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CATALYTIC HYDRODESULFURIZATION OVER THE
Mo(100) SINGLE CRYSTAL SURFACE II:
THE ROLE OF ADSORBED SULFUR AND MECHANISM OF THE DESULFURIZATION STEP

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A B S T R A C T

The study of thiophene hydrodesulfurization over initially clean Mo(100) surfaces has been extended to include sulfided surfaces. Low sulfur coverages ($0 \leq \theta_s < 0.67$) inhibit HDS activity. Increasing the sulfur coverage in the range $0.67 \leq \theta_s \leq 1.0$ produces a surface with an HDS activity of about half that of the clean Mo(100) surface. Excessive exposure of the surface to a sulfur containing environment results in the formation of a MoS_2 layer which is, at least in part, responsible for complete catalytic deactivation. Radiotracer (^{35}S) labelling techniques have been used to measure rates of hydrogenation of sulfur adsorbed on the Mo(100) surface. In ambient atmospheres of both hydrogen (1 atm.) and the thiophene HDS reaction mixture ($P(\text{H}_2) = 1 \text{ atm.}$, $P(\text{Th}) = 2.5 \text{ Torr}$) the rate of hydrogenation of adsorbed sulfur is two orders of magnitude less than the HDS rate. This fact has been used to suggest that the desulfurization step of the reaction does not proceed via the formation of a tightly bound Mo-S species.

1. INTRODUCTION

The preceding paper has shown that Mo single crystal surfaces can be used to model and study the molybdenum sulfide based catalysts used for the hydrodesulfurization process.¹ The overall mechanistic pathway is initiated by a desulfurization step leading to the formation of butadiene. Subsequent hydrogenation of an adsorbed hydrocarbon intermediate results in butene and butane production. The mechanism of the initial step is in question and it is the aim of this work to ascertain the nature of this reaction and to determine the effect of adsorbed sulfur on the activity of the catalyst.

The model most frequently proposed for the desulfurization step is that originally described by Lipsch and Schuit.³ Initial adsorption of the sulfur containing organic molecule is postulated to be at an anion vacancy on the catalyst surface (in this case an oxygen or sulfur vacancy). The exact geometry and nature of the bonding is not specified although on the basis of theoretical calculations^{4,5} it was suggested that thiophene should bond through the electron lone pair on the sulfur atom. On the other hand, surface science studies of molecular thiophene adsorption on Cu, Pt and Mo surfaces point to a π -bonded configuration.^{6,7,8} Subsequent hydrogenation of the C-S bonds leads to production of butadiene and deposition of sulfur onto the catalyst surface. Final steps involve the hydrogenation of the adsorbed sulfur to H_2S and the further hydrogenation of the hydrocarbon. It should be noted, however, that there is very little direct evidence for this mechanism other than a series of experiments using a catalyst labelled with ^{35}S .⁹ These showed that for the HDS reaction of dibenzothiophene over a sulfided Mo catalyst there is a labile sulfur species, present on the catalyst, that is an intermediate in the reaction leading to H_2S .

It is possible to envision a number of HDS mechanisms that do not proceed via the formation of an Mo-S species. Direct hydrogenation of C-S bonds to yield H_2S and a surface bound hydrocarbon intermediate is one such possibility. Such a mechanism has been proposed leading from dibenzothiophene to mercaptobiphenyl which is then hydrogenated to biphenyl and H_2S .¹⁰ In the case of thiophene HDS, a mechanism has been proposed similar to that of an alcohol dehydration reaction, in which the desulfurization occurs by an intramolecular hydrogenation of the sulfur atom leaving diacetylene as the hydrocarbon product.¹¹ Investigations of the HDS of thiophene in D_2 showed

that the sulfur containing product was H_2S rather than D_2S , in direct agreement with this mechanism.¹² Such a reaction does not require the formation of a metal-sulfur bond but is impossible in the case dibenzothiophene.

This study extends the investigation of the catalytic activity of Mo(100) single crystal surfaces to study the effect of adsorbed sulfur. We have measured the rate of thiophene HDS as a function of sulfur coverage and the stability of adsorbed sulfur under reaction conditions. Using a ^{35}S isotope we have been able to make direct measurements of the rate of sulfur removal from the metal surface during exposure to either H_2 or the reaction mixture. Periodic removal of the crystal from the reaction environment allows determination of the amount of ^{35}S remaining on the surface by monitoring of its β^- emission. Using this approach it is possible to discriminate between sulfur that has been deposited directly on the metal surface under UHV conditions and sulfur that has been deposited in the form of adsorbed thiophene or via the decomposition of thiophene under reaction conditions.

2. Experimental

The surface analysis chamber and methods used to perform high pressure catalytic reactions have been described in the previous paper of this pair.

In addition to the equipment described previously, a solid state β^- detector was installed specifically for this work. The details of its operating characteristics and the data collection system have been described elsewhere¹⁵. Briefly, the detector consists of an n-type silicon wafer with a 300 micron thick depletion region. A potential of 100 volts is applied across the silicon wafer via thin film gold contacts on either side of the wafer.

High energy electrons impinging on the silicon wafer create free charge carriers that are separated by the potential bias and measured as a current pulse at the contacts. The amplitude of the current pulse is proportional to the energy of the impinging electron. The detector is held in a rotatable mount allowing it to be directed away from the crystal when the crystal is exposed to $C^{35}S_2$ and during atmospheric pressure reactions. The detector mount was attached to a liquid nitrogen reservoir via copper braids. During operation, the detector was cooled to approximately $-35^{\circ}C$ in order to minimize the dark current.

Beta emission from the ^{35}S adsorbed on the Mo(100) surface was measured by rotating the detector so that it faced the center of the crystal. The crystal was then moved up to a position approximately 2mm from the front face of the detector. The detecting surface is 8mm in diameter and is smaller than the single crystal which has a diameter of 10mm. Furthermore, the detecting surface is recessed by 2mm into the detector unit itself resulting in a geometry in which the detecting surface is quite well screened from all surfaces other than the one under study.

The background β^{-} emission from the support rods could be estimated quite simply by first adsorbing a saturation amount of sulfur on the sample and then cleaning it by heating to $1600^{\circ}C$. The sample was mounted between two thick (0.125" dia.) tantalum support rods and was attached to these via two small tantalum wires (0.02" dia. x 0.05"). Thermal insulation from the thick support rods was such that they did not heat to more than $600^{\circ}C$ while heating the sample to $1600^{\circ}C$. At these temperatures sulfur will not desorb from the tantalum supports. The supports were observed to contribute a background count rate of 300-400 cpm which was subtracted from the total count rate to

determine the contribution from sulfur adsorbed to the Mo(100) surface. The background represents about 25% of the total measured count rate. The tantalum supports became saturated with sulfur within a couple exposures of the crystal to the $C^{35}S_2$ after which the background current remained constant.

^{35}S deposition was accomplished by decomposition of labelled $C^{35}S_2$. The labelled compound was obtained from New England Nuclear Corp. at an initial activity of 100 mCi/mole (^{35}S half-life = 87.9 days) and a radiochemical purity of better than 99%. The material was stored in a breakseal tube with a teflon stopcock. The crystal was exposed to the $C^{35}S_2$ vapor via a doser attached to a leak valve. Use of the doser allowed exposure of the crystal while minimizing the exposure of the remainder of the chamber to $C^{35}S_2$. Sulfur overlayers were produced by exposure of the crystal to $C^{35}S_2$ followed by annealing to 800-1000°C. Heating of the crystal serves to dissociate the $C^{35}S_2$ and causes the carbon to dissolve into the bulk of the sample. In general heating a Mo crystal will cause segregation of carbon to the clean surface, however, in the presence of surface sulfur, carbon dissolves into the crystal bulk. A similar effect was reported in the case of nickel in which surface sulfur alters the thermodynamics of carbon segregation.¹⁶ Two or three such treatments with exposures totalling approximately 45×10^{-9} torr sec were sufficient to produce a sulfur overlayer at a coverage of $\theta_s = 0.75$ in a c(4x2) structure identical to that produced using exposures to either H_2S or S_2 . It was not possible, however, to produce overlayers of higher coverage using this approach. The calibration of AES signal and LEED patterns versus sulfur coverage on the Mo(100) surface has been discussed elsewhere.^{8,17}

The procedure used in performing this set of experiments began with cleaning of the surface by flashing to 1600°C followed by a measurement of the beta emission from the clean surface to determine the background count of the sample holder. The surface was sulfided with labelled ^{35}S and the coverage determined. The coverage was determined with the aid of AES, LEED and β^- emission measurements. The sulfided surface was enclosed in the isolation cell which was then pressurized with either H_2 or a mixture of H_2 and thiophene. In the cases in which mixtures were used the gases were circulated through a batch reactor loop for approximately 30 minutes to ensure mixing of the gases before heating the crystal. The reactor loop was made of 1/4" stainless steel and was attached with both an inlet and an outlet to the cell. After mixing was complete the crystal was heated resistively to the desired temperature, usually for a period of five minutes. The temperature was maintained by a controller which monitored the potential across the Pt-Pt/Rh 10% thermocouple attached to the crystal. After heating, the crystal was allowed to cool in the gas mixture which was then pumped out of the cell using a mechanical pump followed by an oil diffusion pump. In the case of a pure hydrogen atmosphere the cell was evacuated for 15 minutes while on the occasions in which a hydrogen/thiophene mixture was used, the evacuation time was about 2 hours. The cell was then opened exposing the crystal to ultra-high vacuum conditions and a measurement was made of the beta emission from the surface to determine the coverage of ^{35}S remaining on the surface. The procedure was repeated using either the existing surface or a freshly prepared surface as necessary.

