

# Surface Chemistry of Tribochemical Reactions: Molecular Beam Experiments\*

<sup>a</sup>J. LARA-ROMERO, <sup>a</sup>R. MAYA-YESCAS, <sup>a</sup>J. L. RICO-CERDA, <sup>a</sup>J. L. RIVERA-ROJAS,  
<sup>b</sup>F. CHIÑAS CASTILLO, <sup>c</sup>M. KALTCHEV, and <sup>d</sup>W. T. TYSOE

<sup>a</sup>*Faculty of Chemical Engineering, Universidad Michoacana de San Nicolás de Hidalgo, MX-58000 Morelia  
e-mail: lararom@zeus.umich.mx*

<sup>b</sup>*Mechanical Engineering Department, Instituto Tecnológico de Oaxaca, MX-68030 Oaxaca*

<sup>c</sup>*Department of Chemistry and Physics, Milwaukee School of Engineering, WI-53211 Milwaukee*

<sup>d</sup>*Department of Chemistry and Biochemistry, University of Wisconsin-Milwaukee, WI-53211 Milwaukee*

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The thermal decomposition of model chlorine- and sulfur-containing extreme-pressure lubricant additives on clean iron was studied in ultrahigh vacuum conditions using molecular beam strategies. Methylene chloride and chloroform react to deposit a solid film consisting of FeCl<sub>2</sub> and carbon, and evolve only hydrogen into the gas phase. No gas-phase products and less carbon on the surface are detected in the case of carbon tetrachloride. Dimethyl and diethyl disulfide react on clean iron to deposit a saturated sulfur plus carbon layer at low temperatures (~ 600 K) and an iron sulfide film onto an Fe + C underlayer at higher temperatures (~ 950 K). Methane is the only gas-phase product when dimethyl disulfide reacts with iron. Ethylene and hydrogen are detected when diethyl disulfide is used.

Extreme-pressure (EP) lubricants are used in a wide range of metalworking applications such as severe stainless steel-forming operations or fine blanking heavy parts for the auto industry. Chlorine- and sulfur-containing hydrocarbons are commonly added to a base fluid for the synthesis of lubricants, which are used under the conditions where interfacial temperatures exceeding 1000 K could be attained. These additives thermally decompose at the hot interface to reactively form a solid lubricating film [1–5]. Extreme-pressure lubrication can be described as a dynamic process where the resulting film thickness at the lubricated interface arises from a balance between the film growth rate and the removal rate. The nature of the film and the growth rate depends on the chemical structure of the additive used. Chlorinated hydrocarbons (methylene chloride, chloroform, and carbon tetrachloride) have been used as model additives [6–8]. It has been shown that methylene chloride and chloroform form films that consist of FeCl<sub>2</sub> incorporating carbonaceous particles [6, 7]. When using carbon tetrachloride, iron carbide is formed leading to a much more effective lubrication [8]. Sulfur-containing EP additives generally comprise molecules with sul-

fur linkages, *e.g.* dimethyl disulfide and diethyl disulfide [9–11]. These substances thermally decompose to form films consisting of FeS [12].

Molecular beam experiments carried out in ultrahigh vacuum conditions can mimic the tribological interface where a hot and clean iron surface can be exposed to the EP additive. The advantage of this strategy is that the gas-phase products can be monitored, the nature of the films can be determined, and the film growth rate can also be measured. The main goal of this work is to provide a better understanding of the chemical interaction that may take place in a tribological interface by using molecular beam experiments.

## EXPERIMENTAL

Tribological behaviour of the model chlorine- and sulfur-containing EP additives was measured using a pin and v-block apparatus, which is able to reproduce extreme-pressure conditions [1, 2]. The model lubricants were synthesized by dissolving the model additive in poly- $\alpha$ -olefin. The steel pin and steel v-blocks were immersed in the EP lubricant. Concentration of the EP additive was measured using infrared spec-

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troscopy (FTIR Nicolet 550) throughout the whole experiment in order to guarantee a constant concentration of the additive. The pin, while clamped between the v-shaped blocks, was rotated at a constant angular velocity ( $290 \text{ min}^{-1}$ ) and both the applied load and the torque required to rotate the pin were simultaneously monitored. As the applied load was increased, the torque increased correspondingly. When the lubricant failed, a sudden rise in the torque was detected and the corresponding load was designated as the seizure load. A plot of seizure load *vs.* additive concentration was used to describe the tribological performance of all model additives.

