains carbon,[20] so that the density of the film is likely to differ slightly from that of pure $FeCl_2$ so that absolute values of the film thickness measured in this way will reflect this approximation. However, relative values of the film thickness will be accurate.

Control experiments were performed in which the iron sample was heated to 600 K in 700 Torr of hydrogen for 300 min prior to film growth. However, it was found that merely annealing in vacuo rather than in hydrogen prior to growth yielded exactly identical growth kinetics in both cases. This behavior can be understood since the native oxide layer on iron is ~40 Å thick.[26] Films grow by thermal decomposition of the chlorinated hydrocarbon up to 10⁴ Å thick (Figures 7 and 8) by oxidation of the substrate. The resulting oxygen contamination in the layer due to any native oxide is ~1% and therefore not likely to substantially effect layer growth.

Results

Shown in Figure 2 are a series of plots of seizure load versus additive concentration obtained with the pin and v-block apparatus using a range of chlorinated hydrocarbon additives. The abscissa in Figure 2 has been normalized with respect to the chlorine content of the additives. When using CH_2Cl_2 as additive the seizure load initially increases rapidly with concentration and reaches a plateau after the addition of ~0.7 wt % chlorine from methylene chloride. This behavior is designated type I. Other

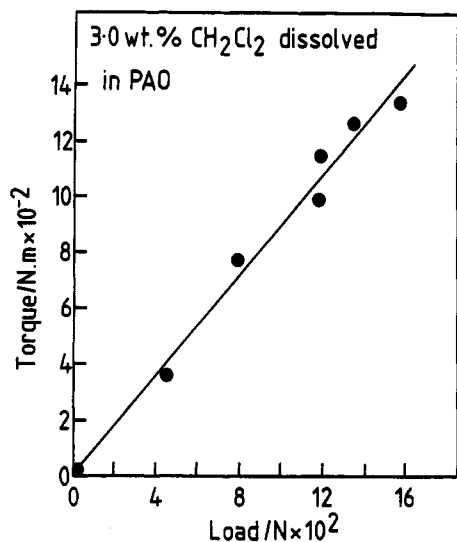(26) Vernon, W. H. J.; Calnan, E. A.; Clews, C. J. B.; Nurse, T. J. *Proc. R. Soc. London* **1953**, *A216*, 375.

Figure 3. Plot of torque versus load in the pin and v-block apparatus obtained when using 3.0 wt % CH_2Cl_2 dissolved in poly-α-olefin as lubricant.

additives that show this type of behavior are 1,4- and 2,3-dichlorobutane, 1-chloropropane, and 1-chlorodecane. In contrast the seizure load when using CCl_4 continues to increase with additive concentration and shows no sign of reaching a plateau within the limits of applied load attainable using the pin and v-block apparatus. This is designated type II behavior. Some additives show both types of behavior, being type I for low additive concentrations and converting to type II at higher concentrations. This type of behavior is exemplified by C_2Cl_6 (in Figure 2) and C_2HCl_5 (not shown). The results presented in this paper focus primarily on understanding the behavior of methylene chloride as an additive (a type I additive, in which a plateau region is observed).

The temperature T at any point close to the interface between the pin and the v-block rises as a function of applied load L because of frictional energy dissipation between the two moving surfaces. The temperature T increases linearly with the applied load assuming that the interfacial coefficient of friction μ remains constant (see Appendix) and is given by