3. Results

3.1 The Effect of Adsorbed Sulfur on Thiophene HDS

Figure 1a depicts the rate of thiophene hydrodesulfurization over the Mo(100) surface as a function of sulfur coverage. The initial sulfiding of the surface, under UHV conditions, prior to the reaction resulted in a decrease in activity at low coverages which continued to decrease up to a coverage of approximately 0.6, beyond which the further addition of sulfur had very little effect. The activity of the surface at these coverages was reduced to almost half that of the clean surface. The fact that the addition of sulfur to the surface can inhibit the reaction suggests that this adsorbed sulfur species remains on the surface during the reaction and thus cannot be an intermediate species in the reaction mechanism. It is also interesting to note in Fig. 1b that the HDS reaction products are not uniformly affected by the presence of sulfur. While the rates of butene and butane production follow the behavior described above, the rate of butadiene production is virtually unaffected by adsorbed sulfur.

The inhibition of the reaction rate at low coverages is caused by sulfur atoms adsorbed in fourfold hollow sites on the surface⁸. This sulfur must remain adsorbed on the surface during the reaction. At high coverages ($\theta_S > 0.67$) the sulfur atom is adsorbed in a second, less tightly binding site.⁸ The fact that the addition of sulfur to the surface at these high coverages has little additional effect on the reaction rate suggests that the sulfur in this second binding site is easily reduced and that removal of sulfur from this site is relatively fast. This implies that a reaction that is initiated on a metal surface that is initially covered with one monolayer

of sulfur results in an immediate reduction of this coverage to the point at which only hollow sites are occupied. Immediate reduction implies a reaction that is fast on the time scale by which HDS rates are measured (~15 min).

3.2 Deactivation of the Mo(100) Catalyst

Extended exposure of the Mo(100) surface to the HDS reaction mixture resulted in a very high surface sulfur coverage that was accompanied by formation of an MoS₂ compound overlayer and a lower HDS activity. This is a process that is distinct from the inhibition of activity by sulfur pre-adsorbed under UHV conditions in that it involves the formation of an MoS₂ compound overlayer.

After a period of steady state activity of about 90 min. the reaction rate over the single crystal surface begins to fall until, after ~ 12 hours there is no further activity under our experimental conditions. Although turnover numbers at this point are in excess of 1500 the total conversion of reactants is <15%. The long term deactivation of the catalytic surface has not been investigated thoroughly as yet but several possible causes exist. Competition for reactant adsorption sites by the H₂S product has been observed over dispersed catalysts. In our batch reactor this could lead ultimately to the complete deactivation of the catalyst as the H₂S partial pressure is continuously increasing. A second effect that may lead to catalyst deactivation is the growth of a MoS₂ overlayer oriented to expose its inactive basal plane. A typical AES spectrum of the crystal surface after a long reaction time yields a S₁₅₀:Mo₂₂₁ AES ratio that approaches the value of ~12:1 observed for a MoS₂ single crystal.¹³ In general no LEED pattern can be observed from the surface unless the duration of the reaction is fairly short, in which case the sulfur coverage is less than a monolayer and a square lattice due to diffraction from the Mo(100) substrate can be observed.

Annealing of a heavily sulfided surface to 800-1100K will produce the LEED pattern shown in Ref. 2 with no significant change in the AES spectrum. This LEED pattern has diffraction spots forming a square lattice, again produced by the substrate, and a circle of diffraction intensity with twelve maxima about its perimeter. These are due to diffraction from two domains of a hexagonal overlayer rotated at 30° with respect to each other. The lattice spacing of this hexagonal overlayer is $3.11\text{\AA} \pm 0.05\text{\AA}$ which is almost identical to that of MoS_2 (3.15\AA).¹⁴ This sulfide structure has been grown on both the Mo(100) and Mo(111) surfaces by exposures to H_2S (~1 torr) at high temperatures (>500°C) and has been determined to be the basal plane of MoS_2 . This assessment has been made based upon the above observations and the comparison of electron energy loss (ELS) and LEED I/V measurements with those made on bulk MoS_2 .²¹⁻²³ On occasion this structure has been observed immediately following an HDS reaction without the need for annealing. This suggests that the surface after most reactions is composed of an MoS_2 overlayer having a high $S_{150}:\text{Mo}_{221}$ AES ratio but not sufficiently well ordered to produce a LEED pattern. The effect of annealing is to induce long range order. Deactivation of the Mo(100) catalyst apparently occurs by reversible adsorption of H_2S onto active HDS sites and by formation of the inactive MoS_2 basal plane at the surface of the single crystal.

3.3 Mo(100)-³⁵S Reduction in H₂

The ³⁵S overlayer on the Mo(100) surface produced a β^- emission signal of approximately 1800 counts per minute (cpm) at a coverage of $\theta_s=0.75$ on initial receipt of the C^{35}S_2 . Exposure of the surface to H_2 (1 atm) at 340°C for 5 minutes results in no measureable loss of ³⁵S from the surface. Figure 2 shows the loss of ³⁵S from the surface at a temperature of 525°C. A fit to

a first order kinetic equation:

$$r = \frac{d\theta_s}{dt} = k\theta_s$$

yields the rate constant for removal, $k = 3.0 \times 10^{-4} \text{ site}^{-1} \text{ sec}^{-1}$. Note that this rate constant contains any dependence on θ_H , and even at this temperature it is less than the measured rate of thiophene HDS at 340° of 0.11 molecules site⁻¹ sec⁻¹. Kinetic measurements of the rate of sulfur removal find an activation energy of 13.9 kcal/mole in the temperature range 400-550°C, and an order in hydrogen pressure of 0.34 over the pressure range 50-780 torr (Figures 3 and 4). Extrapolation of the Arrhenius plot to 340° yields a rate of approximately $2 \times 10^{-5} \text{ sec}^{-1}$, about four orders of magnitude less than the observed HDS rate of thiophene. The reduction of sulfur, bound to the metal surface, by hydrogen is clearly not a step that is involved in the HDS of thiophene.

The rate of sulfur removal from the surface was measured at several initial sulfur coverages (Figure 5). Although the rate was measurable at 500°C for coverages of 0.75, at coverages of $\theta_s \leq 0.67$ there was no measurable reduction in the ³⁵S signal after treatment with H₂ for 5 minutes. Repetitive exposures would result in the buildup of contaminant sulfur and carbon from the reaction loop and the displacement of sulfur. It is interesting to note that the coverage at which it becomes impossible to remove the sulfur is $\theta_s = 0.67$. It is at this coverage that the sulfur atoms begin to populate the high coverage binding site rather than the fourfold hollow sites.⁸

3.4 Mo(100)-S Reduction under HDS Conditions

In addition to studying the reduction of sulfur overlayers in H₂, similar measurements have been carried out in the presence of the HDS reaction mixture.

The kinetic measurements show that the reaction is much different from that in pure H_2 (Figs. 6,7,8). The most pronounced effect of the addition of thiophene to the reaction mixture is a marked increase in the rate of sulfur removal. Under conditions of $T=345^\circ C$, $P(H_2)=780$ torr and $P(Th)=1$ torr, very close to those used to study the HDS reaction, the removal rate constant is $6.8 \times 10^{-4} \text{ sec}^{-1}$, greater than 30 times that observed in pure H_2 , but still two orders of magnitude lower than the observed thiophene HDS rate.

An Arrhenius plot of the rate over a temperature range of $225-440^\circ C$ shows a distinct break at approximately $380^\circ C$ with a change of activation energy from 7.2 kcal/mole in the low temperature regime to 32.2 kcal/mole in the high temperature regime. The sulfur removal rate has been measured at $325^\circ C$, in the low temperature regime, over a range of reactant concentrations and been shown to be independent of both thiophene and hydrogen pressures. This is true even for very low concentrations of thiophene ($<10^{-3}$ torr). After performing reactions with thiophene it was necessary to flush the reaction loop with H_2 for several hours before measuring sulfur removal rates characteristic of those in pure H_2 .

