A molecular beam study of the tribological chemistry
of dialkyl disulfides

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Molecular beam studies carried out in ultrahigh vacuum show that dimethyl disulfide reacts with initially clean iron to evolve methane. The reaction is proposed to proceed via a methyl thiolate intermediate. Reaction ceases at ~600 K, an effect that is proposed to be due to the surface being blocked by an overlayer of sulfur and carbon. Reaction recommences above ~950 K as sulfur diffuses into the iron. The activation energy for the film-forming reaction is 52.5 ± 2.1 kcal/mol, in good agreement with the activation energy for the growth of FeS films from dimethyl disulfide at higher pressures measured using a microbalance. A depth profile of the film grown in ultrahigh vacuum shows that the sulfur-containing film grows on a Fe + C underlayer. Similar molecular beam experiments with diethyl disulfide suggest the formation of an intermediate ethyl thiolate species which decomposes via a β-hydride elimination reaction to evolve ethylene. The activation energy for film growth, in this case, is 60 ± 2.4 kcal/mol. The results of tribological experiments using a pin and v-block apparatus are consistent with FeS forming the anti-seizure film.

KEY WORDS: molecular beams; Auger spectroscopy; dimethyl disulfide; diethyl disulfide; iron; tribological chemistry

1. Introduction

A general model has been developed for the operation of extreme-pressure (EP) lubricant additives which proposes that they thermally decompose at the hot interface (where temperatures of the order of 1000 K can be attained) to reactively form a lubricating film [1–14]. Since this film is continually worn from the surface under the high loads encountered during extreme-pressure lubrication, the resulting thickness of the interfacial lubricating film arises from a balance between the rate of its reactive formation and tribological removal. The nature of the film that is formed depends on the additive that is used. It has been shown that methylene chloride and chloroform form films that consist of $FeCl_2$ and which incorporate small (~50 Å in diameter) carbonaceous particles [8,9]. In contrast, when carbon tetrachloride is used as an additive, iron carbide is formed leading to a much more effective additive [13,14]. Sulfur-containing extreme-pressure additives generally comprise molecules with sulfur–sulfur linkages and are modeled here using dialkyl disulfides (R–S–S–R, where R is CH_3 or C_2H_5) [15–28]. It has been shown previously that dialkyl disulfide thermally decomposes to form a lubricating film that consists of FeS [29]. Ferrous sulfide is significantly harder than ferrous chloride (3.5–4.5 for FeS versus ~1.0 for $FeCl_2$ on the Mohs scale [30,36]) and would therefore be expected to lead to a significantly higher interfacial coefficient of friction. Although the friction coefficients of interfacial films formed using sulfides *are* higher than when using chlorinated hydrocarbons, these differences are small. For example, the interfacial coefficient of friction found when using methylene

chloride is $(11 \pm 1) \times 10^{-2}$ [8], when using chloroform $(7.1 \pm 0.7) \times 10^{-2}$ [9] while when using dimethyl disulfide, it is $(12 \pm 1) \times 10^{-2}$ [29]. The difference between friction coefficients of films formed from methylene chloride and chloroform has been ascribed to the effect of small carbonaceous particles incorporated into the film [9].

We have shown previously that the decomposition kinetics of chlorinated hydrocarbons measured using molecular beams mimic those found using higher pressures [14]. The advantage of this strategy is that the gas-phase products can be monitored in the ultrahigh vacuum environment used for the molecular beam experiments, and the nature of the resulting film can also be measured. It was found, using these strategies, that chlorinated hydrocarbons thermally decompose to form a halide film and evolve hydrogen. The dialkyl disulfides are somewhat more complicated and are therefore likely to have more complex surface chemistries. This is borne out experimentally by the results presented below where methane is formed from dimethyl disulfide and ethylene is evolved from diethyl disulfide. In addition, it is found that the FeS forms on a carbided substrate. This observation may account for the relatively low friction coefficients of these sulfide layers.