Molecular beam experiments were carried out in a stainless steel, ultrahigh vacuum chamber pumped after bake-out down to  $\sim 1.3 \times 10^{-8} \text{ Pa}$  by means of a combination of ion and sublimation pumps (Varian ion pump model 912-7000 and a Leybold titanium sublimation pump model TSP45, respectively). A pure iron foil sample (Aesar, 99.999 %) was mounted at the end of a carousel manipulator and could be heated to  $\sim 1200 \text{ K}$ . The chamber was equipped with a cylindrical mirror analyser used for Auger surface analysis (PHI model 15-255) and a quadrupole mass spectrometer for monitoring the gas-phase reaction products. The mass spectrometer (Hiden HAL 301/3F) was able to monitor up to 5 different masses simultaneously. The EP additive molecular beam was generated by leaking the reactant through a 1 mm internal diameter capillary tube connected to a leak valve. The beam of molecules was incident at  $\sim 70^\circ$  to the normal onto the iron sample. The iron foil was located in front of the mass spectrometer and heated at a constant rate of  $3.5 \text{ K s}^{-1}$ . The iron sample was analysed with Auger before and after the reaction. Prior to the reaction, the sample was cleaned by repeated cycles of annealing and argon bombardment until no species were detected with the Auger analyser. Methylene chloride, chloroform, carbon tetrachloride, dimethyl disulfide, and diethyl disulfide (Aldrich, 99 %) were purified by repeated freeze-pump-thaw cycles and dosed to the chamber using the gas-handling glass line attached to the system [13].

## RESULTS

Fig. 1 shows results of the tribological experiments using the pin and v-block apparatus. The plot depicts the seizure load *vs.* concentration of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ), and carbon tetrachloride ( $\text{CCl}_4$ ) as model EP lubricant additives. The concentration was normalized to chlorine concentration for each additive. Two clearly differing types of behaviour were found. The first one characterised the seizure load changes in the presence of methylene chloride and chloroform. In this case, the seizure load was initially increasing with the additive concentration. However, at certain chlorine concentration the

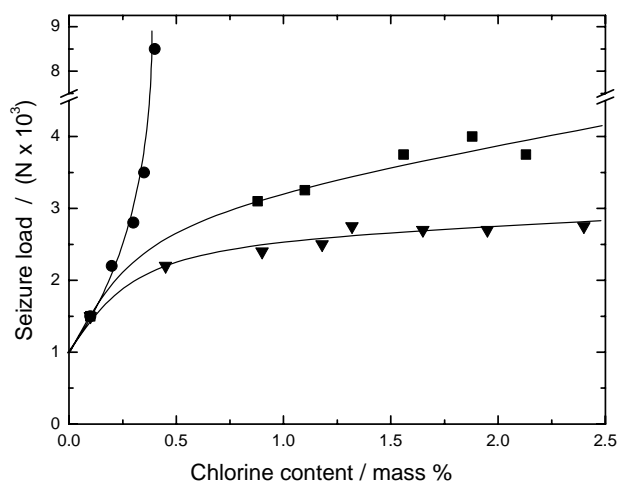


Fig. 1. Seizure load variation with chlorinated additive content:  $\text{CH}_2\text{Cl}_2$  ( $\blacktriangledown$ ),  $\text{CHCl}_3$  ( $\blacksquare$ ), and  $\text{CCl}_4$  ( $\bullet$ ).

seizure load reached a plateau. In contrast, the experiments in the presence of carbon tetrachloride showed a continuous increase of the seizure load at low concentration. It has been shown that the temperature at the interface between a pin and v-block can be estimated using the expression [4]