There was no significant difference in rates between surfaces starting with $\theta_s = 0.5$ and $\theta_s = 0.75$ as was observed in the case of pure H_2 . In the cases in which thiophene was included in the reactant mixture even sulfur atoms bound in the fourfold hollow sites could be displaced, although their residence time on the surface was still very long, i.e. approximately 30 min. The sulfur deposited on the surface before an HDS reaction remains on the surface for periods of time much longer than the residence times of either reactants or products.

4. Discussion

The implications of the results of this study for HDS catalysis can be understood by comparing the rates of sulfur removal from the Mo(100) surface and of thiophene HDS over these surfaces. The rate of hydrogenation of adsorbed sulfur to H_2S is much slower than the rate of hydrodesulfurization under the same conditions. The rates of these processes, under comparable conditions are depicted in Figure 9. These findings eliminate the Lipsch-Schuit mechanism of desulfurization (depicted in Figure 10a) in which the sulfur is first adsorbed onto the catalyst as a result of hydrogenolysis of C-S bonds and is subsequently hydrogenated. In this circumstance, the sulfur hydrogenation reaction would be rate limiting, and the HDS reaction rates would be much slower than those observed. It is not, of course, possible to rule out a mechanism in which the sulfur atom is deposited onto the surface in a very weakly bound state (Figure 10b) from which it is easily reduced. The nature of such a state, however, would be much different from any observed during the adsorption of sulfur on the Mo(100) surface under UHV conditions (i.e. the Mo-S bond strength must be $\ll 75$ kcal/mole). Its bonding to the metal must be sufficiently weak that reduction to H_2S is much faster than any exchange reaction with sulfur bound directly to the metal. It is difficult to understand what the driving force would be for the breaking of C-S bonds to form such a species. Instead, the desulfurization step must be one in which H_2S is produced without the formation of an adsorbed sulfur atom (Fig. 10c).

The kinetic studies of thiophene HDS have shown that the initial steps to produce butadiene are independent of hydrogen pressure and first order in thiophene pressure. This has been discussed in terms of a rate determining step that occurs prior to any hydrogenation steps. The fact that butene

production is fractional order in hydrogen pressure has suggested that the hydrogen coverage is low and the first order dependence in thiophene pressure rules out a mechanism in which one of the hydrocarbon intermediates leading to butadiene is saturating the surface. Finally, the activation energy of the rate determining step has been found to be approximately 14 kcal/mole. Two mechanisms for the initial desulfurization step are consistent with the observations of this work. One would lead to a reaction in which hydrogenolysis of C-S bonds by adsorbed hydrogen proceeds without the intermediate formation of an Mo-S bond, yielding H₂S and an adsorbed hydrocarbon intermediate that is readily reduced to butadiene. In this case the rate determining step is one occurring prior to the hydrogenolysis step, either the adsorption of thiophene or the production of some activated adsorption state in which the hydrogenolysis can occur. It is unlikely that simple chemisorption is activated. However, studies of thiophene chemisorption on the Mo(100) surface⁸ showed the existence of a molecular adsorption state, stable to high temperatures (>450K), that was produced only upon heating to approximately 200K (i.e. activated). Although no direct correlation to the high pressure reaction can be made, such a species might be hydrogenated at high pressures to yield the HDS products. The second mechanism that is consistent with the current work is that proposed by Kolboe¹¹, which is a dehydrodesulfurization reaction. The production of H₂S occurs intramolecularly leading to adsorbed diacetylene. It seems reasonable to suggest that such an initial step would be activated and might be rate limiting. Furthermore the hydrogenation of diacetylene to butadiene would be expected to be very fast.¹⁹ Such a mechanism would not be possible in the case of dibenzothiophene, but labelling studies of the HDS of this compound show that it does proceed by a Lipsch-Schuit type mechanism⁹

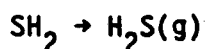
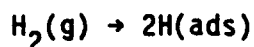
(as in Fig. 10a).

The measurements of sulfur hydrogenation in H_2 show that the hydrogenation of the high coverage sulfur species is faster than that of the low coverage species ($\theta_s > 0.67$). This was predicted from the study of the rates of thiophene HDS reactions at various different initial sulfur coverages in which the low coverage sulfur was found to have a strong inhibiting effect, while increasing the coverage caused little additional change. Previous work has shown that at high coverages the Mo(100)-S bond strength is 75-90 kcal/mole, reduced from its low coverage value of 110 kcal/mole (24). The suggestion is that this weakly bound sulfur species may be readily reduced to H_2S and thus has little effect on the HDS activity. Calculations of the equilibrium coverages of sulfur in H_2 (1 atm, 340°C), using 110 kcal/mole and 80 kcal/mole respectively for the two Mo-S species show that the steady state coverage of the tightly bound species is almost unity while that of the weakly bound species is approximately 5×10^{-4} . The coverage at which sulfur can be reduced is that at which the high coverage binding site, postulated to be a bridging site, becomes populated. The present results provide further evidence that there is some change in the bonding of sulfur to the surface on going from the $\begin{bmatrix} 2\bar{1} \\ 11 \end{bmatrix}$ ($\theta_s=0.67$) structure to the $c(4 \times 2)$ ($\theta_s=0.75$) structure.

The details of the mechanism by which preadsorbed sulfur determines the reaction rate are unclear. In the presence of thiophene all of the ^{35}S can be reduced from the metal surface, but on a time scale that is much longer than the reaction rate. The preadsorbed sulfur selectively inhibits the hydrogenation reactions leading to the butenes and butane, but not the desulfurization reaction leading to butadiene. Kinetic studies suggest that

the hydrogenated products are formed via a partially hydrogenated intermediate that saturates its available binding sites on the surface, thus leading to the very weak dependence of the rates of butene and butane production on thiophene pressure. The presence of preadsorbed sulfur blocks binding sites for such an intermediate. The simplest explanation for the shape of the rate versus θ_s curve would be that sulfur adsorbed in the fourfold hollow sites ($\theta_s \leq 0.67$) remains on the surface permanently, blocking adsorption sites for the intermediate leading to the hydrogenated products. Sulfur adsorbed on the surface at coverages greater than 0.67 is present in the high coverage binding site and is reduced from the surface very quickly, and thus has no effect on the reaction rate. Such an ideal situation would be expected to result in a linear decrease of the rate in the coverage regime $0 < \theta < 0.67$, and for $\theta_s \geq 0.67$, a rate equal to that at $\theta_s = 0.67$. While the results presented here approximate such a process, the situation is clearly much more complicated due to the fact that the removal of sulfur from the high coverage sites is not infinitely fast, nor is the removal rate of sulfur from the low coverage sites equal to zero. Furthermore, in the presence of thiophene there is some deposition of sulfur onto the surface, albeit at a rate much less than that of the reaction.

The sulfur reduction kinetics in pure hydrogen can be modelled by a simple scheme of hydrogen adsorption followed by a sequential hydrogenation of sulfur atoms and, finally, desorption of H_2S .



The fact that the hydrogen pressure dependence is not one-half order indicates that the first step of hydrogen adsorption is not rate limiting.

Unfortunately, it was not possible to cover a great enough range of hydrogen pressures to allow determination of which step among the remainder is rate limiting.

The final point of interest in this study is the dramatic influence of thiophene on the rate of sulfur reduction. Very low pressures of thiophene resulted in an enhancement of the reduction rate by more than an order of magnitude. The rate increase may be caused by a change in the metal-sulfur bonding due to the presence of coadsorbed thiophene or by a change of reaction mechanism.

The reduction of sulfur in pure H_2 has been noted to occur at a faster rate as the Mo-S bond is weakened on increasing the coverage past 0.67 monolayers. This bond weakening is due to the change in the sulfur adsorption site with coverage, induced by repulsive interactions between adsorbed sulfur atoms. If such an effect were produced by the presence of thiophene, a similar increase in the reaction rate would be expected. Such an effect, however, would be expected to manifest itself in a decrease in the reaction activation energy. At temperatures of 390-440°C this is clearly not the case as the apparent activation energy increases from 14 kcal/mole to 32 kcal/mole on introducing thiophene. In the lower temperature range, outside that accessible when working with pure H_2 , the activation energy is lowered by the presence of thiophene. The pre-exponential factor and the kinetics, however, are also different suggesting a new sulfur removal mechanism.

It is interesting to note that the removal rate of sulfur in the HDS mixture is independent of both thiophene and hydrogen pressures. Studies of

the HDS kinetics point to the existence of a hydrocarbon intermediate that is saturating the surface and is in equilibrium with adsorbed hydrogen. Its concentration is independent of both thiophene and hydrogen pressures. It is possible that such a species serves as a source of hydrogen for sulfur removal, accounting both for the enhancement in the reaction rate and the change in the observed kinetic parameters. The presence of a carbonaceous deposit serving as a source of hydrogen during hydrogenation reactions has been discussed elsewhere.²⁰ In the case of ethylene hydrogenation over Pt(111) and Rh(111) surfaces, such deposits have been identified as ethylidyne moieties.^{2,18} In this case, however, the nature of such a species is unknown, and should be the subject of further investigation.