2. Experimental

The experiments were carried out in a stainless-steel, ultrahigh vacuum chamber operating at base pressures of 1×10^{-10} Torr following bakeout, which has been described in detail elsewhere [14]. The sample was mounted to a carousel geometry manipulator and the iron foil sample could be resistively heated to 1200 K where the temperature

was monitored by means of a chromel–alumel thermocouple spot-welded to the back of the foil.

Molecular beam data were collected by continually impinging a beam of reactant onto the sample while it was heated at a constant rate of ~3.5 K/s. Desorbing species were detected using a Hiden HAL 301/3F quadrupole mass spectrometer, located in line of site of the sample, which allows five masses to be monitored sequentially during the same desorption sweep. The mass spectrometer was enclosed in a shroud having a 1 cm diameter hole in the front to minimize extraneous signals not coming from the sample. The chamber also contained a double-pass, cylindrical-mirror analyzer for Auger spectroscopic analyses of the sample following reaction.

The sample was cleaned using a standard procedure [31] which consisted of bombarding with argon ions (3 keV, 1 μA/cm^2) at 300 K and annealing to 1000 K *in vacuo* to remove any remaining surface species. The cleanliness of the sample was monitored by means of Auger spectroscopy and the sample was judged clean when no signals not due to the iron substrate could be detected.

Tribological data of seizure load versus additive concentration were measured using a pin and v-block apparatus and the experimental protocol has been described in detail elsewhere [3]. The model lubricants were synthesized by dissolving the dialkyl disulfides in a poly α-olefin. The additive concentration was measured using infrared spectroscopy following completion of the experiments to ensure that none had been lost.

In the case of molecular beam experiments, the dimethyl (Aldrich, 99%) and diethyl disulfide (Aldrich, 99%) were transferred to glass vials which were attached to the gas-handling line of the vacuum system and further purified by repeated freeze–pump–thaw cycles and their cleanliness monitored mass spectroscopically.

3. Results

Shown in figure 1 are the results of a molecular beam experiment for the reaction of dimethyl disulfide ($(CH_3)_2S_2$) with an initially clean iron foil. The reflected fluxes at 45 amu (from dimethyl disulfide) and 16 amu (methane) are monitored as a function of sample temperature which was ramped at a uniform rate of 3.5 K/s. The assignment of these masses to dimethyl disulfide and methane was confirmed by monitoring various masses and comparing the signals with the mass spectrometer ionizer fragmentation patterns of the pure compounds. No significant amount of hydrogen was detected. There are clearly two reaction regimes. The first commences at ~450 K and results in the reactive loss of dimethyl disulfide and the concomitant formation of methane. Reaction ceases as the temperature reaches ~650 K and commences once again as the temperature exceeds ~950 K, where the rate continues to increase with increasing temperature. An Auger analysis of the sample following reaction at 1000 K reveals the presence of relatively large amounts of sulfur on the surface,
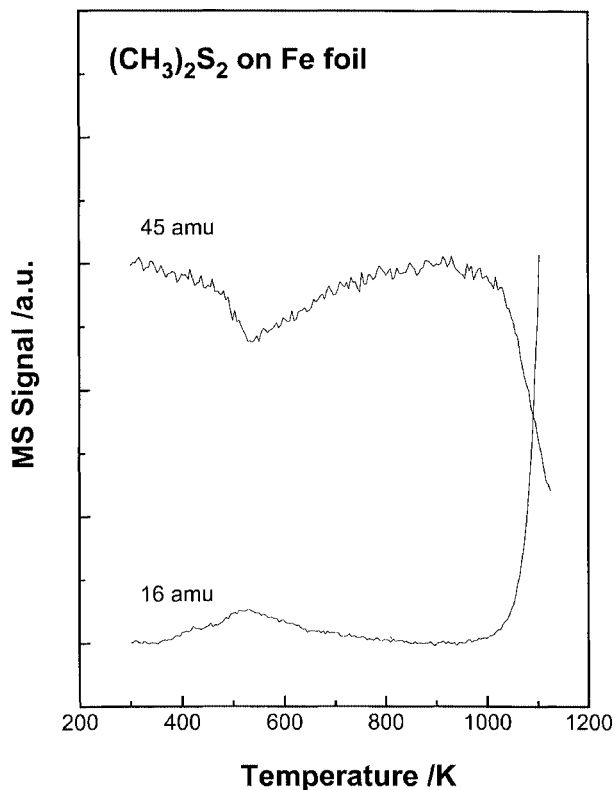