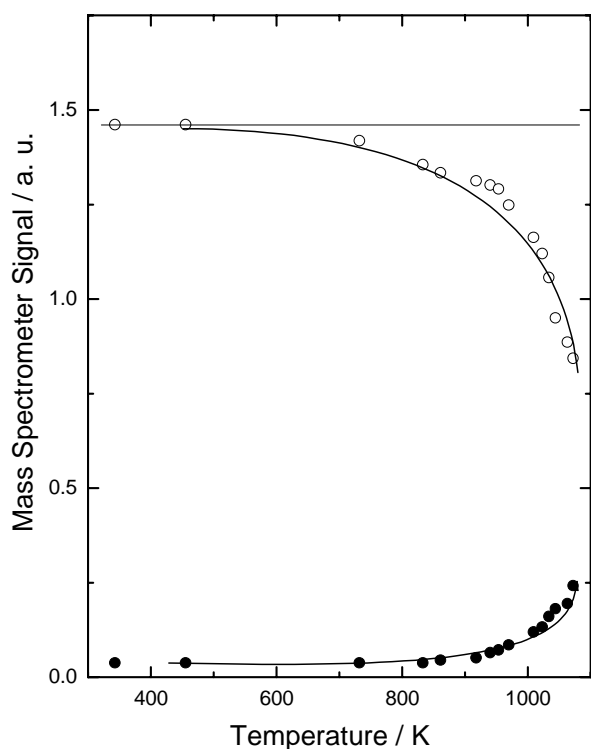
$$T = T_0 + \alpha L \quad (1)$$

where  $T_0$  is the bath temperature and  $\alpha$  is a constant depending on the friction coefficient characteristic of each additive.

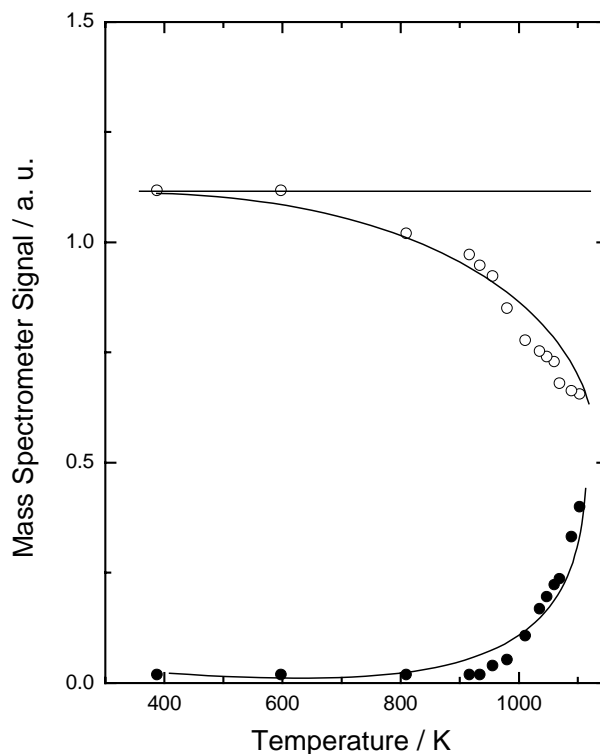
The temperature estimated at the plateau found during experiments with methylene chloride and chloroform was about 940 K. Carbon tetrachloride allowed reaching much higher interfacial temperatures showing better tribological performance. These results suggest that the presence of carbon tetrachloride in lubricant enables faster growth of the tribological film. Moreover, the film chemical nature differs from that of the films formed by methylene chloride and chloroform.

In Figs. 2–4 results of the molecular beam experiments are plotted showing the variation of signal for  $\text{CH}_2\text{Cl}_2$  (49 amu),  $\text{CHCl}_3$  (83 amu), and  $\text{CCl}_4$  (118 amu) with the sample temperature, respectively. The signals were corrected for their respective mass spectrometer ioniser sensitivities. Figs. 2 and 3 show the decrease of methylene chloride and chloroform signals at about 700 K and a corresponding increase of the hydrogen signal (2 amu). No gas-phase products were detected in the case of carbon tetrachloride (Fig. 4); only a decrease of the  $\text{CCl}_4$  signal at  $\sim 700 \text{ K}$  was observed as well.

These temperature data can be plotted in Arrhenius form by calculating a rate flux  $\theta$  by multiplying the mass spectrometer signal by  $\sqrt{T}$  to take into account the variation of desorbing species as a func-



**Fig. 2.** Variation of  $\text{CH}_2\text{Cl}_2$ , 49 amu ( $\circ$ ) and  $\text{H}_2$ , 2 amu ( $\bullet$ ) amount with the sample temperature during molecular beam experiments with  $\text{CH}_2\text{Cl}_2$  on iron foil at  $2.4 \times 10^{-7}$  Pa.