5. Conclusion

The primary mechanistic implication of this work on thiophene hydrodesulfurization over Mo(100) single crystal surfaces is that the desulfurization step does not occur via the Lipsch-Schuit mechanism. Carbon-sulfur bonds are not broken to form an intermediate metal-sulfur species such as is observed during sulfur adsorption on the Mo(100) surface in UHV. These sulfur species have high heats of adsorption (75 kcal/mole) and if formed their hydrogenation to H₂S would be reaction rate limiting (Fig. 10a). It is possible that a weakly adsorbed intermediate is produced (Fig. 10b) but it should be noted that its rate of hydrogenation must be much greater than any interconversion with the tightly bound species. Instead, we suggest that the desulfurization step occurs via either the Kolboe mechanism of intramolecular dehydrodesulfurization or a direct hydrogenolysis of C-S bonds to form H₂S (Fig. 10c).

Measurements of the rate of hydrogenation of surface sulfur in 1 atmosphere of pure H₂ at various sulfur coverages show a discontinuity as the coverage exceeds $\theta_s = 0.67$. At the lower coverages the rate is below the detection limits of the experiment, while for $\theta_s > 0.67$ it is quite significant but still two orders of magnitude lower than the rate of HDS of thiophene. This result points to a distinct change in the Mo(100)-S bonding at this coverage. It supports the suggestion made previously that it is at this coverage that adsorbed sulfur atoms begin to occupy a weakly binding site different from the fourfold hollow site occupied at $\theta_s \leq 0.5$.

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FIGURE CAPTION

Fig. 1. A) Rate of thiophene HDS vs. initial sulfur coverage of the Mo(100) — surface. Rates are given relative to those on the clean surface. $P(H_2) = 780$ torr, $P(Th) = 2.5$ torr, $T = 340^\circ C$. B) Rates of butadiene, butene and butane production vs. θ_s . Rates are relative to those on the clean surface.

Fig. 2. A) Decrease in ^{35}S signal with time during reduction in H_2 . Initial coverage was $\theta_s = 0.75$, $T = 525^\circ C$, $P(H_2) = 780$ torr. B) Plot of $\ln(\theta_s/0.75)$ vs. t shows first order kinetics.

Fig. 3. Arrhenius plot of the rate constant for sulfur removal in hydrogen. $P(H_2) = 780$ torr.

Fig. 4. Order plot of the rate constant for sulfur removal vs. hydrogen pressure. $T = 550^\circ C$.

Fig. 5. Rate constant for sulfur removal vs. sulfur coverage. Reaction times were limited to 5 min. to minimize the effects of contamination by background hydrocarbons. $T = 500^\circ C$, $P(H_2) = 780$ torr. The detection limit for sulfur removal rate constant was $2 \times 10^{-5} \text{ atom}^{-1} \text{ sec}^{-1}$.

Fig. 6. Arrhenius plot of rate constants for sulfur removal in both thiophene and hydrogen. $P(Th) = 1.0$ torr, $P(H_2) = 780$ torr.

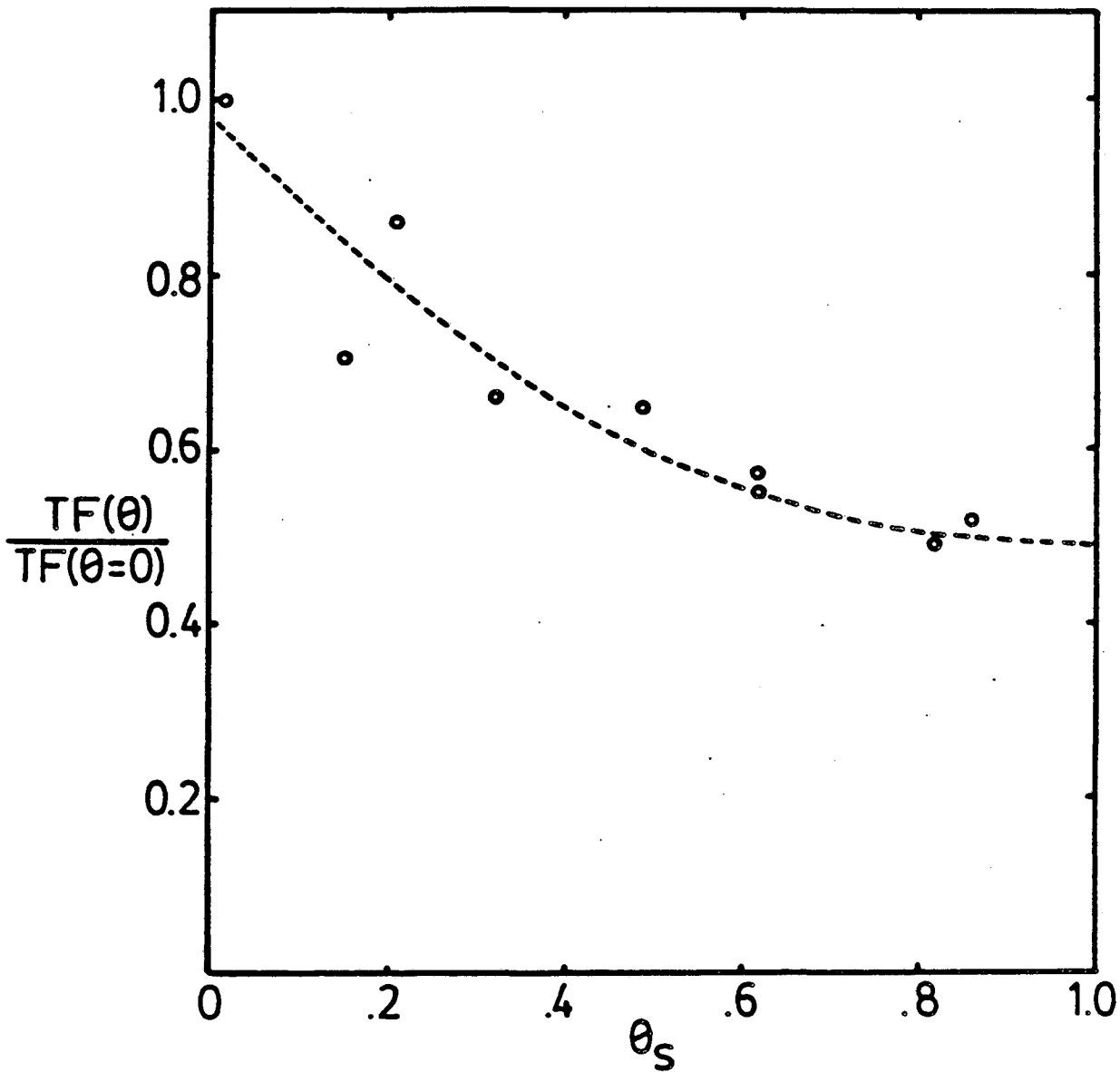
Fig. 7. Order plot of the rate constant for sulfur removal vs. hydrogen pressure. $P(\text{Th}) = 1.00$ torr, $T = 345^\circ\text{C}$.

Fig. 8. Order plot of the rate constant for sulfur removal vs. thiophene pressure. $P(\text{H}_2) = 780$ torr, $T = 345^\circ\text{C}$.

Fig. 9. Relative rates of thiophene HDS, sulfur hydrogenation in a pure H_2 environment and sulfur hydrogenation in a thiophene/ H_2 atmosphere on the Mo(100) surface.

Fig. 10. Possible mechanisms for the initial desulfurization of thiophene. A) The Lipsch-Schuit mechanism involving deposition of sulfur onto the catalyst followed by reduction by surface hydrogen. B) Deposition of sulfur into a weakly bound adsorption state followed by hydrogenation. C) Direct extrusion of sulfur from the thiophene ring to form H_2S without the intermediate formation of an Mo-S species.

