JOURNAL OF CATALYSIS **127**, 190–200 (1991)

Tetrahydrothiophene Desulfurization on Co–Mo/γ-Al_2O_3: A Temporal Analysis of Products (TAP) Investigation

WILLIAM R. MOSER,* GEORGE A. ROSSETTI, JR.,* JOHN T. GLEAVES,† AND JERRY R. EBNER†

**Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, Massachusetts 01609; and †Specialty Chemicals Division, Monsanto Chemical Company, 800 North Lindberg Boulevard, St. Louis, Missouri 63167*

Received November 13, 1989; revised July 2, 1990

The catalytic reactions of tetrahydrothiophene, thiophene, 1-butene, 1,3-butadiene, and *n*-butane with hydrogen were studied at low pressure over a commercial cobalt molybdate catalyst. The formation sequence of tetrahydrothiophene desulfurization products was monitored with submillisecond time resolution using the temporal analysis of products (TAP) transient microreactor technique. The TAP experiments showed that butene and butadiene were the only hydrocarbon desulfurization products formed, although rapid dehydrogenation to thiophene was also observed. The exceptional time resolution of the TAP spectrometer provided evidence that the butene formed could not be accounted for by a mechanism involving butadiene hydrogenation. The results suggested a desulfurization mechanism for tetrahydrothiophene wherein C_4 hydrocarbon formation proceeds via a surface butene thiolate intermediate produced by a single β-hydride elimination. It is proposed that 1,3-butadiene is formed by a slow subsequent β-hydride elimination of the intermediate, while rapid C–S bond hydrogenolysis involving surface hydrogen is responsible for butene formation.

INTRODUCTION

Relatively few studies have examined the catalytic hydrodesulfurization mechanism of saturated sulfur heterocyclics, desipte evidence that they may be key intermediates in the desulfurization of the technologically more important thiophenic compounds (*1*, *2*). Detailed mechanistic studies of the saturated C_4S heterocycle, tetrahydrothiophene, might prove particularly profitable, since this heterocycle can be considered the simplest prototypic model compound for the hydrodesulfurization thiophene and related molecules. At present, there is no general agreement regarding even the major mechanistic features of tetrahydrothiophene desulfurization.

Mechanistic information for tetrahydrothiophene desulfurization has been largely deduced from kinetic data obtained on sulfided cobalt molybdate catalysts in conventional microreactor studies (*1*, *3–5*). Based on the observation that no 1,3-butadiene was formed in the desulfurization of tetrahydrothiophene, Deskian and Amberg (*3*) first proposed that the primary path to hydrocarbon products is by hydrodecyclization to 1-butanethiol, followed by β-hydride elimination or C–S bond hydrogenolysis to 1-butene or *n*-butane, respectively. In subsequent work, however, Kolboe (*4*) observed that tetrahydrothiophene desulfurization in fact resulted in an even greater butadiene yield than did the desulfurization of thiophene. This suggested a dehydrosulfurization mechanism involving double β-hydride elimination, analogous to the dehydration reactions of alcohols, wherein the primary gas phase product would be 1,3-butadiene (or 3-butenethiol, if desorption occurs prior to scisson of the second C–S bond) which could then be rapidly hydrogenated to butene on the same or other sites. Support for Kolboe's mechanism was later provided by the low conversion microreactor studies of

0021-9517/91 $3.00

Hargreaves and Ross (*1*). While surface spectroscopic data for tetrahydrothiophene adsorption is scant, the above mechanisms assume a Lewis base interaction with the catalyst surface through a lone electron pair on the heteroatom. Still another mechanism has been proposed based on a multipoint adsorption configuration (*5*).

More recently, Roberts and Friend (*6*) used temperature-programmed reaction spectroscopy to study tetrahydrothiophene desulfurization on Mo(110) surfaces. No butadiene formation was observed on the single crystal Mo catalyst and a desulfurization mechanism was proposed wherein hydrogenation of tetrahydrothiophene at the α-carbon produces a surface butylthiolate intermediate. Depending on the surface concentration of hydrogen, the butylthiolate may be either hydrogenated or dehydrogenated to *n*-butane or 1-butene, respectively.