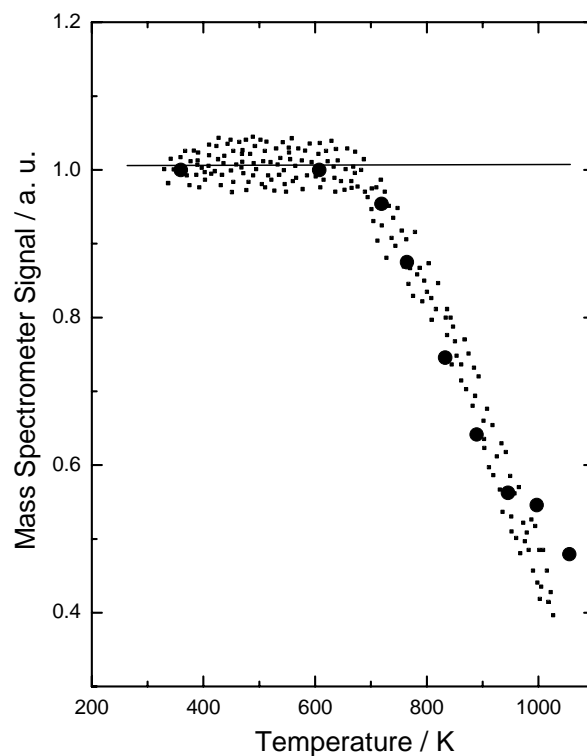


**Fig. 3.** Variation of  $\text{CHCl}_3$ , 83 amu ( $\circ$ ) and  $\text{H}_2$ , 2 amu ( $\bullet$ ) amount with the sample temperature during molecular beam experiments with  $\text{CHCl}_3$  on iron foil at  $2.7 \times 10^{-7}$  Pa.

tion of sample temperature (not shown). This yields activation energies for the consumption of methylene chloride, chloroform, and carbon tetrachloride of  $41.0 \pm 3.8 \text{ kJ mol}^{-1}$ ,  $34.7 \pm 3.8 \text{ kJ mol}^{-1}$ , and  $59.4 \pm 2.1 \text{ kJ mol}^{-1}$ , respectively. These values were compared with the corresponding activation energies obtained directly from the film growth measurements at high pressures. After each experiment, the surface of the sample was analysed using X-ray photoelectron and Auger spectroscopy to determine the products in the solid phase. A Cl 2p X-ray photoelectron spectrum is displayed in Fig. 5. In this picture, the characteristic feature centred at 198.6 eV corresponds to iron halide,  $\text{FeCl}_2$ .

Auger analysis showed large Cl (180 eV) and Fe (590 eV, 650 eV, and 710 eV) signals confirming formation of  $\text{FeCl}_2$ . In addition, small amount of carbon was detected at  $\sim 273$  eV. Fig. 6 represents the Auger chlorine-to-iron intensity ratio measured for methylene chloride and carbon tetrachloride.

The amount of carbon deposited on the iron foil surface at low temperature was higher when  $\text{CH}_2\text{Cl}_2$  was used compared to the amount corresponding to the  $\text{CCl}_4$  carbon deposits. By heating the sample, the amount of carbon on the surface decreased due to diffusion into the sample bulk since no carbon-containing species were detected in the gas phase. Carbon deposited from carbon tetrachlo-



**Fig. 4.** Variation of  $\text{CCl}_4$  amount (118 amu) with the sample temperature during molecular beam experiments with  $\text{CCl}_4$  on iron foil at  $2.7 \times 10^{-7}$  Pa.