THIOPHENE HDS on Mo(100) vs. θ_S
RATE RELATIVE to CLEAN SURFACE
T=340 °C P_{H_2} =780t P_{Th} =2.5t

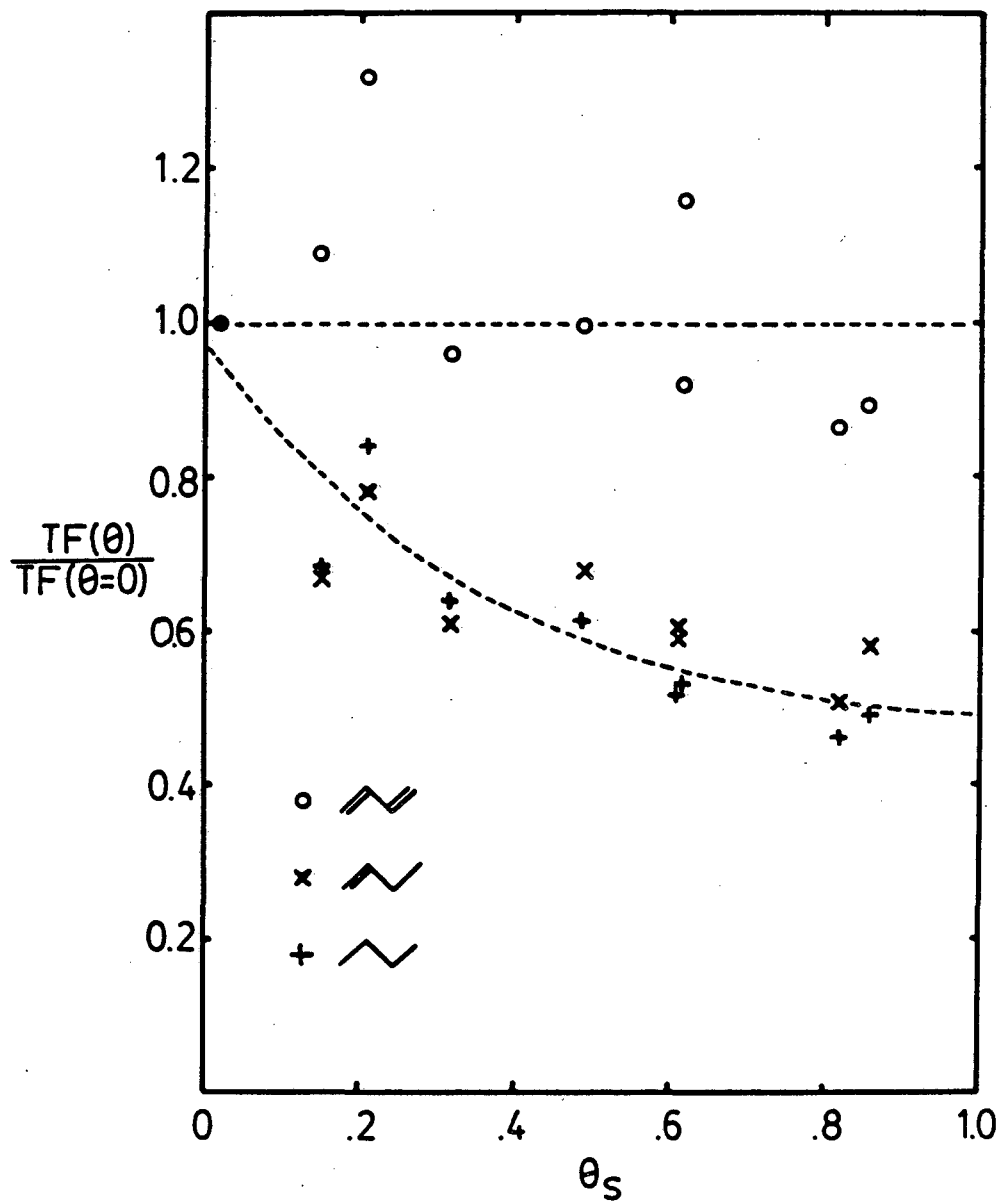


XBL 848-3440

Fig. 1A.