In the present communication, initial findings of tetrahydrothiophene desulfurization experiments carried out at low hydrogen exposures using the temporal analysis of products (TAP) transient microreactor technique (*7*) are reported. The TAP technique permits the real-time observation of reaction products and intermediates with submillisecond time resolution, thereby providing time resolution two or more orders of magnitude better than that of conventional transient microreactor methods (*7*). Due to the short contact times and low surface coverages employed, the TAP technique often reveals intermediates or reaction pathways impossible to detect in conventional microreactor studies (*8*). The exceptional time resolution of the TAP spectrometer provides new evidence suggesting an alternative mechanism to those previously proposed for tetrahydrothiophene desulfurization on supported cobalt molybdate catalysts. The results of the TAP studies are most consistent with a tetrahydrothiophene desulfurization mechanism wherein butadiene is formed by a sequential double β-hydride elimination, while butene is formed by a single β-hydride elimination followed by rapid C–S bond hydrogenolysis of the adsorbed butenethiolate intermediate.

EXPERIMENTAL

Materials and Catalysts

The tetrahydrothiophene and thiophene used were obtained from Eastman Kodak (Rochester, NY) and were 99+% pure. The *n*-butane, 1-butene, 1,3-butadiene, and hydrogen gases were all of research grade purity.

The catalyst used was a commercial material supplied by American Cyanamid (Stamford, CT). The composition of the catalyst as reported by the manufacturer was 16.5 wt% MoO_3 and 5 wt% CoO supported on γ-Al_2O_3. It had a BET surface area of 235 m^2/g. The as-received catalyst was presulfided prior to study in the TAP spectrometer. The sulfiding was performed in a tubular 316 stainless steel microreactor at 760 Torr and 340°C using hydrogen saturated with thiophene at 0°C. Conversion of thiophene was monitored with a Perkin–Elmer Sigma 2000 gas chromatograph employing a 6-ft carbowax column and flame ionization detector. After essentially quantitative conversion of thiophene to C_4 hydrocarbons was observed ($\approx$1 h), the catalyst was left on stream for 24 h and subsequently cooled to room temperature under flowing argon. The catalyst was then placed in polyethylene bags and lightly crushed to facilitate efficient packing in the TAP microreactor.

TAP Microreactor Experiments

A schematic of the TAP spectrometer used in these studies is shown in Fig. 1. The details of the system hardware and principles of operation have previously been reported (7), so only a brief description is provided here. The TAP spectrometer was comprised of four essential components: a catalytic microreactor, a fast pulse gas delivery system, a real-time mass spectrometric detection system, and a differentially pumped high throughput ultrahigh vacuum system. Reactant gases were introduced to

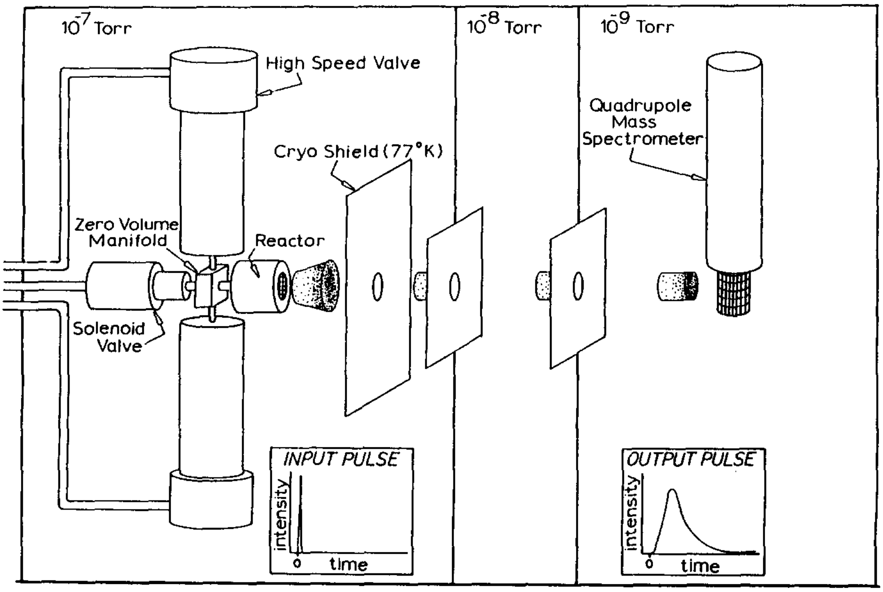

FIG. 1. Schematic of the temporal analysis of products (TAP) microreactor.

the microreactor by either of two high-speed pulse valves or through a continuous feed solenoid valve. The flow rate of reactants through the continuous feed valve was controlled using a micrometer metering valve downstream of a low-pressure gas reservoir. The pulse valves could be adjusted to produce reactant transients having a minimum temporal width of 100 μs and could be operated while the continuous feed valve was open. Reactant gases were delivered to the pulse valves from a stainless steel mixing manifold that could be evacuated. Gas mixtures were prepared at the desired molar ratios by monitoring the pressure in the manifold with a Setra electronic manometer precise to 0.5 Torr.