Figure 1. Molecular beam data collected using a heating rate of 3.5 K/s for a beam of dimethyl disulfide incident onto an initially clean iron foil monitoring 45 amu (from dimethyl disulfide) and 16 amu (methane), plotted versus sample temperature. The sample temperature is plotted along the abscissa.

but apparently no carbon. The depth profile of the resulting film is measured by bombarding with argon ions (with energy 3 keV at a current of 1 μA/cm^2) for various times and collecting Auger spectra at various intervals. The resulting data are shown in figure 2 which plots the normalized sulfur (152 eV kinetic energy) and carbon (272 eV kinetic energy) signals as a function of bombardment time. The initially large sulfur signal decreases with increasing time so that after 2 min of ion bombardment, it has decreased to ~10–15% of its original value, while the carbon signal grows. Further ion bombardment causes a further decrease in sulfur signal and a concomitant increase in carbon. These results indicate that the sulfur-containing film grows on a carbon-rich underlayer. Note that the iron film was completely free of carbon prior to commencement of the experiment.

Shown in figure 3 are the corresponding molecular beam data for the reaction of diethyl disulfide ($(C_2H_5)_2S_2$) with initially clean iron. Again two distinct reaction regimes are detected, one that commences at ~500 K and evolves ethylene and hydrogen, which is complete by ~750 K, and a high-temperature region where reaction starts once again at 950 K. The nature of these species were again confirmed by comparison with the mass spectrometer ionizer fragmentation pattern of the pure compounds. Note that no significant ethane formation was detected.
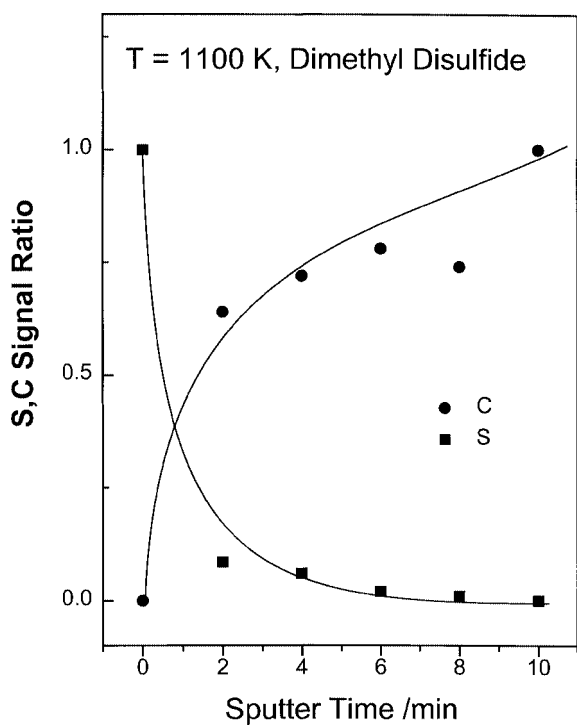
Figure 2. Depth profile of the relative carbon and sulfur concentrations as a function of sputtering time (using an argon ion current of 1 μA/cm^2) for a film grown from dimethyl disulfide at 1100 K.