THIOPHENE HDS on Mo(100) vs. θ_s
RATE RELATIVE to CLEAN SURFACE

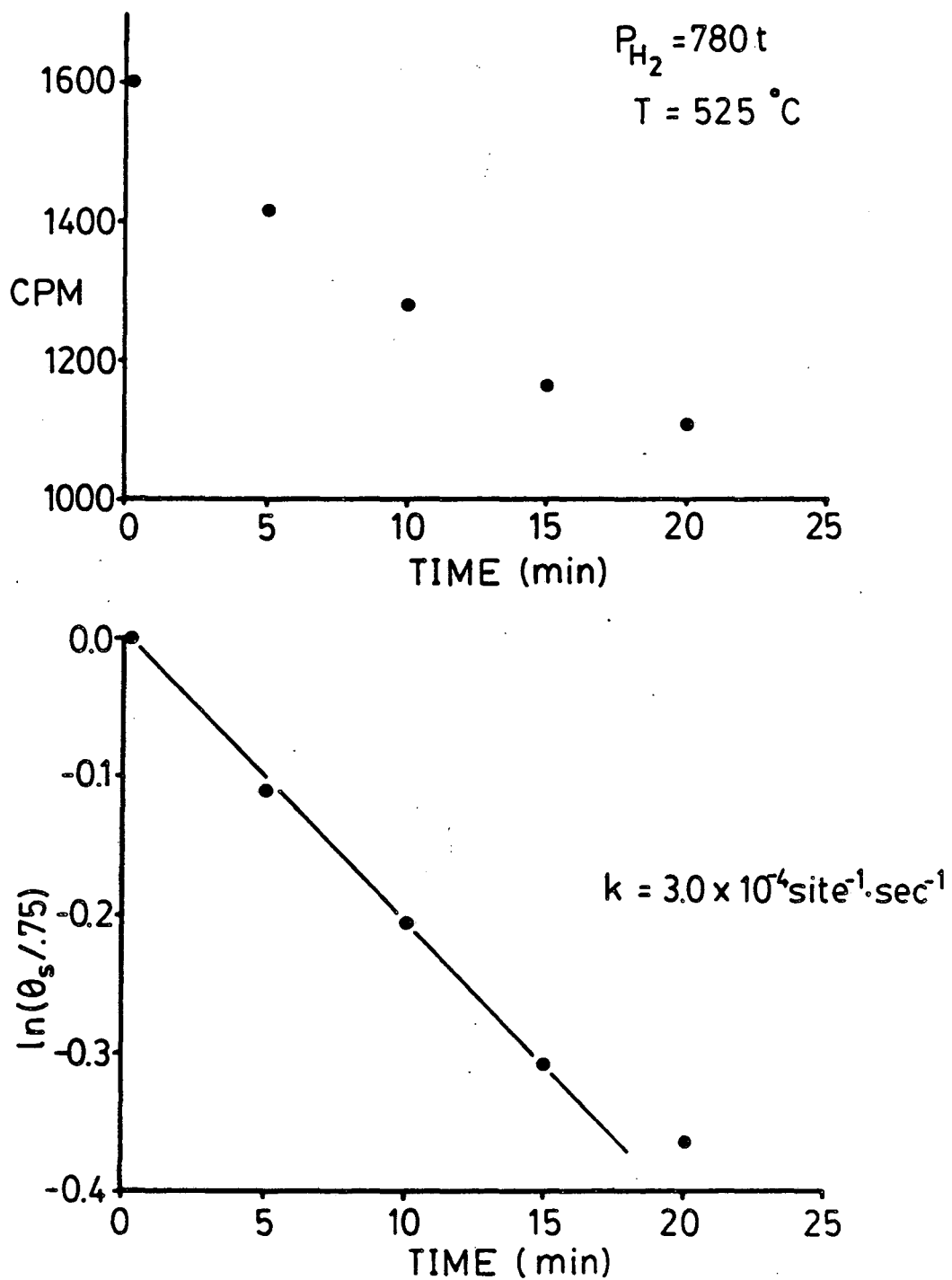
T = 340 °C P = 780t P = 2.5t



XBL 848-3440 A

Fig. 1B

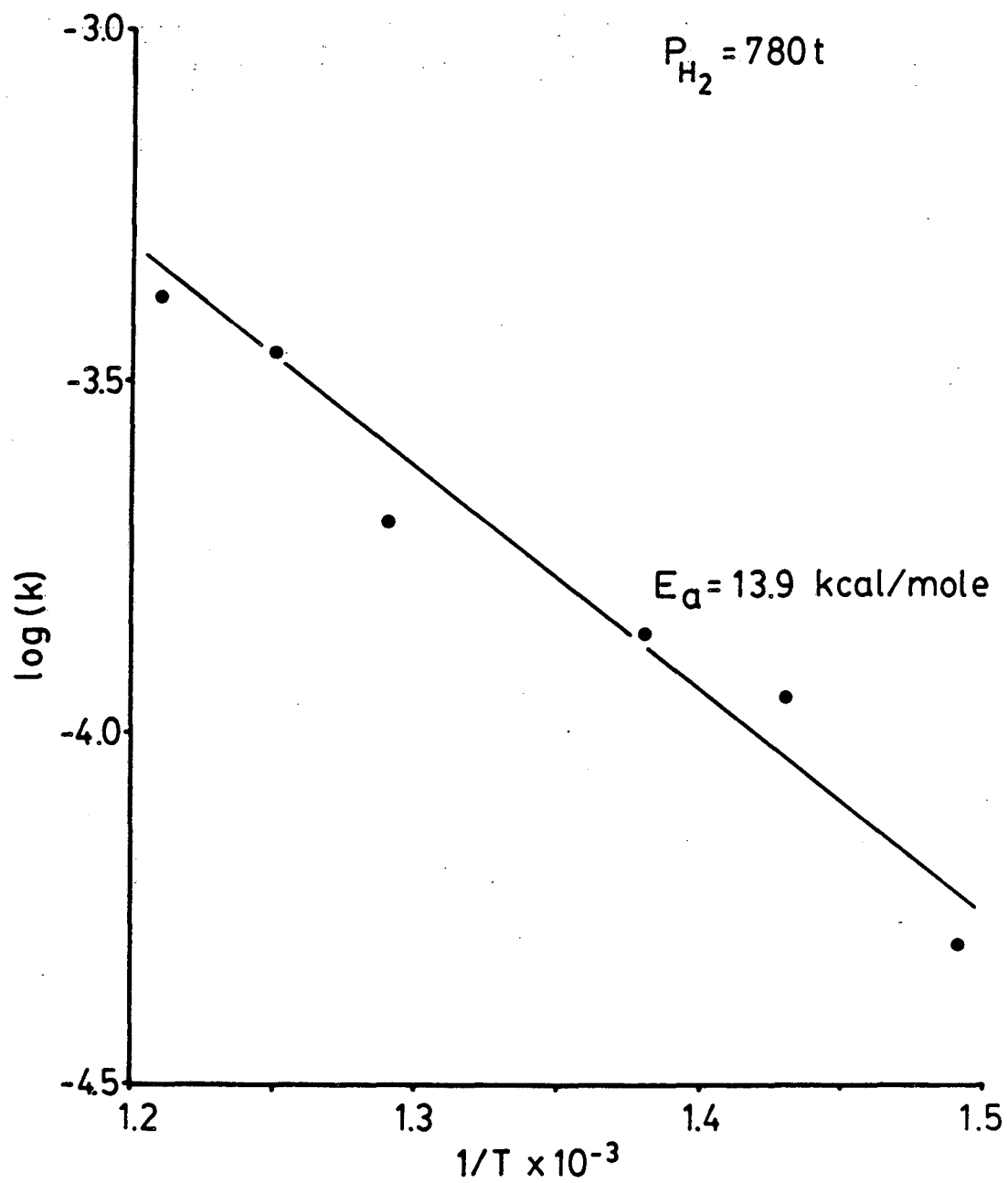
^{35}S HYDROGENATION on Mo(100) at $\theta_s = .75$