Mass spectra of the reaction mixtures were obtained with a UTI 100C quadrupole mass spectrometer. A digital voltmeter precise to 1 mV was connected to the output of the spectrometer to provide accurate alignment of peak masses. To improve signal to noise ratio in the spectra, the signal from the spectrometer was fed to a PARC 4203 signal averager. After averaging, the spectra were transferred to a Hewlett–Packard 9816 computer to be stored on disk or plotted.

The TAP spectrometer was used in two basic modes. One mode, called the scan mode, was used to identify the components of the reaction mixture and to determine conversion and product yields. Operation in the scan mode was analogous to that of a conventional microreactor and provided no time-resolved data. A second mode, called the TAP mode, was used to establish reaction sequences and adsorption characteristics. The TAP mode provided the fast, real-time resolution of the formation sequence of reaction products. Prior to each experiment in both the TAP and scan modes, the catalyst was reduced under flowing hydrogen for 15 min at the reaction temperature of ≈445°C.

In scan mode experiments, reactant gases were admitted to the microreactor from the low pressure (≈77.5 Torr) gas reservoir. The reactants were delivered to the catalyst at a constant rate through the continuous feed solenoid while the mass spectrum (typically m/e 24–60) was monitored. More complete scans (*m*/*e* 0–100) were performed when changing reaction conditions to ensure that no unsuspected products were formed. Sufficiently refined data were obtained by averaging 25 mass spectral scans. The reaction conditions and the spectrometer ionization voltage were adjusted so that mass fragments characteristic of a particular reactant or product could be identified for study in the TAP mode. These fragments were established by comparing the authentic spectra of all suspected reaction components against spectra obtained under reaction conditions. Spectra from calibration mixtures were used to estimate the hydrocarbon product yields. The individual reactions of tetrahydrothiophene, thiophene, 1-butene, 1,3-butadiene, and *n*-butane at various concentrations with hydrogen were studied.

In TAP mode desulfurization experiments, the high-speed pulse valves were used to impose hydrogen transients onto a continuous reactant feed of 10 : 1 (by mole) hydrogen : tetrahydrothiophene or hydrogen : thiophene. The hydrogen pulse intensity was controlled by the valve backing pressure in the mixing manifold, which was maintained at either 517 or 1034 Torr. In performing the TAP experiments, the quadrupole mass spectrometer was tuned to a single mass fragment characteristic of a component in the reaction mixture. A synchronization signal from the valve driver was used to trigger the signal averager, which was set to monitor the quadrupole signal for a duration slightly greater than that of the product pulse. A TAP curve was produced by monitoring the mass intensity of the characteristic fragment as a function of time relative to the synchronization signal. Refined TAP curves were obtained by averaging 50 such spectra.

The characteristic fragments monitored for tetrahydrothiophene, thiophene, butene, and 1,3-butadiene (chosen on the basis of signal intensity and specificity) occurred at *m*/*e* 46, 45, 41, and 39, respectively. Butene isomerization was not examined since the fragmentation patterns of the isomers are not readily distinguishable with a quadrupole spectrometer. While the fragments chosen were not unique to each reaction component, experiments in which unique (but far less intense) fragments were monitored showed that partial peak overlap in no way prejudiced the assignment of the relative temporal peak positions for the various components (*9*). The enhancement of signal to noise ratio achieved by monitoring the most intense fragments more than justified the concomitant loss in signal specificity. H_2S could be detected and its formation in TAP experiments was monitored; however, these studies did not yield useful time-resolved data due to the broad desorption behavior. Monitoring this peak was useful in indicating the optimum presulfidation conditions for the catalyst.