$$T = T_0 + aL \tag{2}$$

where T_0 is the ambient temperature, L is the applied load, and a is a constant. Note that the constant a is a function of position (see Appendix). In order to measure the coefficient of friction, the torque required to rotate the pin at a constant angular velocity is shown plotted versus applied load in Figure 3 when using 3.0 wt % CH_2Cl_2 dissolved in PAO. This clearly increases linearly indicating a constant coefficient of friction since this is proportional to the ratio of the torque to load. The corresponding plot of the temperature measured *close* to the interface using a thermocouple spot-welded to the v-blocks, but as close as possible to its interface with the pin, is shown in Figure 4 when using both a type I (3.0 wt % CH_2Cl_2) and a type II additive (2.4 wt % C_2HCl_5). Note that this is not the temperature *at* the interface. The thermocouple temperature indeed varies linearly with applied load up to the onset of seizure where the temperature increases precipitately. Note that, in both of the cases shown and for all cases so far measured, the temperature shows a drastic increase at a thermocouple temperature of $\sim$390 K. However, when using a "type II" additive, seizure does not occur at this temperature but the additive maintains its antiseizure properties at higher
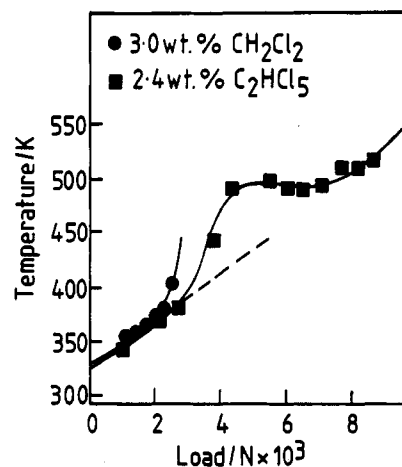

Figure 4. Temperature measured close to the interface between the pin and the v-block using a thermocouple plotted versus load when using 3.0 wt % CH_2Cl_2 (●) and 2.4 wt % C_2HCl_5 (■).
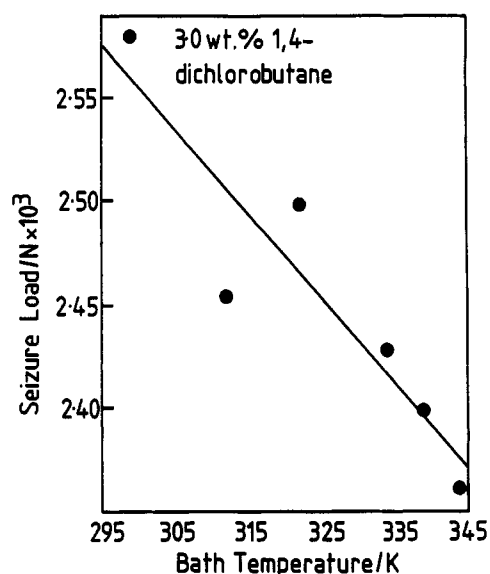

Figure 5. Plot of seizure load versus fluid temperature when using 3.0 wt % 1,4-dichlorobutane dissolved in poly-α-olefin as lubricant. Dichlorobutane is used rather than methylene chloride in this case since it is less volatile.

applied loads (and interfacial temperatures). The consistent measurement of a significant rise in interfacial temperature when the thermocouple reads $\sim$390 K suggests that seizure occurs when the temperature at the interface reaches a critical value T_c. Assuming that eq 2 applies *at* the interface, and assuming that seizure does occur when the interface reaches a critical temperature T_c, then, by rearrangement of eq 2, the seizure load L_s should vary with the bath temperature T_0 according to

$$L_s = (-1/a_0)T_0 + (T_c/a_0) \tag{3}$$

Note that the constant a in this equation is position dependent (see Appendix) and the value in this case is for the temperature *at* the interface (and designated a_0). The corresponding experimental results for the variation in seizure load L_s with bath temperature T_0 are shown in Figure 5, in this case using 3.0 wt % 1,4-dichlorobutane rather than methylene chloride dissolved in PAO. This was done since methylene chloride is sufficiently volatile that a substantial loss of methylene chloride occurs at higher fluid temperatures. The tribological properties of 1,4-dichlorobutane (i.e., the plot of seizure load versus additive concentration) are identical to those of methylene
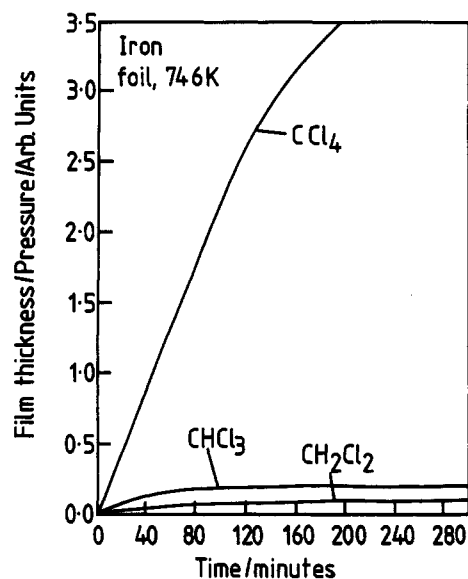
Figure 6. Film thickness normalized to the pressure of the chlorinated hydrocarbon plotted versus time for a number of volatile chlorinated hydrocarbons obtained with a microbalance using 15.0 Torr of methylene chloride, 7.5 Torr of chloroform, and 4.0 Torr of carbon tetrachloride.