XBL 861-329

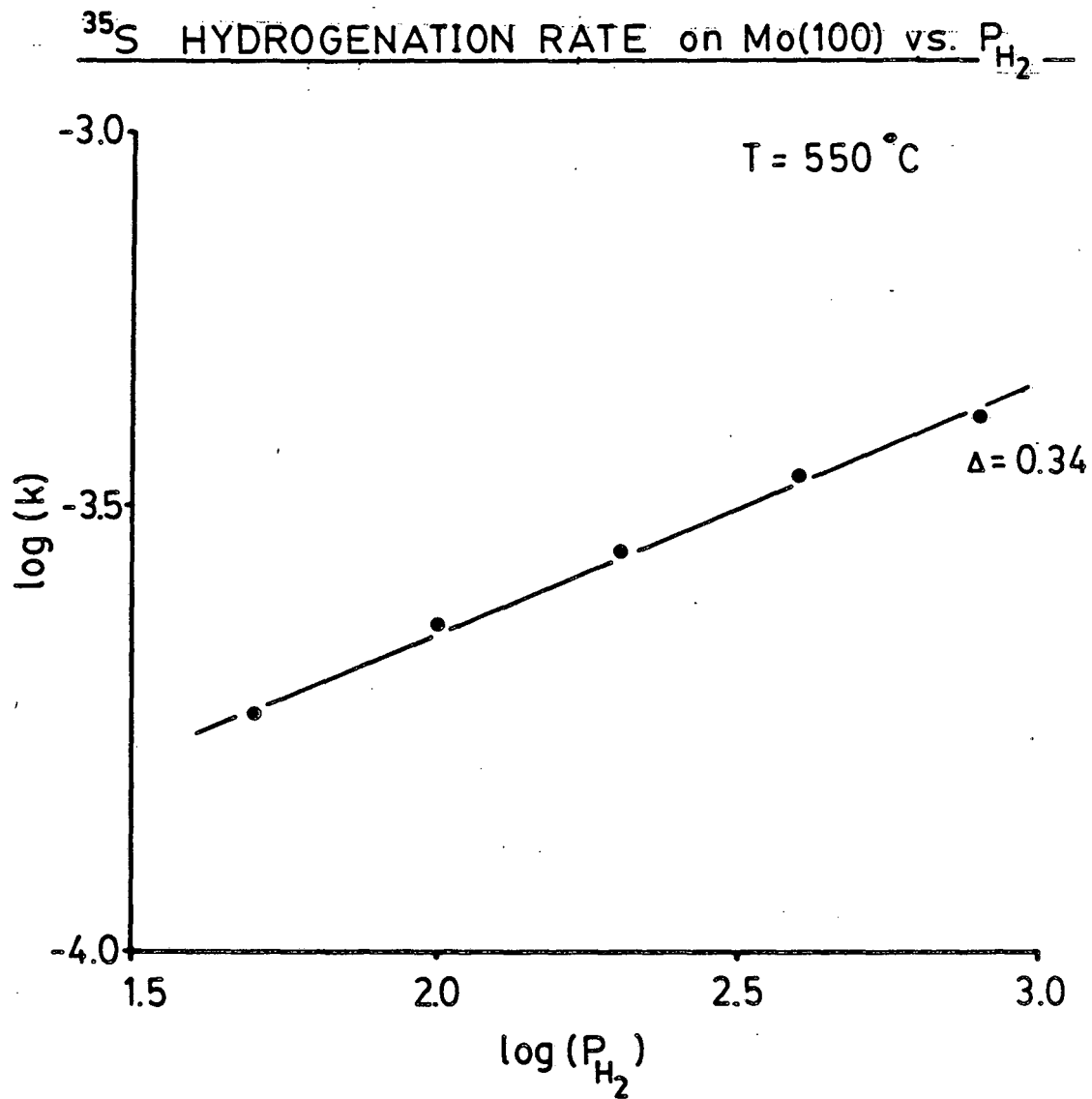
Fig. 2

³⁵S HYDROGENATION RATE on Mo(100) vs. T



XBL 861-328

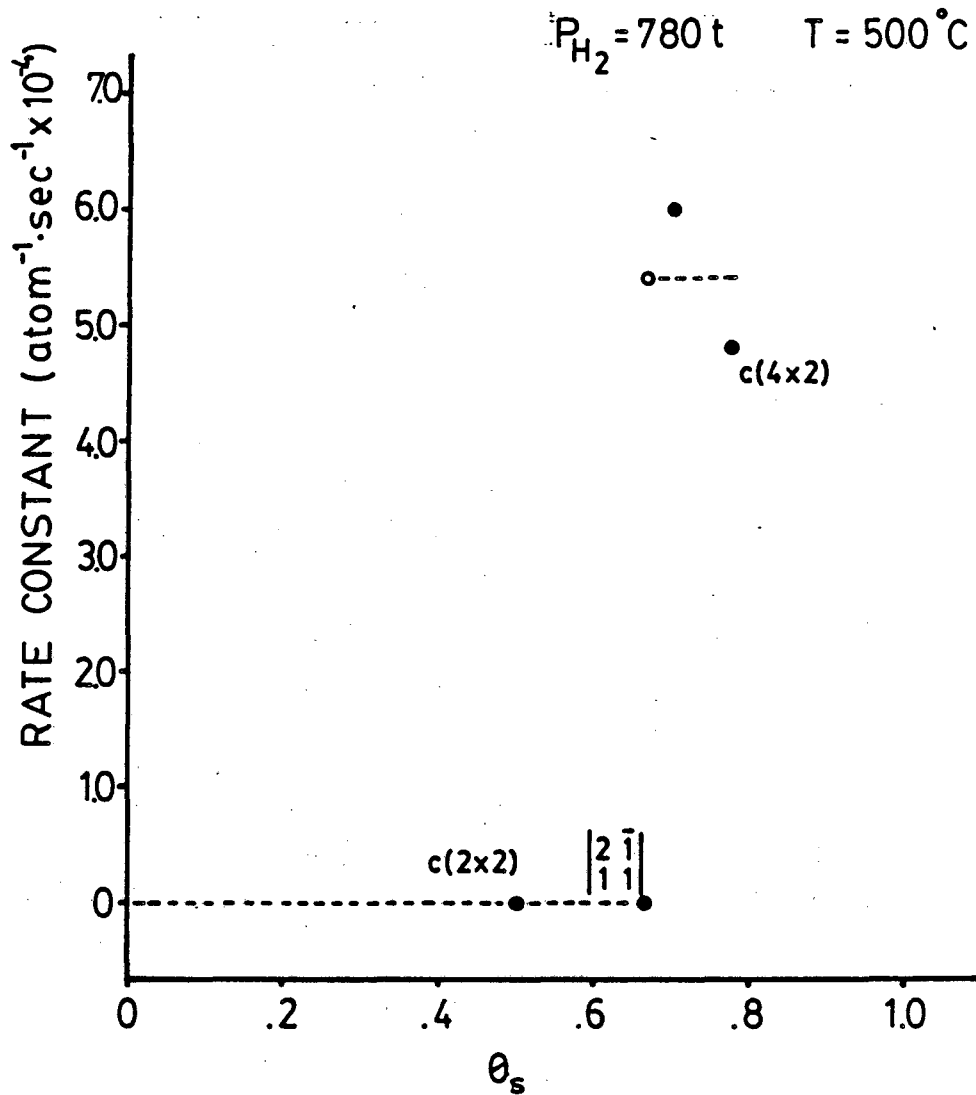
Fig. 3



XBL 861-327

Fig. 4

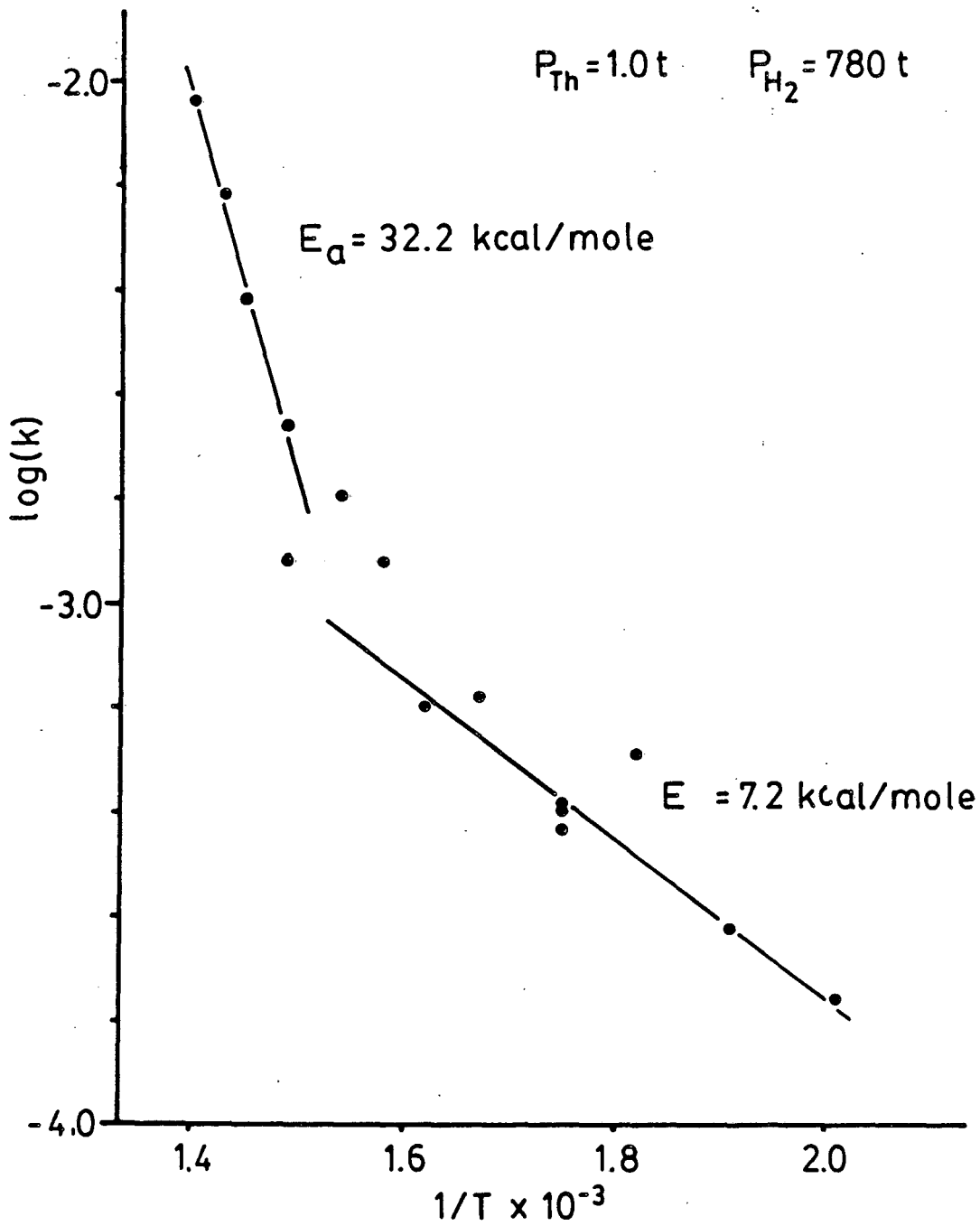
^{35}S HYDROGENATION RATE on Mo(100) vs. θ_s



XBL 861-326

Fig. 5

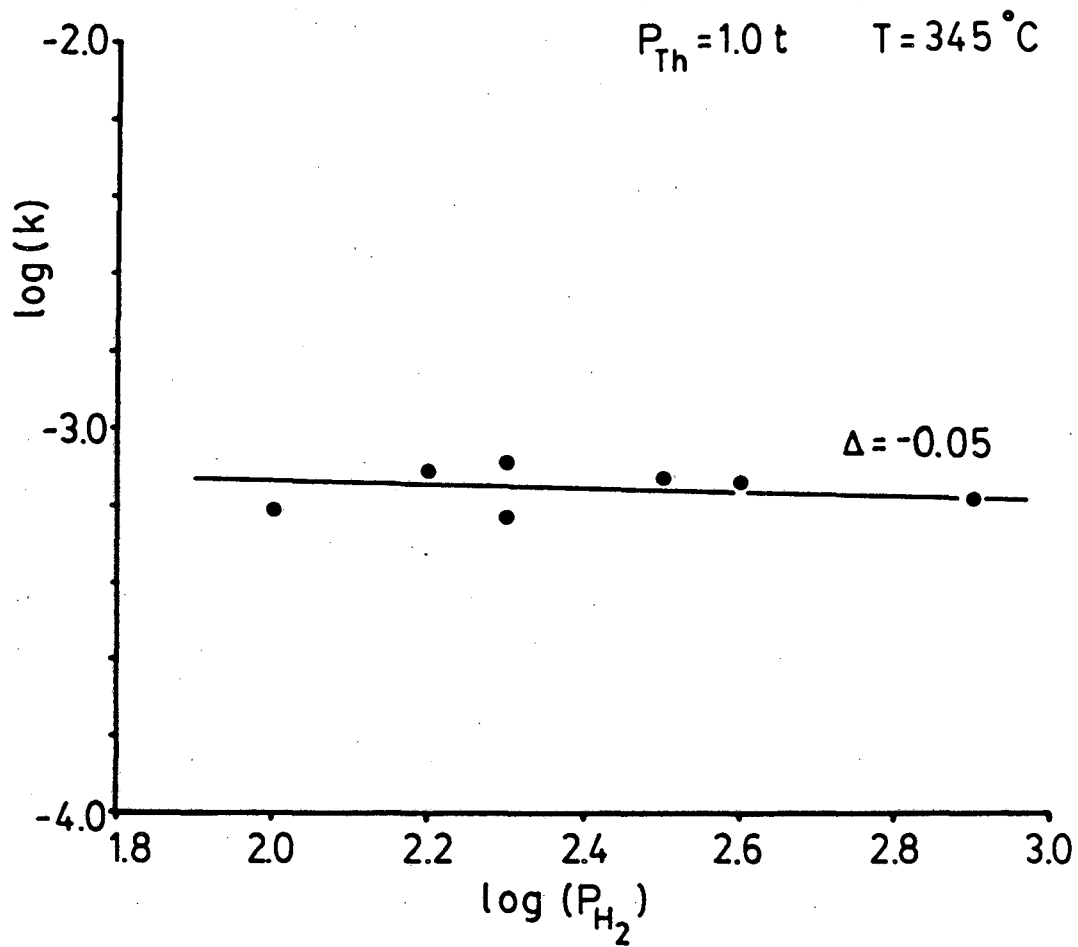
³⁵S HYD. RATE on Mo(100) vs. T (in Thiophene)