RESULTS AND DISCUSSION

Scan Mode Experiments

The results of the scan mode experiments are given in Table 1, which summarizes the products observed during individual reactions of tetrahydrothiophene, thiophene, 1-butene, 1,3-butadiene, and *n*-butane at various concentrations with hydrogen. Under all conditions, Table 1 shows that tetrahydrothiophene reacted to complete conversion to produce butene and butadiene hydrocarbon products. No butane was detected in the hydrocarbons. The addition of hydrogen to the reactant stream at increasing levels up to 10 : 1 (*m*/*m*) hydrogen : tetrahydrothiophene increased the butene to butadiene ratio. Higher concentrations of hydrogen had no effect on the butadiene yield. In addition to the tetrahydrothiophene desulfurization reaction, dehydrogenation to thiophene also occurred at all hydrogen concentrations examined. As a rough indication of the amount of thiophene formed relative to butene, the signal intensity ratio (*m*/*e* 45 : 41) for thiophene : butene is given as a function of hydrogen concentra-

TABLE 1

Hydrocarbon Product Distributions for the Reactions of Tetrahydrothiophene, Thiophene, Butene, 1,3-Butadiene, and *n*-Butane at Various Concentrations with Hydrogen

Reactant	H_2/reactant molar ratio	Conversion (%)	Butene (%)	1,3-Butadiene (%)	*n*-Butane (%)
Tetrahydrothiophene	0	100	14	86	0
	5	100	23	77	0
	10	100	32	68	0
	30	100	32	68	0
Thiophene	0	0	0	0	0
	10	0	0	0	0
1,3-Butadiene	0	0	0	0	0
	10	22	22	88	0
Butene	0	45	55	45	0
	10	18	82	18	0
n-Butane	0	0	0	0	100
	10	0	0	0	100

tion in Table 2. Table 1 shows that on increasing the H_2/reactant molar ratio from 0 to 30, the relative amount of butene to butadiene increases. Thus, comparison of Table 2 with the data in the third column of Table 1 suggests that the inclusion of hydrogen in the feed also discourages thiophene formation. The product distribution data in Tables 1 and 2 are qualitatively consistent with the low conversion results obtained in conventional microreactor studies (*1*). It is believed that this agreement derives from the very low surface coverage and short contact times attainable in the scan mode experiments.

An important aspect of the data in Table 1 is that while tetrahydrothiophene reacted readily to produce butene and butadiene, no conversion of thiophene could be detected. Thiophene does not react in the absence of hydrogen (*4*), and it is likely that the very low system pressures (≪760 Torr) employed in these experiments resulted in insufficient hydrogen surface coverage to enable thiophene conversion (*7*). It should be noted that 100% conversion of thiophene to products was observed over the same catalyst during the presulfiding procedure performed in the conventional atmospheric pressure microreactor. The relative inertness of thiophene to the hydrogen exposures employed here is a distinct advantage, since independent reactions of thiophene and tetrahydrothiophene to products need not be considered. This greatly simplifies the interpretation of the hydrocarbon product distribution data.

TABLE 2

Relative Thiophene and Butene Yields for Tetrahydrothiophene Desulfurization at Various Hydrogen Concentrations

H_2/tetrahydrothiophene molar ratio	Thiophene : butene mass intensity ratio (*m*/*e* 45 : 41)
0	1.95
5	0.80
10	0.40
30	0.35

Table 1 further shows that interconversion of butene and butadiene occurred, even when hydrogen was included in the reactant stream. This result is to be expected, since the equilibrium constant for the reaction,

$$\text{butene} = \text{butadiene} + \text{hydrogen}$$

has been given as 10^{-6} at ≈350°C (*1*). While this implies only a 0.1% equilibrium conver-