chloride. A straight line fit is shown plotted onto these data and yields a value of a_0 = 0.25 ± 0.04 K/N and T_c = 950 ± 100 K *at* the interface. These results demonstrate that the temperature at the interface between the pin and the v-block shows a substantial rise with applied load and that the local interfacial temperature at seizure is ~950 K.

Typical growth kinetics (calculated from measurements of Δm versus time) for the surface decomposition of a range of chlorinated hydrocarbons on iron are displayed in Figure 6, in this case normalized to the pressure of the chlorinated hydrocarbon using 15.0 Torr of methylene chloride, 7.5 Torr of chloroform, and 4.0 Torr of carbon tetrachloride. Clearly films are formed most rapidly from the thermal decomposition of carbon tetrachloride with both methylene chloride and chloroform reacting significantly more slowly. These relative film formation rates correspond well to their relative tribological activities (Figure 2).

Film growth kinetics from the decomposition of methylene chloride on an iron foil were measured as a function of both methylene chloride pressure and sample temperature using a microbalance to monitor the change in mass of the sample and therefore the average thickness of the film that is deposited (eq 1). The growth curves for film formation from the decomposition of methylene chloride on an iron surface are displayed as a function of temperature using a pressure of 15.0 Torr in Figure 7. Films are deposited and both the rate of film deposition and the ultimate thickness depend on the sample temperature. Thus growth is initially rapid with the rate decreasing as the film is deposited and ultimately reaching a plateau. In addition the growth rate increases with increasing temperature as is expected for an activated process. Figure 8 shows the corresponding film growth kinetics taken at a constant temperature of 620 K measured as a function of methylene chloride vapor pressure. Similarly shaped kinetic growth curves are noted as those shown in Figure 7 and the growth rate increases with reactant pressure.

An X-ray photoelectron spectroscopic analysis of the film that is formed on the iron foil (not shown[21]) reveals the presence of an iron halide and carbon; a surface composition that strongly resembles that found on the
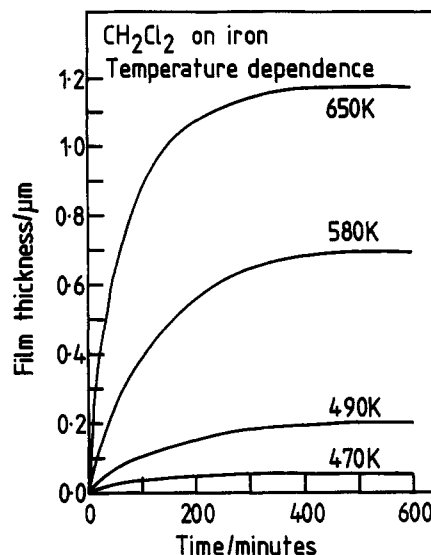

Figure 7. Plots showing the thickness of the film deposited on an iron foil versus time from the thermal decomposition of methylene chloride vapor at a pressure of 15.0 Torr for several deposition temperatures.
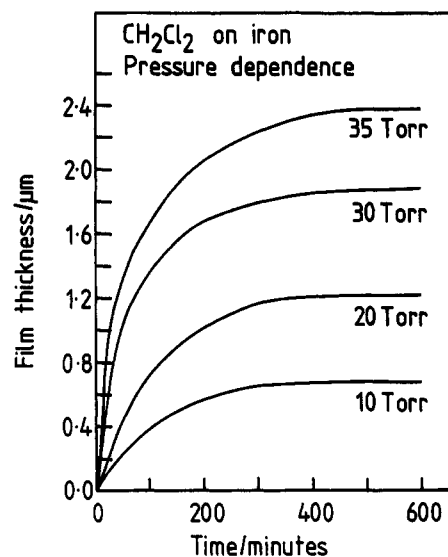