XBL 861-332

Fig. 6

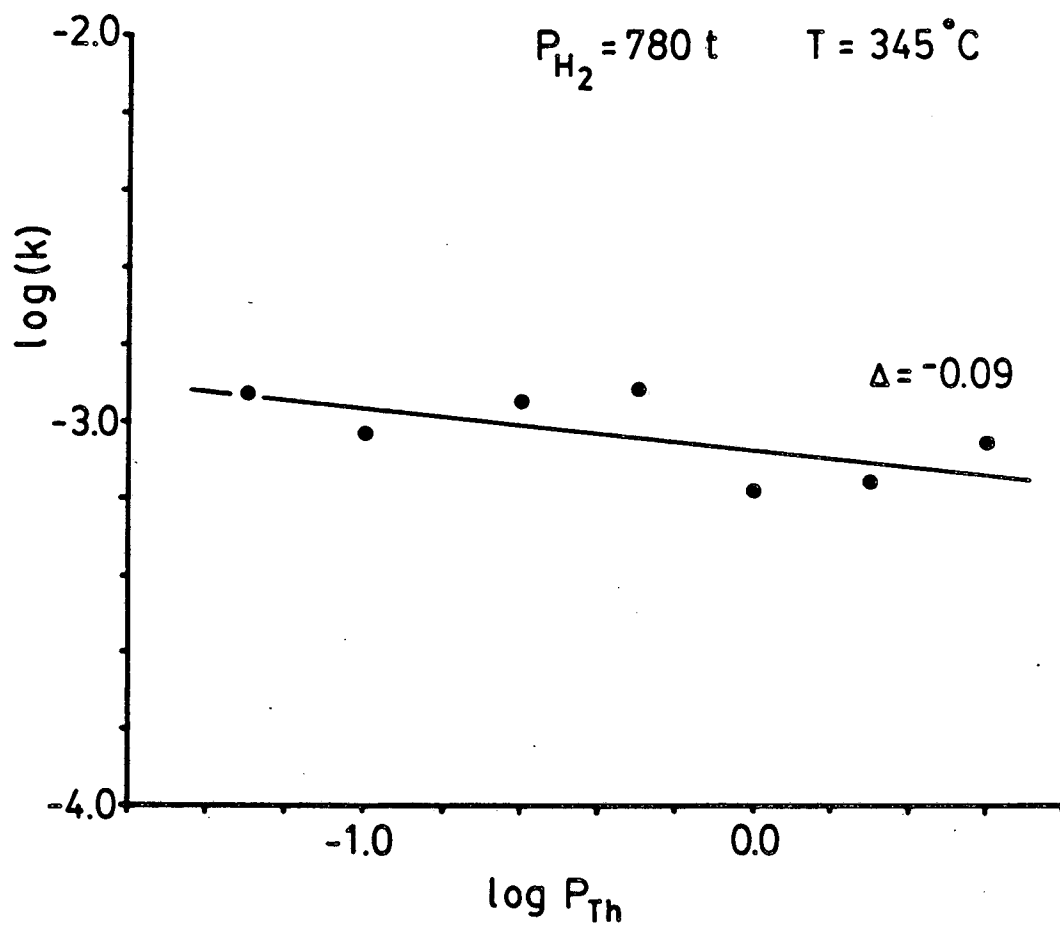
^{35}S HYD. RATE on Mo(100) vs. P_{H_2} (in Thiophene)



XBL 861-331

Fig. 7

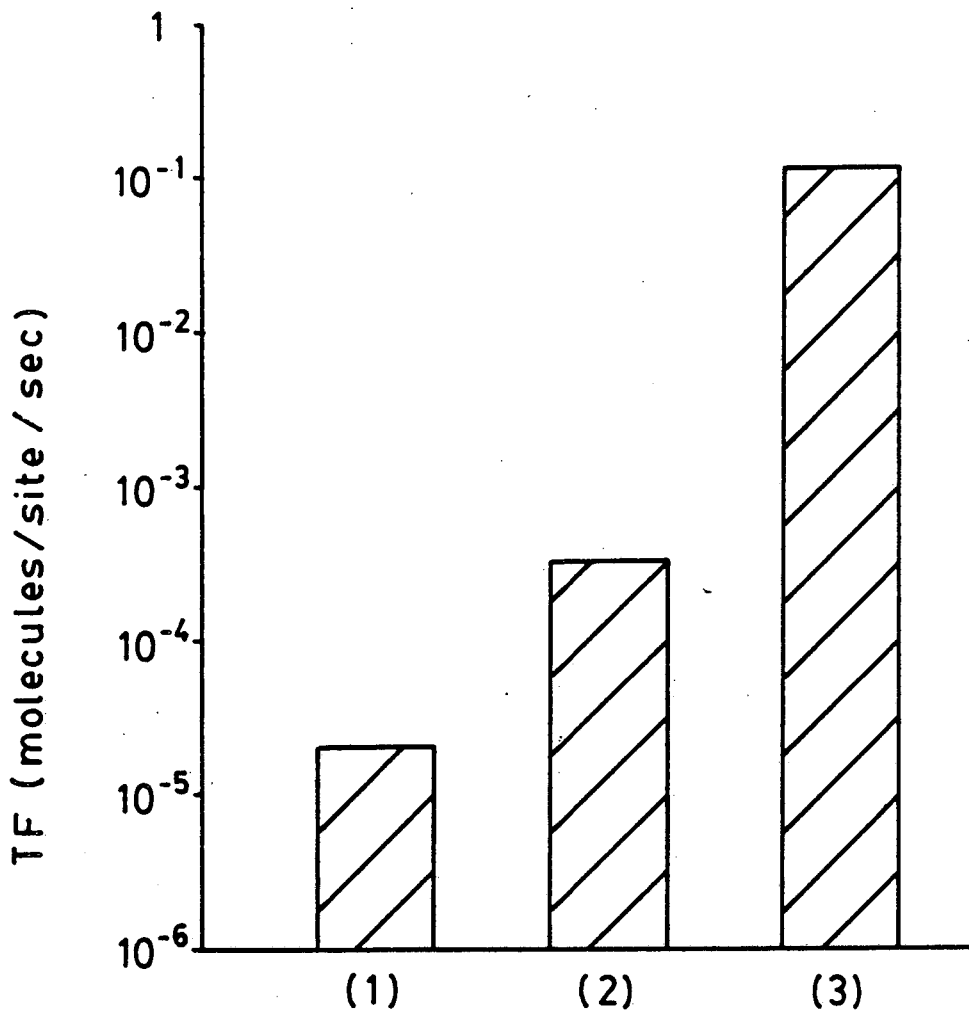
^{35}S HYD. RATE on Mo(100) vs. P_{Th} (in Thiophene)



XBL 861-330

Fig. 8

SURFACE REACTION RATES

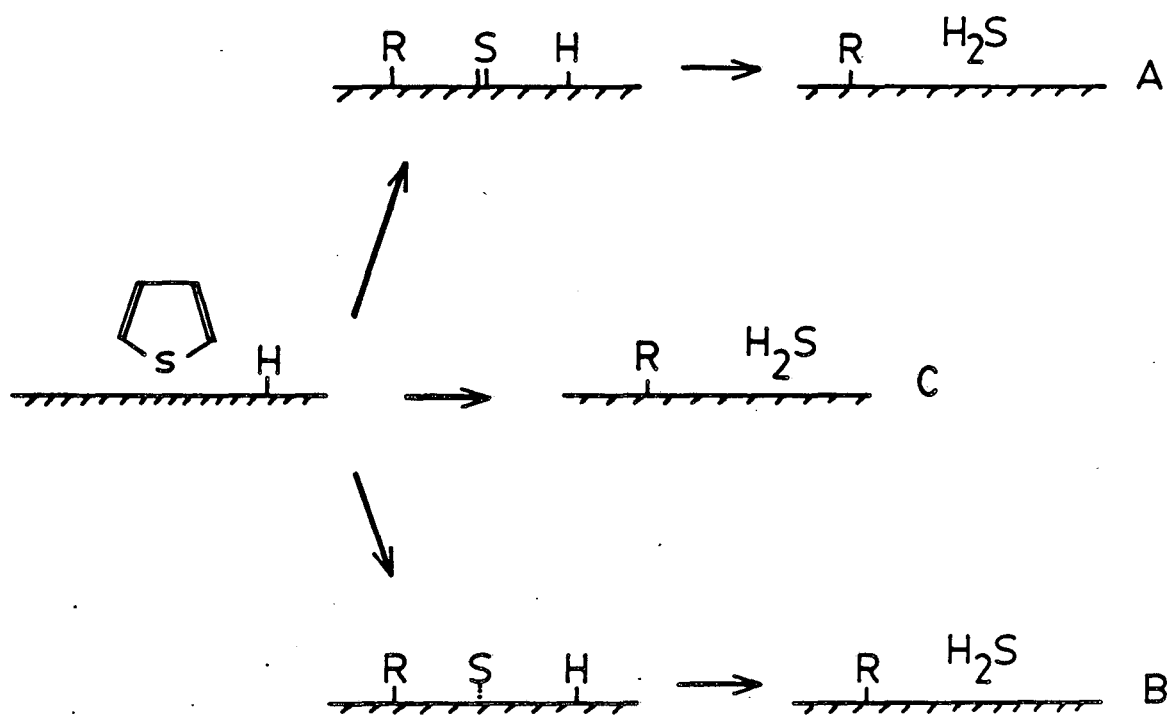


- (1) ³⁵S Hydrogenation T=340°C P_{H₂}=780t
(2) ³⁵S Hydrogenation T=340°C P_{H₂}=780t P_{Th}=2.5t
(3) Thiophene HDS T=340°C P_{H₂}=780t P_{Th}=2.5t

XBL 866-2365

Fig. 9

THIOPHENE DESULFURIZATION MECHANISMS



XBL 866-2366

Fig. 10

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