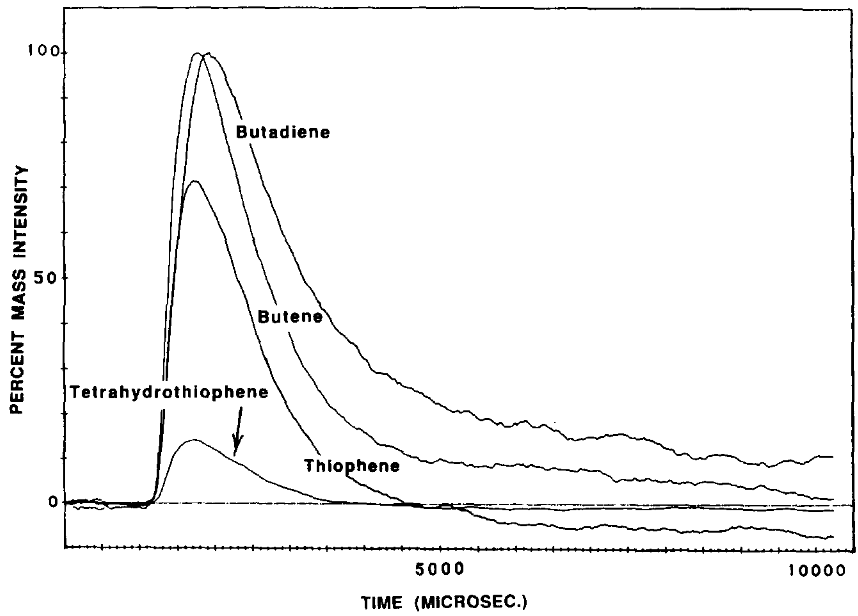

FIG. 2. TAP curves for the desulfurization of tetrahydrothiophene obtained by imposing a hydrogen pulse of intensity 517 Torr onto a 10:1 (by mole) hydrogen : tetrahydrothiophene continuous background. (Relative residence times: tetrahydrothiophene ≈ thiophene = 1730 μs; butene = 1790 μs; 1,3-butadiene = 1940 μs.)

sion of butene to butadiene at atmospheric pressure, when the pressure is reduced to the regime indicated by Fig. 1, equilibrium conversions on the order of 50% are predicted. Although equilibrium conversions of the hydrocarbons are unexpected, appreciable conversion of butene to butadiene at the low pressure employed is nonetheless not surprising. No conversion of butene or butadiene to butane was observed, and butane itself was inert under the conditions studied.

TAP Mode Experiments

The relative TAP curves for the desulfurization of tetrahydrothiophene are shown in Fig. 2. These curves were obtained by imposing a hydrogen transient on a 10:1 (*m*/*m*) hydrogen : tetrahydrothiophene gas mixture. As with the scan mode experiments, tetrahydrothiophene was rapidly converted to thiophene, butene, and butadiene in the TAP mode. Again, no butane was found in the hydrocarbon products. In the TAP mode, the conversion of tetrahydrothiophene to products was less than 100% because introduction of the hydrogen pulse reduced the contact time relative to the scan mode experiments. The relative intensities of the curves in Fig. 2 reveal that roughly 56% of the hydrocarbons formed consisted of butene. It should be noted that the amount of butene formed in the TAP mode experiments is nearly twice that achieved during the lower hydrogen pressure and longer contact time scan mode experiments. No TAP curves for the hydrodesulfurization of thiophene are shown, since under the present conditions, no conversion of thiophene to products was observed in the TAP mode experiments.

The time-resolved data of Fig. 2 shows that the characteristic peaks for tetrahydrothiophene and thiophene were both centered close to 1730 μs. Dehydrogenation of tetrahydrothiophene to thiophene obviously occurred very rapidly. It is therefore expected that the increase in the *m/e* 45 : 41 ratio in the TAP mode experiment of Fig. 2 relative to that of the scan mode experiment of Table 2 is associated with the reduction in the reactor contact time. As noted above, the tetrahydrothiophene conversion in the scan mode experiment exceeds that of the TAP mode experiment. Butene was also formed rapidly, having its characteristic peak centered at 1790 μs. With a characteristic peak centered at 1940 μs, butadiene was apparently the slowest product to form.

Since butadiene is lighter than butene, the transit time from reactor to detector (which increases as the square of molecular weight) could not have controlled the relative residence times of these two molecules (*7*). Since no desulfurization of thiophene was observed, formation of butene and butadiene by independent reactions of thiophene and tetrahydrothiophene can be excluded. At the temperature employed here (445°C) marked differences in the adsorption characteristics of butene and butadiene are considered unlikely. Indeed, TAP curves obtained by pulsing butene and butadiene separately to the catalyst at the reaction temperature showed them to exhibit no significant differences in adsorption behavior (*9*). Furthermore, TAP studies of C_4 hydrocarbon reactions over the same catalyst (*9*) showed that when butene was in fact formed by butadiene hydrogenation, the butene exited the reactor last.

The TAP data of Fig. 2 may provide new evidence that tetrahydrothiophene desulfurizes more rapidly to butene than to butadiene. These results are in conflict with the mechanism of Kolboe (*4*), which proposes that tetrahydrothiophene primarily undergoes dehydrosulfurization to butadiene followed by hydrogenation to butene. On the other hand, dehydrogenation of butene cannot be a major path to butadiene formation. Table 1 shows that even in the absence of hydrogen, only about one-half of the butadiene formed in tetrahydrothiophene desulfurization can be accounted for by butene dehydrogenation; when hydrogen is present, only about one-fourth can be accounted for. Consequently, the combined data of Table 1 and Fig. 2 suggest that butene and butadiene are formed by essentially independent reaction paths. The significant yield of butadiene observed in these and previous studies argue against mechanisms involving intermediates like 1-butanethiol or a surface butylthiolate, since these intermediates lead logically only to more highly saturated products.