Figure 8. Plots showing the thickness of the film deposited on an iron foil versus time from the thermal decomposition of methylene chloride vapor at 620 K for several pressures.

surface of the pins or v-blocks following a tribological experiment.[20]

The rate of material removal during a tribological experiment can be evaluated separately using the pin and v-block apparatus by measuring the width of the wear scar formed on the surface of the v-block because of material removed due to the rubbing of the cylindrical pin. In this experiment the pin and v-block apparatus is run at a constant applied load for a fixed period of time. Here it is assumed also that the surface film is continually replenished by reaction with the chlorinated hydrocarbon dissolved in the PAO. The total volume V of material that is removed during the experiment can be calculated from the width of the wear scar w from the formulas

$$\theta = 2 \sin^{-1}(w/d) \qquad (4)$$

and

$$V = d^2 l(\theta - \sin \theta)/8 \qquad (5)$$

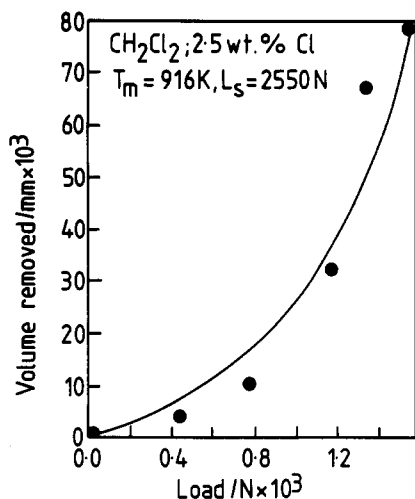where θ is the angle subtended at the center of the pin of

Figure 9. Volume of material removed in 600 s plotted versus load measured using the pin and v-block apparatus with methylene chloride (2.5 wt % chlorine) dissolved in poly-α-olefin as lubricant.

diameter d by the wear scar and l is the total length of the scar (Figure 1b). Note that the surface of the pin wears as well as the face of the v-block which leads to a decrease in the diameter d of the pin. This wear at the surface of the pin is ~50 μm so that d decreases by less than 1% during the course of the experiment so that d can be taken to be a constant in eqs 4 and 5. Figure 9 shows the volume of material removed in a period of 600 s in pin and v-block experiments at less than seizure loads calculated using eqs 4 and 5. This is plotted as a function of the applied load L when using 2.5 wt % Cl from methylene chloride as additive to the PAO (a type I additive in its plateau region). It has been demonstrated that the volume of material removed varies linearly with time[22] so that the rate of material removal dV/dt is constant at any particular applied load below seizure. Thus material is removed from the surface of the v-block during the experiment, and the volume of material removed increases rapidly as a function of the applied load.

Discussion

A body of work on the chemistry of chlorinated hydrocarbons on iron surfaces[23-28] has aimed at understanding the role of these compounds as "extreme pressure" (EP) additives. As emphasized above, a number of theories have been proposed to explain how they work.[1-3] The results described above indicate that chlorinated hydrocarbons can decompose at an iron surface to deposit a film over the temperature range encountered at the interface between the pin and the v-block (from room temperature to ~950 K) and that this film can be removed at the interface due to the relative motion of the two contacting surfaces. Analyses of the material removed from the surfaces of the pins and v-blocks using X-ray photoelectron spectroscopy indicate the presence of an iron halide and carbon.[20] A similar analysis of the surfaces of the iron foil after film formation by reaction with methylene chloride vapor shows the formation of a film of similar composition.[21] It is postulated that the film grown from methylene chloride forms a tribologically significant layer that effectively lubricates the surfaces and prevents their seizure. The validity of this postulate will be demonstrated below.