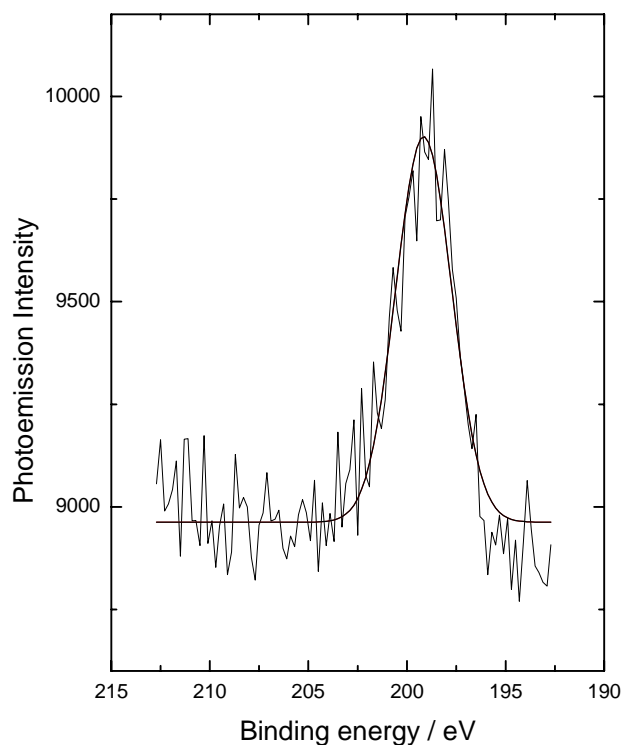


Fig. 5. Typical Cl 2p X-ray photoelectron spectrum obtained after the reaction of  $\text{CCl}_4$  with iron foil at 900 K.

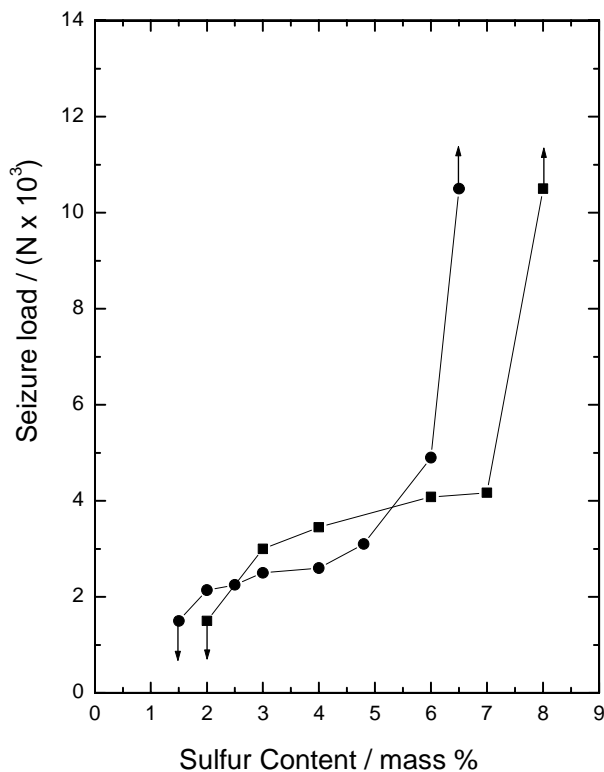


Fig. 7. Seizure load variation with sulfur-comprising additive content: dimethyl disulfide (■) and diethyl disulfide (●).

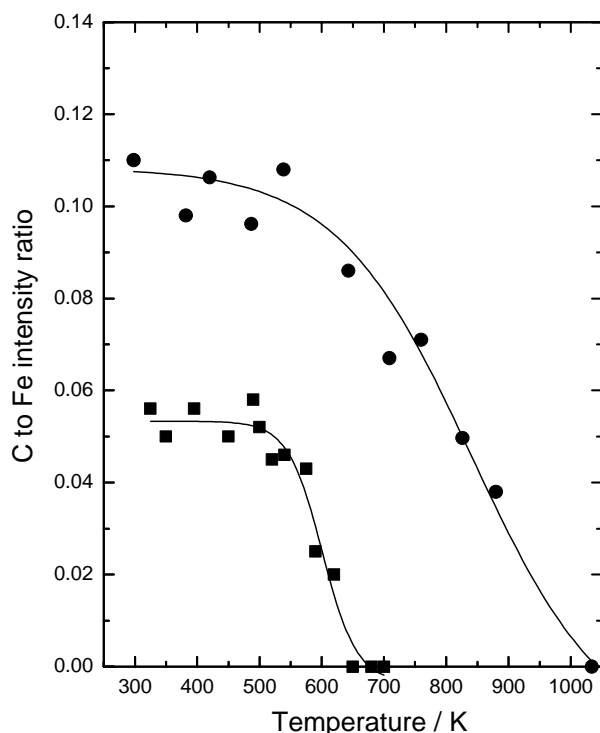


Fig. 6. Variation of carbon to iron peak intensity ratio measured by Auger spectroscopy. Samples of clean iron foil saturated with  $\text{CH}_2\text{Cl}_2$  (●) and  $\text{CCl}_4$  (■).

ride diffused from the surface into the sample bulk much faster than that formed from methylene chlo-

ride. This indicates why carbides are formed more easily from  $\text{CCl}_4$  than from  $\text{CH}_2\text{Cl}_2$ . Moreover, the presence of a large amount of co-adsorbed chlorine seems to facilitate the surface-to-bulk transport of carbon.