Figure 3 shows the effect on butene and butadiene yields when the hydrogen pulse intensity used in the TAP experiment of Fig. 2 was doubled. As expected from Table 1, doubling of the hydrogen pulse intensity led to a further increase in the relative butene yield, as can be seen by comparing Fig. 2 with Fig. 3(a). The increase in pulse intensity reduced the reactor contact time relative to that in the experiment of Fig. 2, so that butene and butadiene had their characteristic peaks shifted down to 1420 and 1650 μs, respectively. It should be noted that despite the decrease in average contact time, the peak separation between butadiene and butene fragments increased relative to that in Fig. 2 on increasing the hydrogen pulse intensity. If parallel reaction pathways are assumed, the increase in peak separation distance specifically indicates an increase in the butene formation rate relative to that of butadiene. Comparison of Figs. 2 and 3(a) also shows that the increased hydrogen pulse intensity caused the butene peak to narrow, while the butadiene peak became correspondingly more broad. This is more apparent in Fig. 3(b), where the curves of Fig. 3(a) are replotted using a normalized intensity scale. The observed increase in the butene yield upon increasing the hydrogen pressure which simultaneously resulted in a sharpening of the butene peak, a broadening of the butadiene peak, and an

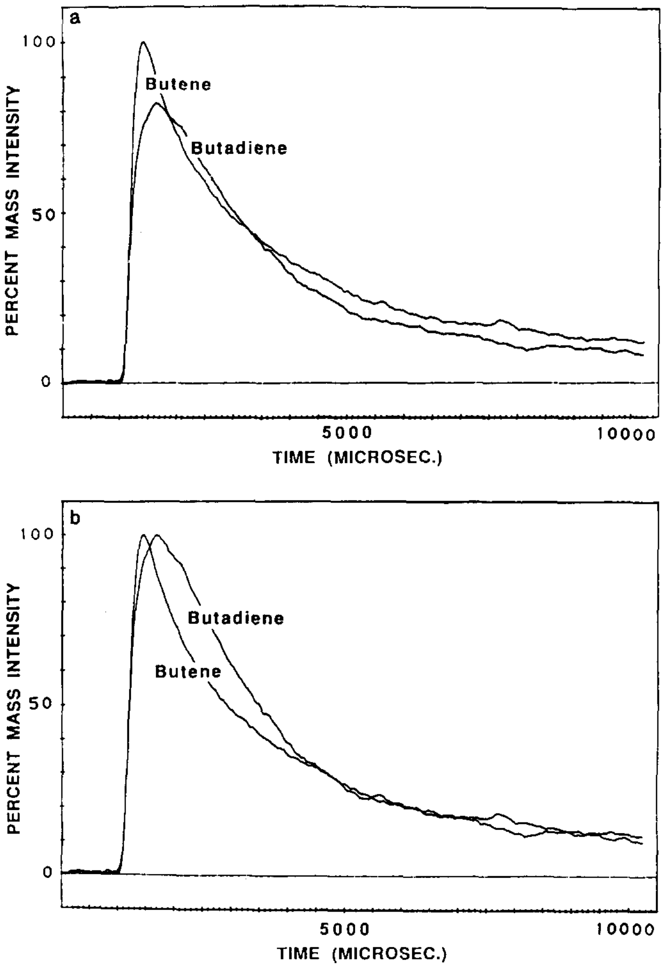

FIG. 3. TAP curves for the desulfurization of tetrahydrothiophene obtained by imposing a hydrogen pulse of intensity 1034 Torr onto a 10 : 1 (by mole) hydrogen : tetrahydrothiophene continuous background. Tetrahydrothiophene and thiophene curves are omitted. The curves in (b) are the same as those in (a) replotted on a normalized intensity scale. (Relative residence times: butene = 1420 μs; 1,3-butadiene = 1650 μs.)

increase in their appearance separation times, suggests that the additional yield of butene was formed at the expense of butadiene by a branching mechanism; and that a second minor mode of butadiene formation arose through dehydrogenation of the higher concentration of butene. While this minor route to butadiene is possible under the low pressure conditions employed, it will be negligible in atmospheric pressure reactions due to thermodynamic equilibrium limitations. Rapid dehydrogenation of tetrahydrothiophene to thiophene also occurs, but is not shown in the figure.