If, under a particular set of experimental conditions, the film-growth rate is given by r_g and the corresponding film-removal rate by r_r, then the resulting film thickness at any time is proposed to arise from a dynamic balance between the growth and removal rates. If the instantaneous film thickness at any time is given by X, then the resulting rate of change in film thickness is given by

$$\mathrm{d}X/\mathrm{d}t = r_g - r_r \qquad (6)$$

In fact, the film grows and is removed sequentially as the pin rotates through the jaws of the v-block; material is removed at a particular point on the pin as it passes the face of the v-block and is deposited as it moves through the fluid. The values of X in eq 6 represent an average of these processes. Since the iron chloride + carbon film is proposed to form the antiseizure layer, complete removal of this layer will lead to seizure. That is, seizure is proposed to occur at an applied load L_s when X becomes zero. Measurement of r_g and r_r is described in the following.

Rate of Film Removal. The rate of film removal as a function of applied load is given by the data shown in Figure 9. It is usually assumed that the rate of film removal at constant relative velocity of the surfaces is given by

$$r_r = c\, L/S \qquad (7)$$

where L is the load, S the shear strength at the interface, and c a constant.[29] Since the pin rotational velocity is maintained at a constant value (290 revolutions/min) and the diameter of the pin d remains essentially constant throughout the experiment, the relative velocity at the interface between the pin and the v-block remains constant. The shear strength S has been shown by thermodynamic arguments to have a temperature dependence given by[30]

$$S = S_0 \ln (T_m/T) \qquad (8)$$

where T is the interfacial temperature, T_m is the melting point of the material at the interface between the pin and v-block (consisting of an iron halide + carbon), and S_0 depends on the latent heat of formation and the density of the material at the interface.[30] Note that a temperature (and therefore load)-dependent shear strength might be expected to imply that the coefficient of friction at the interface also varies as a function of load. However, the linear variation of torque with load (Figure 3) means that the coefficient of friction remains constant.

Note that, according to eq 2 and the results shown in the Appendix, the interfacial temperature increases linearly with load L yielding an overall theoretical dependence of the film removal rate on load as

$$r_r = C\, L/\ln[T_m/(T_0 + a_0 L)] \qquad (9)$$

where C is another constant. A best fit function of this type is shown plotted onto the experimental data of Figure 9, and the agreement between the theoretical fit and the experimental data is good. The best fit was obtained by minimizing the standard deviation between the experimental values and the function shown in eq 9. Fitting was initially performed by fixing T_0 (at 322 K) and a_0 (at 0.25 K/N) and allowing the independent parameters T_m and C to vary. The resulting values of T_m and C and the above values of a_0 and T_0 were then used as input in an unconstrained fit to ensure that a global minimum had been reached. The parameters used to obtain the fit were

(27) Jones, R. G. *Surf. Sci.* **1979**, *80*, 269.
(28) Textor, M.; Mason, R. *Proc. R. Soc. London* **1977**, *A356*, 47.

(29) Rabinowicz, E. *Friction and Wear of Materials*; John Wiley: New Yrok, 1965.
(30) Ernst, H.; Merchant, M. E. *Proc. Spec. Summer Conf. Frict. Surf. Finish, MIT Rep.* **1940**, *15*, 76.

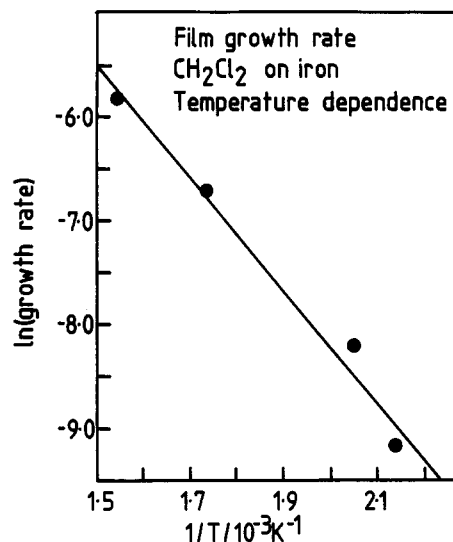**Figure 10.** Arrhenius plot (ln(rate) versus $1/T$) for film growth from the thermal decomposition of methylene chloride on an iron foil.

Figure 11. Plot of film growth rate versus methylene chloride pressure for film growth from the thermal decomposition of methylene chloride on an iron foil.

