

NON-STATIONARY EXPERIMENTS ON THIOPHENE AND TETRAHYDROTHIOPHENE HYDRODESULPHURIZATION

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The reactions of tetrahydrothiophene and thiophene in hydrogen on sulphided Mo/Al₂O₃, Co-Mo/Al₂O₃, and Ni-W/Al₂O₃ catalysts have been studied using pulse-flow, stopped flow, and started flow techniques. The composition of the effluent from the reactor was analyzed after a perturbation and the observed response curves have been interpreted from the point of view of the reaction mechanism and influence of the promotor (Co) in the Co-Mo/Al₂O₃ catalyst. The results confirm that at least partial saturation of the thiophene ring is necessary for hydrodesulphurization and that at least one C—S bond is splitted by hydrogenolysis, the second one either by hydrogenolysis or by elimination. Cobalt increases the hydrogenolytic activity of molybdenum, in its absence the predominant reaction of tetrahydrothiophene is dehydrogenation to thiophene.

Perturbation methods are suitable for obtaining detailed information on kinetic scheme and mechanism of surface processes in heterogeneous catalysis¹⁻³. The purpose of the present work has been to obtain, using this approach, some new knowledge on the mechanism of hydrodesulphurization of thiophene (T) and tetrahydrothiophene (THT) on cobalt-molybdenum, molybdenum, and nickel-tungsten catalysts.

Recently, Zdražil⁴ has examined critically the ideas on hydrodesulphurization mechanism and has shown, on the basis of the chemistry of sulphur-containing heterocycles, that the hydrodesulphurization reaction must begin with partial or total saturation, followed by elimination or hydrogenolytic opening of the ring. Next step is β -elimination of hydrogen sulphide under formation of an alkene which is then hydrogenated to the corresponding alkane. Two questions remained open: *a*) Whether the ring hydrogenation must be complete or the ring may be opened after partial saturation. *b*) Whether the ring opening proceeds by hydrogenolysis, that is under direct participation of hydrogen, or by acid catalyzed step in which hydrogen serves only to the regeneration of the active centres by removal of S.

EXPERIMENTAL

The experimental arrangement was described in our previous papers^{3,5}. At the entry of the pseudodifferential flow reactor, the following concentration perturbations were introduced: *a*) step start of feeding of the compound A (START(A)) into a stream of hydrogen; *b*) step stop

of feeding of A (STOP(A)); c) a pulse of A superposed on the steady-state feeding of compound B (PULSE(A/B)). The step changes were realized by switching a two-way valve, the pulses were introduced by a microsyringe. The continuously flowing gas was hydrogen. The parameters

TABLE I

Conditions of the experiments (W catalyst weight, p_i^0 partial pressure of the component i in the feed, F_i^0 its feed rate, x conversion of i)

Compound	Pulse μmol	Steady-state operation					
		Catalyst	W mg	T $^{\circ}\text{C}$	p_i^0 kPa	F_i^0 $\mu\text{mol s}^{-1}$	x %
Tetrahydrothiophene	5.45	Mo/Al ₂ O ₃	76	300	1.84	0.61	2.2
		Co-Mo/Al ₂ O ₃	35	200	1.84	0.61	0.35
			23	300	1.84	0.61	8.3
		Ni-W/Al ₂ O ₃	37	260	1.84	0.61	1.1
			37	300	1.84	0.61	9.9
Thiophene	6.30	Mo/Al ₂ O ₃	83	300	8.5	2.84	1.4
		Co-Mo/Al ₂ O ₃	38	300	8.5	2.84	7.9
		Ni-W/Al ₂ O ₃	41	260	8.5	2.84	0.23
Hydrogen sulphide	0.40	all	—	—	—	—	—
Hydrogen	—	all	up to total	—	120	40	—

TABLE II

Catalysts used

Composition wt %	Origin	Surface area $\text{m}^2 \text{g}^{-1}$	Helium density g cm^{-3}
Co-Mo/Al ₂ O ₃ (4.2 CoO, 12.6 MoO ₃)	Cherox 36-01 ^a	131	2.58
Mo/AlO ₃ (10 MoO ₃)	laboratory	160	3.10
Ni-W/Al ₂ O ₃ (10.8 NiO, 32.8 WO ₃ , 15.1 SiO ₂ , 1.5 F)	Cherox 34-03 ^a	117	3.98

^a Chemical Works, Litvňnov.

of the components at the entry of the reactor are given in Table I. For obtaining the response curves, the perturbations were repeated and the stream of the products analyzed at different times after the perturbation³.

The catalysts are characterized in Table II. The samples were sulphided *in situ*, using $\text{H}_2\text{S} + \text{H}_2$ (1 : 4) at 450°C for 0.5 h. The reaction temperature was reached during 15 min in a flow of hydrogen and first 10–20 perturbations were introduced until reproducible responses were obtained (better than 95%).

The chemicals used were: Tetrahydrothiophene (*puriss.*, Fluka) was rectified and dried over anhydrous CaCl_2 . Its purity was 99.98% (GLC) and contained traces of thiols and thiophene. Thiophene (*puriss.*, Fluka) was pretreated in the same way as tetrahydrothiophene and its purity was 99.99%. Hydrogen sulphide (Fluka, 99.9%) was taken from a pressure bottle. Hydrogen (Technoplyn) was purified in a deoxo unit and in a column containing molecular sieve 4A. The impurities were less than 20 ppm. Nitrogen (Technoplyn) was purified to the same grade.