Mechanistic Considerations

The TAP spectrometer results presented here suggest a desulfurization mechanism for tetrahydrothiophene other than those previously proposed. As noted above, the key observation in these experiments that butene may in fact be the first desulfurized product formed argues against a simple dehydrosulfurization mechanism as first suggested by Kolboe (*4*). The observation that butadiene is formed in quantities roughly three times greater than can be accounted for by butene dehydrogenation argues against mechanisms involving intermediates like 1-butanethiol, as suggested by Deskian and Amberg (*3*), or a surface butylthiolate, proposed by Roberts and Friend (*6*), since these lead logically only to the more saturated products, butene and butane. The surface science results of Roberts and Friend (*6*) are not necessarily applicable here, since it is questionable whether the HDS mechanism operating over the single crystal Mo catalyst employed in their study is the same as that encountered with the conventional supported cobalt molybdate materials. The fact that the TAP studies did not produce products resulting from a surface butylthiolate intermediate (*6*), i.e., butane and butene, suggests that the chemistry of the single crystal Mo surface is somewhat different from that of the supported cobalt molybdate surface. Conceptually, a wide range of factors could rationalize these differences; but, the key observations seem to indicate that the Co–Mo system is a somewhat superior dehydrogenation/β-eliminator than pure Mo which in competition is more active for hydrogenolysis. Furthermore, any proposed mechanism must be consistent with the observation here and in previous studies (*1*) that both butene and butadiene can be formed in appreciable quantities in the absence of hydrogen, while the inclusion of hydrogen in the feed, particularly at higher pressures, strongly enhances the selectivity to butene. No butane was formed during the TAP hydrodesulfurization of THT, and neither butene nor butadiene were hydrogenated to butane under the same TAP reaction conditions. These results are similar to those reported by Hargreaves and Ross (*1*) on the hydrodesulfurization of THT at pressures much higher than those used in the TAP experiments described here. Their results showed that the product consisted of less than 2% butane for THT conversion by a cobalt molybdate catalyst either in the presence or absence of hydrogen, and the rate of hydrogenation of butene to butane was very slow as compared to THT hydrodesulfurization. In contrast to these results was their observation that the HDS of 1-butanethiol led to appreciable quantities of butane along with the main butene products. Had a surface-adsorbed 1-butanethiol or butylthiolate intermediate been responsible for the hydrodesulfurization of THT, the TAP studies should have resulted in appreciable amounts of butane. The butenethiolate intermediate proposed here accounts for all of the products observed in the TAP studies as well as those in classical HDS studies. Since it also rationalizes the relative production sequence, the mechanism shown in Fig. 4 seems to best account for the experimental observations.

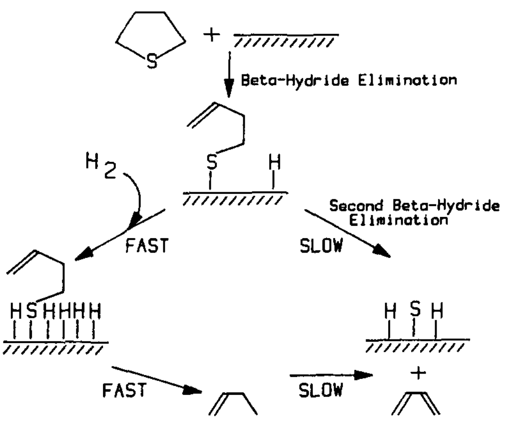

FIG. 4. Proposed tetrahydrothiophene desulfurization mechanism involving a surface butenethiolate intermediate.

The key observation from the TAP studies was the appearance of butene before butadiene when tetrahydrothiophene was hydrodesulfurized under hydrogen over the cobalt molybdate catalyst. Since it is unlikely that the sequential conversion of butene to butadiene is a major pathway for the HDS reaction (*1*), the most reasonable rationalization of the data is that butene and butadiene are formed from either a parallel reaction or a branching reaction from a common intermediate. The observation that the appearance time of butene was considerably shortened relative to that of butadiene when a higher hydrogen pressure was applied confirms this idea. This increase in the separation of the two appearance times would be expected in the TAP experiment if the process conditions specifically increase the rate of formation of one of the parallel reaction products and not the other. In the instant case, the increased hydrogen pressure accelerated the rate of butene formation more than the butadiene rate as judged by the integrated peak intensities. These data are in sharp contrast to prior HDS studies which concluded that butadiene was the primary reaction product, followed by subsequent hydrogenation in a sequential reaction to form butene.