$C = 1.35 \times 10^{-6}$ mm^3/(N/min), $T_0 = 300 \pm 10$ K, $a = 0.24 \pm 0.02$ K/N, and $T_m = 916 \pm 10$ K. The melting temperature of the interfacial material T_m is in good agreement with the critical seizure temperature ($T_c = 950 \pm 100$ K) established above. This value also agrees well with the melting point of $FeCl_2$ (943 K[31]) and indicates that the critical temperature corresponds to the melting of an $FeCl_2$ film formed at the surface and a resulting decrease in the interfacial shear strength S to zero (eq 8) when $T = T_m$. This result is in accord with surface analyses of both the foils[21] and the pins and v-blocks[20] using XPS which indicate the formation of an iron halide + carbon film. These results suggest that the surface film, in fact, consists of mostly ferrous chloride.

Rate of Film Growth. The rate of film growth on the iron foil can be measured from the plots of film thickness as a function of time for various sample temperatures and methylene chloride pressures. The *initial* growth kinetics can be summarized as

$$r_g(t=0) = A \, p(CH_2Cl_2)^n \exp(-E_{act}/RT) \quad (10)$$

where A is a rate constant pre-exponential factor, $p(CH_2Cl_2)$ the methylene chloride pressure, n the reaction order, T the sample temperature, and E_{act} the growth activation energy. The growth rates are measured by fitting a function of the form

$$X = X_m(1 - \exp(-bt)) \quad (11)$$

where X_m is the maximum film thickness and b a constant to the experimental data. The initial growth rate can then be obtained directly by differentiating this equation and yields

$$r_g(t=0) = b \, X_m \quad (12)$$

The initial growth rate derived in this manner from the results shown in Figure 7 is shown plotted in Arrhenius form (i.e., $\ln(r_g(t=0))$ versus $1/T$) in Figure 10. Measurement of the slope of this curve yields an initial growth rate activation energy of 33 ± 2 kJ/mol.

The film thickness versus time curves are displayed in Figure 8 for various reactant pressures. A function of the form shown in eq 11 is fitted to these data and initial rates
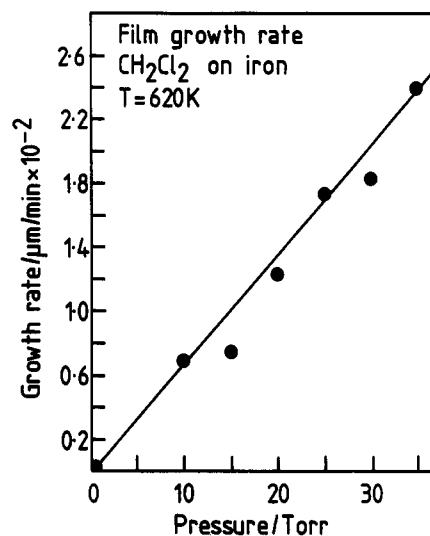
are again calculated from eq 12. A plot of $r_g(t=0)$ versus pressure, where pressure indicates the methylene chloride pressure, is shown in Figure 11. The linearity of this curve indicates that the reaction is first order in methylene chloride pressure. The initial film growth kinetics can therefore be summarized as

$$r_g = A \, p(CH_2Cl_2)^{1.0\pm0.1} \exp(-(3.3 \pm 0.2) \times 10^4/RT) \quad (13)$$

Kinetic Model for the Operation of a Chlorinated Hydrocarbon Extreme Pressure Additive. These results can now be used to calculate the film thickness during a pin and v-block experiment using eq 6. The differential equation is solved numerically using the functional forms for r_g and r_r described in the previous sections (eqs 9 and 13, respectively). The seizure load is taken as that load which causes X to diminish to zero. Note that in order to obtain reproducible experimental results, it is necessary to run the pin and v-block at a low load (1180 N) for a period of time as discussed above. This has two effects. First, it forms an initial wear scar of width w_0 and, second, it deposits an initial $FeCl_2 + C$ film on the surface by the thermal decomposition of the chlorinated hydrocarbon. These values are the initial conditions for the solution of the differential equation as a function of load (or time since the loading rate is constant). The value of w_0 is calculated directly from eqs 4 and 5 and X_0 is taken as the thickness of the film formed during the "run-in" period. X_0 is allowed to vary to optimize the fit and is the only adjustable parameter used. The other values are taken directly from the experimental determinations described above and are allowed to vary slightly within their error limits in order to optimize the overall fit. The results are shown in Figure 12 which plots the theoretical fit (solid line) and the experimental data (●) on the same axes. It is clear that the fit between the experimental values for the seizure load and the simulation is extremely good. The value of the initial film thickness X_0 is 0.22 ± 0.05 μm and is a reasonable value based on the thicknesses of the films that are formed by the thermal decomposition of chlorinated hydrocarbons on metal surfaces[21] and is within the range of thicknesses seen on the pins using argon ion bombardment depth profiling.[20] Strictly speaking, the value of X_0 should be allowed to vary with the additive concentration since film growth kinetics are concentration dependent (Figure 8). However, such a refinement significantly increases the number of adjustable