Figure 4. Plot of seizure load versus additive concentration measured using a pin and v-block apparatus when using dimethyl disulfide (■) and diethyl disulfide (●), as additives.
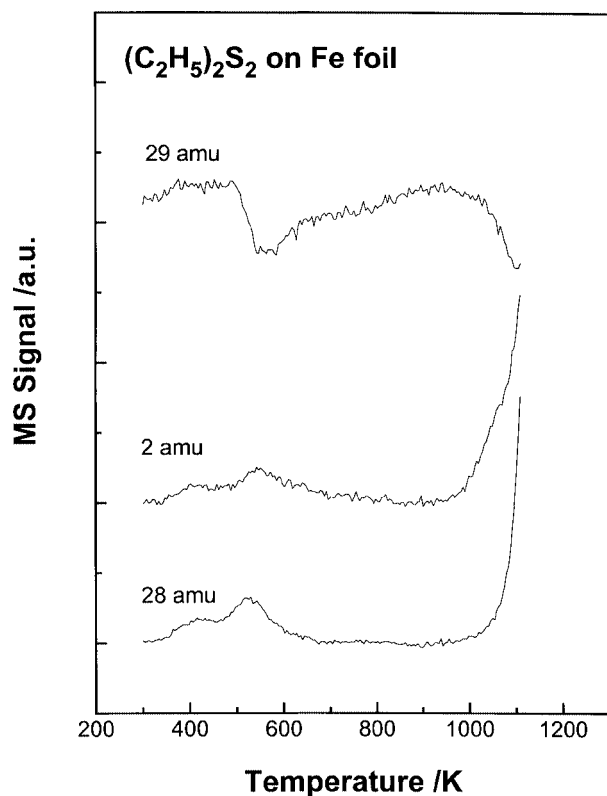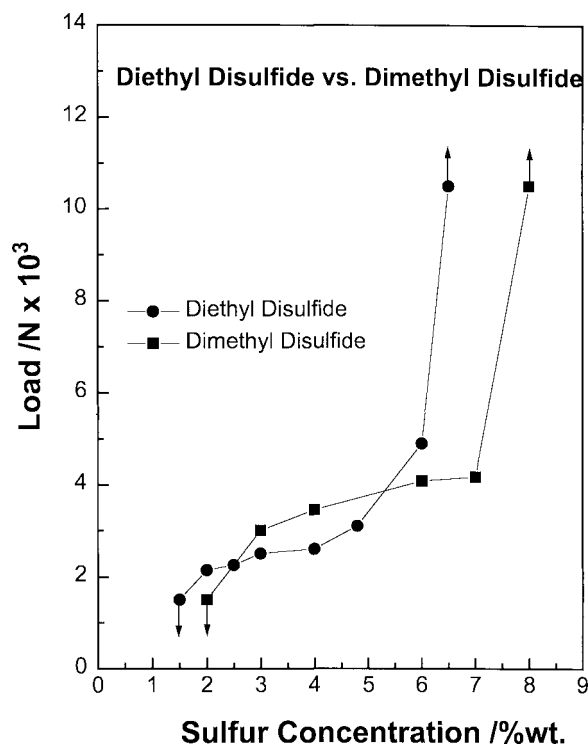

Figure 3. Molecular beam data collected using a heating rate of 3.5 K/s for a beam of diethyl disulfide incident onto an initially clean iron foil monitoring 29 amu (from diethyl disulfide), 28 amu (ethylene) and 2 amu (hydrogen), plotted versus sample temperature. The sample temperature is plotted along the abscissa.

The corresponding plot of seizure load versus additive concentration for a model lubricant consisting of dimethyl disulfide or diethyl disulfide dissolved in a poly α-olefin are displayed in figure 4. In both cases the seizure load increases with increasing additive concentration, reaching initial plateaux at applied loads of $(2.7 \pm 0.1) \times 10^3$ N for diethyl disulfide and $(4.0 \pm 0.1) \times 10^3$ N for dimethyl disulfide. The seizure load continues to increase once again with the addition of further additive. Note that the seizure load in the absence of additive (for pure poly α-olefin) is ~200 N and the friction coefficient measured when using diethyl disulfide is 0.17 ± 0.01 compared to 0.12 ± 0.01 for dimethyl disulfide [29].