Fig. 7 shows the tribological behaviour of dimethyl disulfide and diethyl disulfide in extreme-pressure conditions. In both cases the seizure load increased with increasing additive concentration reaching an initial plateau, at which the estimated interfacial temperature was about 1430 K. At higher sulfur concentrations, even higher seizure loads and interfacial temperatures could be reached indicating the presence of different species at the sample interface.

Fig. 8 shows that dimethyl disulfide (45 amu) and methane (16 amu) were the only products found in the gas phase throughout the whole temperature range studied. From the course of measured curves it can be deduced that the surface reaction proceeds at two different temperature ranges. Dimethyl disulfide conversion and methane formation starts at about 450 K and stops at  $\sim 650$  K. Re-appearance of the reaction products was detected again at approximately 950 K. Starting from this point, the reaction rate was directly proportional to the temperature. The activation energies estimated from Arrhenius plot of the high-temperature processes were  $219.5 \pm 8.8 \text{ kJ mol}^{-1}$  for dimethyl disulfide and  $250.8 \pm 10.0 \text{ kJ mol}^{-1}$  for diethyl disulfide.

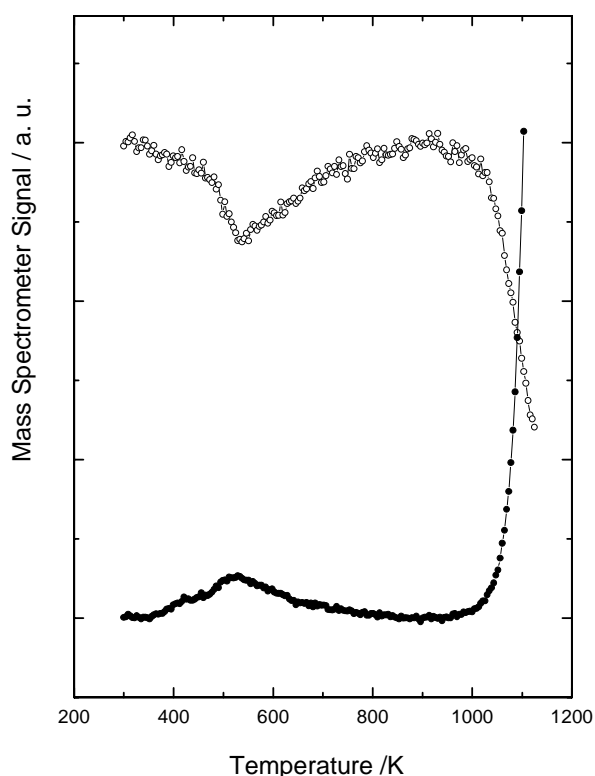


Fig. 8. Variation of dimethyl disulfide, 45 amu (○) and CH<sub>4</sub>, 16 amu (●) amount with the sample temperature during molecular beam experiments with (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> on iron foil at  $2.4 \times 10^{-7}$  Pa.

Auger analysis of the sample, at which the reaction was carried out at 1000 K revealed the presence of large amounts of sulfur (152 eV) on the sample surface. However, apparently no carbon was present at the iron foil surface.

A depth profile of the film after repeated cycles of argon ion bombardments showed a decrease of the sulfur signal and an increase of the carbon signal (273 eV), as displayed in Fig. 9. These results indicate that the sulfur-containing film grew on top of carbon-rich underlayer.

Similarly, in Fig. 10 the corresponding molecular beam data for the surface reaction of diethyl disulfide (29 amu) on a clean iron sample are shown. Again, two regimes of the surface reaction were detected, the first one starting at  $\sim 500$  K and the second one at the high-temperature region (more than 950 K). During the reaction ethylene (28 amu) and hydrogen (2 amu) were detected in the gas phase.