(31) Weast, R. C., Selby, S. M., Eds. *Handbook of Chemistry and Physics*; Chemical Rubber Co.: Cleveland, OH, 1967.
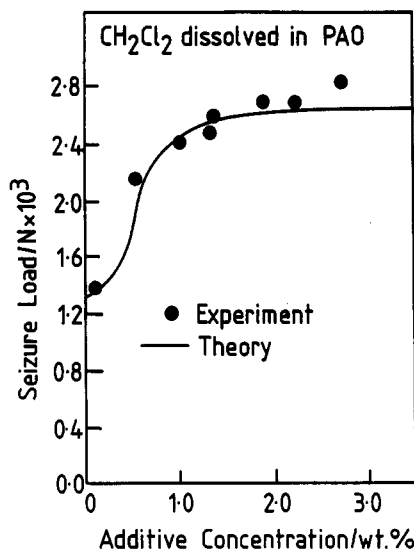
Figure 12. Comparison of a calculation of the seizure load versus additive concentration for methylene chloride (solid line) with experimental results (●) obtained using a pin and v-block apparatus.
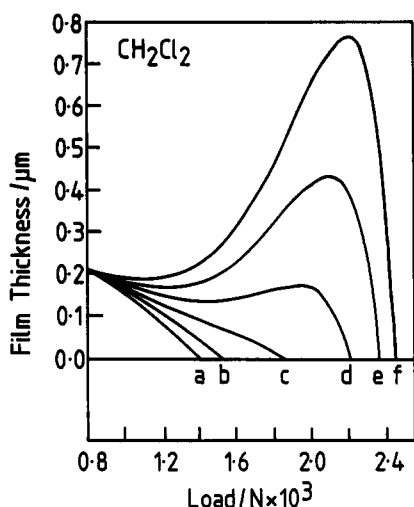

Figure 13. Plot of film thickness versus applied load calculated with the parameters used to obtain the fit shown in Figure 12 for methylene chloride as additive: (a) 0.175, (b) 0.35, (c) 0.525, (d) 0.7, (e) 0.875, and (f) 1.05 wt % of methylene chloride.

parameters and results in only a slight improvement of the fit. Plots of film thickness versus load obtained with the parameters used to obtain the best fit shown in Figure 12 are displayed in Figure 13. It is evident that the film formed during the "run-in" period is merely removed when the additive concentration is low (curves a, b, and c). As the additive concentration increases, the film growth rate starts to increase compared with the film removal rate (curves d and e), and ultimately at higher concentrations film growth dominates so that the film grows to a thickness of the order of 1 μm. However, in all cases the film is completely removed as the interfacial temperature reaches the melting point of the film ($FeCl_2$ + C) resulting in a precipitate decrease in the film thickness around an applied load of 2400 N and the onset of seizure at this load. It should be noted that the persistence of EP activity above a load of ~2400 N (for example when CCl_4 is used as additive) implies that, in these cases, ferrous chloride no longer forms the tribologically-significant film and some other film with a melting point substantially higher than that of $FeCl_2$ is formed. Possible candidates for such a film include carbon or an iron carbide. It is interesting

to note that a stable halide is formed on iron following CCl_4 adsorption.[25,32]