4. Discussion

The data of figure 1 show that dimethyl disulfide reacts with initially clean iron to evolve methane from the surface. The adsorption of methanethiol (CH$_3$SH) on iron single crystals has been shown to form thiolate species [32,33]. This thermally decomposes on a sulfur-covered surface to evolve methane in a broad feature centered between ~350 and 500 K, in the same region as found in the molecular beam data of figure 1. In addition, almost no hydrogen was found to desorb from the sulfur-covered surface in accord with the molecular beam data. This suggests that this species is formed by the thermal decomposition of a thiolate species deposited by reaction with the dimethyl disulfide:

2 CH$_3$-S-S-CH$_3$

2 ... S^{CH_3} S^{CH_3} → S S S S C + 3CH$_4$

Scheme 1.
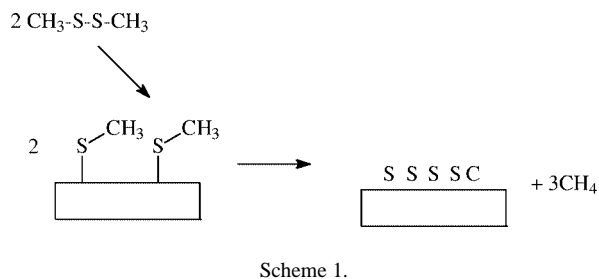
The thiolate decomposes to evolve methane (figure 1) and deposit carbon and sulfur onto the surface. This reaction ceases at ∼650 K because the surface becomes covered by an overlayer of carbon and sulfur. However, as the sample temperature is raised, the carbon and sulfur diffuse into the bulk of the sample. This can be shown by collecting an Auger spectrum of a surface prepared by saturating with dimethyl disulfide at ∼900 K and subsequently annealing *in vacuo* at ∼1000 K; both carbon and sulfur are lost from the surface. The resumption of reaction at above 1000 K (figure 1) is therefore proposed to be due to the diffusion of carbon and sulfur into the surface allowing subsequent surface reactions to take place. It has been shown previously that carbon (when deposited from either CCl$_4$ or CH$_2$Cl$_2$) diffuses into the bulk of the sample at between 600 and 800 K [34], more rapidly than sulfur. This further implies that the resumption of reaction at above ∼1000 K is, in fact, limited by the diffusion of sulfur into the iron sample. The kinetics of film growth by the thermal decomposition of dimethyl disulfide on iron at higher pressures (several Torr) have been measured using a microbalance. In this case, the formation of a slightly non-stoichiometric FeS layer was identified using X-ray diffraction and Raman spectroscopy [29]. The activation energy for film formation under these high-pressure conditions was measured to be 52.5 ± 2.1 kcal/mol. The activation energy for film formation can also be measured using the molecular beam data collected above ∼1000 K by taking the decrease in dimethyl disulfide signal to be proportional to the surface reaction rate. This must be corrected for the effect of the temperature of the desorbing species on the mass spectrometer ionizer sensitivity by multiplying by $\sqrt{T}$, where T is the sample temperature [35]. The resulting Arrhenius plot taken from the data of figure 1 is shown in figure 5. The slope of this curve yields the reaction activation energy directly as 52.5 ± 2.1 kcal/mol, in good agreement with the value measured at higher pressures [29]. These results suggest that similar kinetic processes are being probed in both the high-pressure (microbalance experiments) and low-pressure (molecular beam experiments) regimes. A similar result was found for the film growth kinetics of methylene chloride, chloroform [8,9] and carbon tetrachloride [12,13]. The loss of dimethyl disulfide from the beam at high temperatures (>950 K) is also accompanied by the formation of methane (figure 1) suggesting that reaction still proceeds as shown in scheme 1, but now at a rate limited by the diffusion of sulfur into the bulk of the sample. It is also likely that some thiolate species thermally decompose
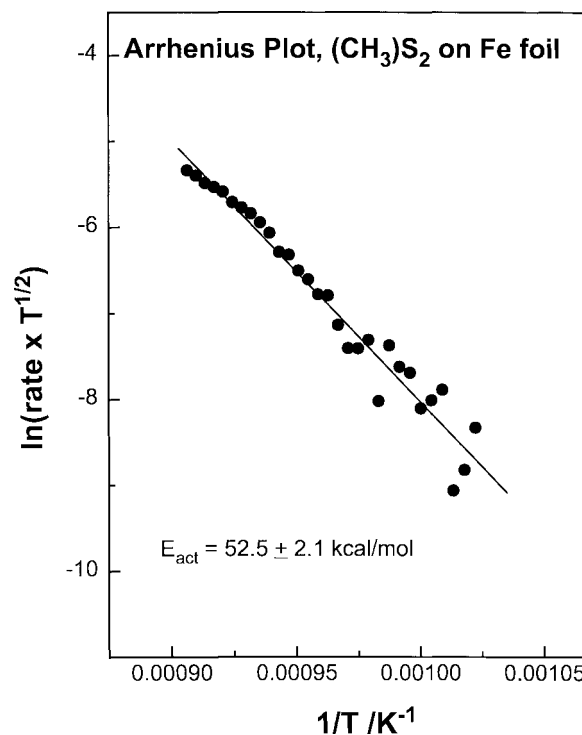