## DISCUSSION

The data shown in Fig. 1 confirmed that CCl<sub>4</sub> exhibits the best tribological performance of all chlorine-containing lubricant additives tested. Based on the molecular beam experiments, carbon from carbon tetrachloride diffuses into the iron substrate much

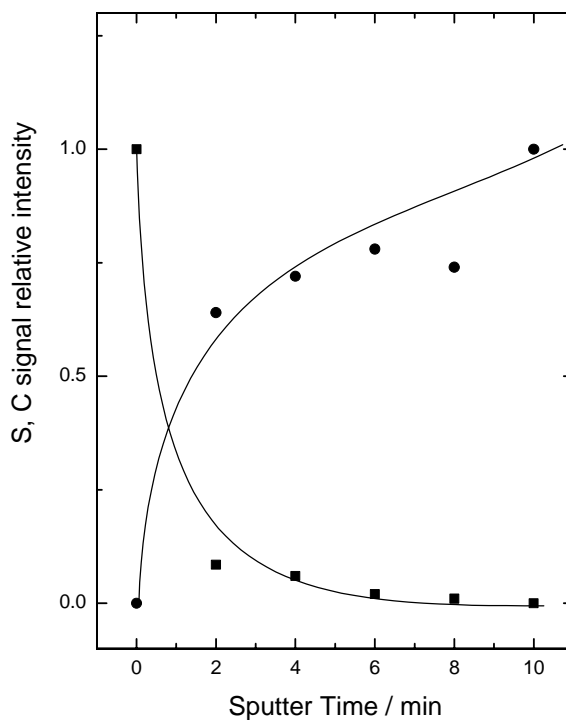


Fig. 9. Auger depth profile of carbon (●) and sulfur (■) signal relative intensity corresponding to a film growth at 1100 K in the presence of dimethyl disulfide.

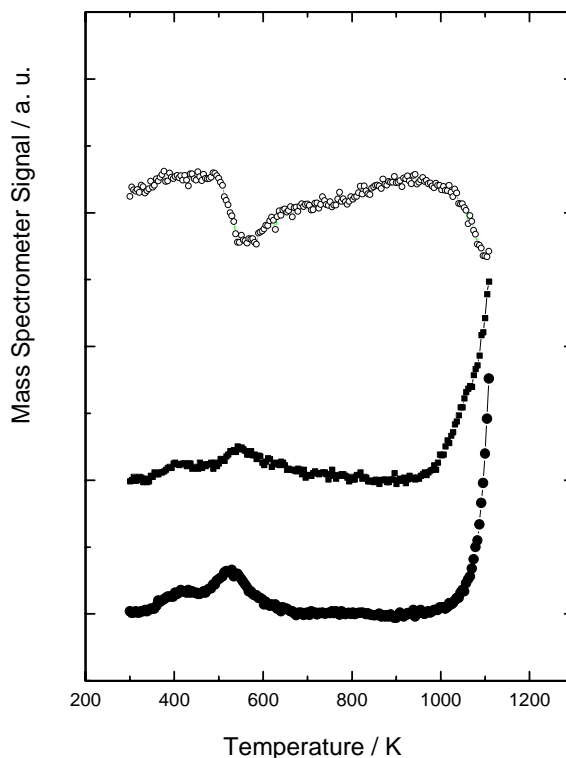


Fig. 10. Variation of diethyl disulfide, 29 amu (○), C<sub>2</sub>H<sub>4</sub>, 28 amu (●), and H<sub>2</sub>, 2 amu (■) amount with the sample temperature during molecular beam experiments with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub> on iron foil at  $2.4 \times 10^{-7}$  Pa.

faster than carbon released from methylene chloride or chloroform. This carbon eventually favours the formation of iron carbide under layer. *Bowden* and *Tabor* suggested that the friction coefficient  $\mu$  of a thin film of share strength  $S_f$  deposited on a substrate of hardness  $H_s$  is given by the equation  $\mu = S_f/H_s$  [14]. Since the hardness of the iron increases with the addition of a small amount of carbon, this will substantially lower the friction coefficient compared to a film grown on pure iron, as the iron carbide hardness is higher than the corresponding one of iron.

The seizure load increase (higher interfacial temperatures) even at such low additive concentration may be explained taking into account the iron carbide presence. Once the iron chloride film has been removed, the iron carbide-containing layer with substantially higher melting point is exposed [15].

Dimethyl disulfide and diethyl disulfide allowed reaching a high seizure load at high additive content in the lubricant. FeS layer growth on top of a carbon-rich iron substrate (iron carbide) was observed. Once the iron sulfide film was removed from the tribological interface, the iron carbide layer was able to sustain the high seizure load and high interfacial temperatures experienced at extreme-pressure conditions.

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