Of the various mechanistic possibilities considered for rationalizing the TAP data, the scheme shown in Fig. 4 is favored. In this mechanism, THT is assumed to adsorb at the catalyst surface by undergoing a single β-hydride elimination to produce a surface butenethiolate intermediate. Rapid equilibration of this intermediate with the gas phase molecule is assumed. When an excess of surface hydrogen is present from an external source, the rate of C–S hydrogenolysis would be expected to greatly increase, thereby enhancing the butene formation rate relative to the rate of the second β-hydride elimination responsible for butadiene formation. This effect was indeed observed (Figs. 2 and 3) in the higher pressure TAP mode experiments and in conventional reactor studies (*1*). Also at higher hydrogen pressures, the appearance position of butene decreased relative to that of butadiene in accord with the expectation based on TAP type experiments (*7*). This data is consistent with the mechanistic step on the left side of the figure, where the common butenethiolate surface species is hydrogenated to butene by hydrogen addition to the α-carbon atom. As this step becomes faster due to higher hydrogen pressures, the butene peak should appear earlier. The appearance of butadiene after the butene peak in the TAP reactions suggests that this product could also have been formed from the butenethiolate common intermediate but at a slower overall rate. This conversion is illustrated on the right side of Fig. 4, where butadiene is shown to be directly formed from the butenethiolate intermediate by a second β-hydrogen elimination. These data clearly demonstrate a detail of HDS not recognized previously, in that butadiene was not formed initially followed by hydrogenation to butene. Higher butene concentrations would then lead to a higher butadiene rate of formation through the butene to butadiene dehydrogenation pathway. This conversion is thermodynamically feasible under the low pressure conditions of the TAP experiment. Indeed, experiments showed that flowing butene over the catalyst at normal reaction conditions led to a modest conversion to butadiene.

CONCLUSIONS

The desulfurization of tetrahydrothiophene on sulfided Co–Mo/γ-Al_2O_3 catalysts has been studied using the temporal analysis of products (TAP) transient microreactor technique. The TAP reactor studies showed that tetrahydrothiophene reacts with hydrogen at low pressures to produce thiophene, butene, and 1,3-butadiene. The exceptional time resolution of the TAP spectrometer provided strong evidence that the butene formed could not be accounted for by a mechanism involving butadiene hydrogenation as had been reported in the prior literature (*4*). This result, coupled with the observation of 1,3-butadiene and butene in nearly equal yields, suggested an alternative tetrahydrothiophene desulfurization mechanism, wherein the major path to C_4 hydrocarbons proceeds via a surface butenethiolate intermediate produced by a single β-hydride elimination. It is suggested that 1,3-butadiene may form by a slow, subsequent β-hydride elimination of the intermediate, while a more rapid C–S bond hydrogenolysis involving surface hydrogen is responsible for butene formation.

ACKNOWLEDGMENT

The authors thank the Specialty Chemicals Division of the Monsanto Company for financial support of this study.

REFERENCES

1. Hargreaves, A. E., and Ross, J. R. H., *J. Catal.* **56,** 363 (1979).
2. Pazos, J. M., and Andreu, P., *Canad. J. Chem.* **58,** 479 (1980).
3. Deskian, P., and Amberg, C. H., *Canad. J. Chem.* **42,** 843 (1964).
4. Kolboe, S., *Canad. J. Chem.* **47,** 352 (1969).
5. Kwart, H., Schuit, G. C. A., and Gates, B. C., *J. Catal.* **61,** 128 (1980).
6. Roberts, J. T., and Friend, C. M., *J. Amer. Chem. Soc.* **108,** 7204 (1986).
7. Gleaves, J. T., Ebner, J. R., and Kuechler, T. C., *Catal. Rev. Sci. Eng.* **30**(1), 49 (1988).
8. Gleaves, J. T., and Ebner, J. R., *in* "Oxygen Complexes and Oxygen Activation by Metal Complexes" (A. E. Martell and D. T. Sawyer, Eds.), Proc. 5th IUCCP Sympos., p. 273. Plenum, New York, 1988.
9. Rossetti, Jr., G. A., M. S. thesis, Worcester Polytechnic Institute, 1987.