Figure 5. Arrhenius plot for the reaction of dimethyl disulfide on an iron foil taken from the data of figure 1.

without forming methane to yield carbon, sulfur and hydrogen and a slight increase in hydrogen signal is noted at these higher temperatures. A depth profile of a film grown at 1100 K from dimethyl disulfide is shown in figure 2. It is clear that the sulfide film is deposited onto a carbon-enriched substrate. This film structure presumably arises since carbon diffuses into iron more rapidly than sulfur, so that the tribological interface consists of an FeS film on a Fe + C substrate. Raman and X-ray diffraction data of a film grown at higher pressures reveal the presence of a slightly non-stoichiometric FeS layer but, in contrast to similar Raman analyses for a chloride layer, the film appears to contain no carbon particles. The molecular beam data are in accord with this observation; at the higher temperatures required to form the FeS layer, carbon diffuses rapidly into the iron to form a carbon-containing underlayer. The tribological data (figure 4) are consistent with this model. It has been shown that the interfacial temperature in the plateau region of a plot of seizure load versus additive concentration corresponds to the melting point of the interfacial material [1,2]. A similar measurement of the interfacial temperature at the plateau load in figure 4 (■) reveals that this is 1430 ± 100 K, close to the melting point of FeS (1460 K [37]). The interfacial coefficient of friction up to this seizure load is $(12 \pm 1) \times 10^{-2}$, close to values measured when using chlorinated hydrocarbon additives. At first sight, it would appear that a halide film should have a lower friction coefficient since it is much softer than FeS. Bowden and Tabor have suggested that the friction coefficient μ of a thin film of shear strength S_f deposited on a substrate of hardness H_s is given by $\mu = S_f/H_s$ [36].

When sulfur-containing additives are used, the tribological films are proposed to consist of an FeS layer which, according to the data shown in figure 2, is deposited onto a carbided iron substrate. Since the hardness of iron increases considerably with the addition of a small amount of carbon [36], this will substantially lower the friction coefficient compared to a film grown on pure iron since H_s for the carbide is higher than for iron, and may rationalize the relatively low value of friction coefficient found for sulfur-containing additives. The increase in seizure load observed in the data of figure 4 at higher additive concentrations may be due to the presence of the carbide remaining after the sulfide layer has been removed since the melting point of iron carbide is substantially higher than that of the sulfide [38]. A similar effect has been observed previously at higher concentrations when using, for example, chloroform as an EP additive [11].

Two analogous reaction regimes are noted when using diethyl disulfide as an additive (figure 3). In this case, an initial reaction of diethyl disulfide between 500 and 700 K is accompanied by the appearance of ethylene and hydrogen. Only very minor amounts of ethane are detected. This suggests that the surface reaction pathway may be similar to that found for dimethyl disulfide (scheme 1) except that the ethyl thiolate species formed on the surface preferentially react by β-hydride elimination rather than hydrogenation as shown below:

$$C_2H_5\text{-}S\text{-}S\text{-}C_2H_5$$

Scheme 2.
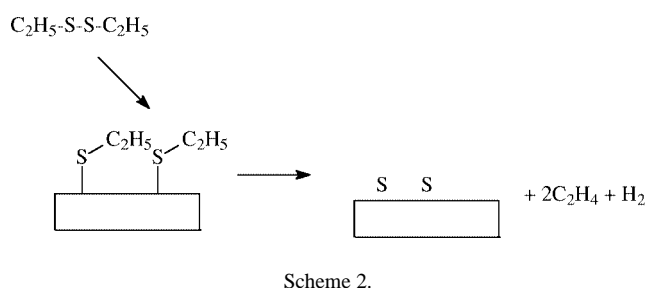
The reaction pathway as written here deposits no carbon onto the surface. It is likely, however, also to be accompanied by a total thermal decomposition of the thiolate species to deposit carbon and sulfur. This reaction ceases at ~600 K again due to the accumulation of sulfur and carbon on the surface, and recommences above ~950 K due to diffusion of sulfur and carbon into the bulk. This process is again accompanied by the formation of ethylene and hydrogen suggesting that reaction still proceeds, as shown in scheme 2. The corresponding Arrhenius plot for this reaction is displayed in figure 6 and yields an activation energy of 60 ± 2.4 kcal/mol; slightly higher than the reaction activation energy for dimethyl disulfide. The origin of this difference is not known. The corresponding plot of seizure load versus additive concentration when using diethyl disulfide as an additive is shown in figure 4 (●). The shape of the curve is very similar to that found when using dimethyl disulfide and the temperature in the plateau region (after correcting for interfacial friction coefficient; 0.17 ± 0.01) is 1400 ± 100 K, again close to the melting point of FeS
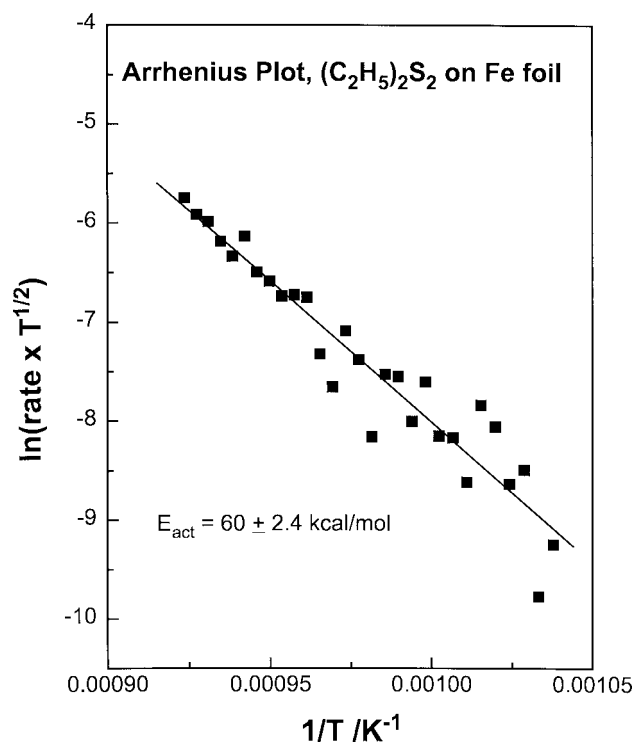

Figure 6. Arrhenius plot for the reaction of diethyl disulfide on an iron foil taken from the data of figure 2.

$(1460 \text{ K } [38])$. The subsequent increase in seizure load at higher additive concentrations is again proposed to be due to the effect of the remaining carbide layer. According to the above discussion, the higher friction coefficient found when using diethyl disulfide compared to dimethyl disulfide $(0.17 \text{ versus } 0.12)$ may be due to the lower amount of carbon deposited from diethyl disulfide (scheme 2) than dimethyl disulfide (scheme 1).

5. Conclusions

Dimethyl and diethyl disulfide react on clean iron in two regimes. Reaction initially ceases due to the formation of a saturated sulfur + carbon overlayer but commences once again at higher temperatures as the sulfur diffuses into the bulk of the film to form a sulfide film deposited onto a Fe + C underlayer. This film structure may account for the relatively low value of friction coefficient found for this sulfide film. Dimethyl disulfide reacts to form surface methyl thiolate species which decompose to yield methane. Similar ethyl thiolate films formed from diethyl disulfide react via a β-hydride elimination reaction to yield predominantly ethylene.

Acknowledgement

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