These results firmly implicate the chemistry of chlorinated hydrocarbons at metal surfaces in the understanding of extreme pressure lubrication. They also show that reaction kinetics measured using a clean iron foil can be used to mimic the performance under tribological conditions. This indicates that an understanding of the film formation chemistry at the surface of a carbon-containing, iron chloride film deposited on iron is important to a full description of extreme pressure lubrication using chlorinated hydrocarbons. These ideas also explain why different metals require different lubricant additives. It further suggests that this mechanism might form the basis for the operation of extreme pressure lubricants in general, since other commonly-used EP additives are sulfur- or phosphorus-containing organic molecules. It might be suggested that these similarly thermally decompose at the hot interface to deposite layers which contain carbon and/or sulfides and phosphides, respectively. Note that in these cases the presence of oxygen or water dissolved in the lubricant might result in further oxidation to form either sulfates or phosphates. Analysis of surfaces lubricated using organosulfur compounds reveals the presence of sulfides, confirming the potential general applicability of these ideas.[33]

Conclusions

A model is proposed for the operation of a chlorinated hydrocarbon, extreme-pressure lubricant additive whereby it thermally decomposes at a clean iron surface to deposit a film that consists of ferrous chloride and carbon. This film acts as an antiseizure layer and is continually removed because of the relative motion of the two surfaces. Independent measurements of both the film formation rate using a microbalance and the film removal rate using the pin and v-block apparatus can be used to provide the parameters to predict the experimental seizure load versus additive concentration curve using a model that assumes that seizure occurs when the protective film thickness diminishes to zero. These results provide a firm basis for discussing the chemistry of an important class of lubricant additives, namely those operating under conditions of extreme pressure. That is, the interaction of chlorinated hydrocarbons with clean metal (in this case iron) surfaces and the resulting film formation reactions are relevant to their tribological properties. These results will allow correlations between the surface chemistry of small chlorine (and possibly sulfur and phosphorus)-containing compounds to be effectively used in scrutinizing their extreme-pressure tribological activities.

Appendix

Consider a power source emitting W watts enclosed in a medium of thermal conductivity κ which depends on position and is therefore designated $\kappa(x,y,z)$. This results in an increase of temperature T of the surrounding medium. The heat flux $\mathbf{j}$ is given by the solution of the usual thermal conduction equation

$$\mathbf{j} = -\kappa \nabla T \tag{14}$$

Imagine an isothermal surface enclosing the heat source. Under steady-state conditions the total heat flux through the isothermal surface equals the total power dissipation

(32) Smentkowski, V. S.; Cheng, C. C.; Yates, J. T., Jr. *Surf. Sci.* **1989**, *220*, 307.

(33) Kajdas, C. *ASLE Trans.* **1985**, *28*, 21.

$$W = \int_s \mathbf{j} \cdot \mathbf{n} \, dS \qquad (15)$$

where $\mathbf{n}$ is the unit vector normal to the isothermal surface. Substitution from eq 14 yields

$$W = -\int_s \kappa(x,y,z) \nabla T \cdot \mathbf{n} \, dS \qquad (16)$$

and writing $\nabla T \cdot \mathbf{n} = (dT/dn)$

$$W = -\int_s \kappa(x,y,z) \, (dT/dn) \, dS \qquad (17)$$

By definition, dT/dn is normal to the isothermal surface S and independent of the coordinates defining S and so can be factored out of the integral. Writing

$$\int_s \kappa(x,y,z) \, dS = B(n) \qquad (18)$$

then

$$W = -B(n) \, (dT/dn) \qquad (19)$$

This can be solved directly on S to give

$$K(\mathbf{r})W = T - T_0 \qquad (20)$$

where T_0 is the ambient temperature and $K(\mathbf{r})$ a constant which depends on position $\mathbf{r}$ with respect to the heat source. The power dissipation W due to the relative motion of the pin and the v-block can be shown to be given by $W = r\omega\mu L$ where r is the pin radius, ω the rotational angular velocity of the pin, and μ the interfacial coefficient of friction, all of which are constant. Substitution into eq 20 yields

$$T = T_0 + a(\mathbf{r})L \qquad (21)$$

where $a(\mathbf{r}) = r\omega\mu K(\mathbf{r})$ so that a also depends on position.