The reaction mixture was analyzed using a temperature-programmed gas chromatograph. The column (2 m) was packed with Carboxpack C + 0.2% picric acid, initial temperature was 40°C for 5 min, then increased by 20 K/min, the upper temperature plateau was 180°C. Flow rate of hydrogen was 20 ml/min, of nitrogen for the FID detector 10 ml/min.

RESULTS AND DISCUSSION

In all experiments, the concentrations of the principal components were determined gas chromatographically at the reactor exit, that is of butenes, butene, C_2 and C_3 hydrocarbons, thiophene, tetrahydrothiophene. Further on, butanethiol, dibutyl sulphide, higher hydrocarbons, and higher-boiling sulphur-containing compounds were detected in traces but not determined. Butadiene was detected in no experiment.

The description of the dynamic behaviour of the reaction system is based on characteristic features of relaxation curves which are recorded as dependences of the rates of production of individual compounds on time. The rate of production of compound i ($\mu\text{mol s}^{-1} \text{g}^{-1}$) is given by

$$r_i = F y_i / W, \quad (1)$$

where F is rate of flow ($\mu\text{mol s}^{-1}$), y_i molar fraction of compound i in the stream, and W catalyst weight (g). In the following graphs, the experimental points are omitted for clarity; however, their density was the same as in our previous paper³. The response curves of 1- and 2-butene were used for calculation of their ratio, denoted $S_{1/2}$, which indicates more sensitively the parallel or consecutive formation of these two products.

Tetrahydrothiophene

The results of the perturbation experiments are presented in Figs 1–4. Each figure consists of four parts, three of them showing the time dependences of the rates of release of reaction products from the reactor following a perturbation of the

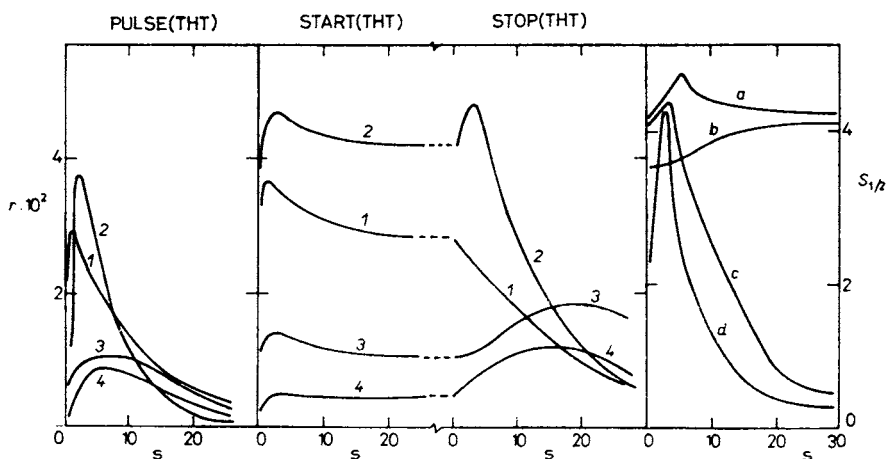


FIG. 1

Response curves of the products from tetrahydrothiophene (THT) on Co-Mo/Al₂O₃ at 200°C. Steady-state conversion 0.35%, r in ($\mu\text{mol s}^{-1} \text{g}^{-1}$). PULSE(THT) denotes experiments with a pulse of THT introduced into the stream of hydrogen, START(THT) denotes initial period of the reaction, after introduction of THT feed into the hydrogen stream, STOP(THT) the period after stopping the THT feed. 1 Hydrogen sulphide (actual rate is twice the given value), 2 1-butene, 3 2-butene, 4 butane, (5 thiophene in Figs 2—4); the 1-butene/2-butene ratio $S_{1/2}$ was calculated: a from experiments with pulses of H₂S superposed onto the steady-state reaction, b from PULSE experiments, c from START experiments, d from STOP experiments

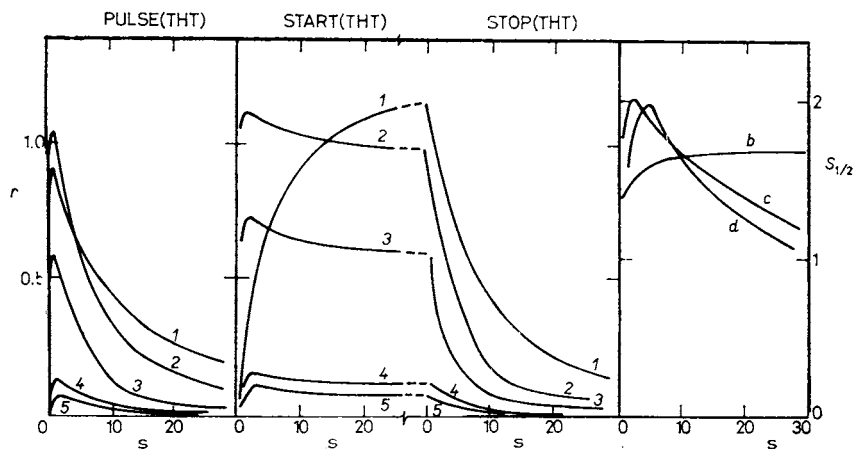


FIG. 2

Response curves of the products from tetrahydrothiophene (THT) on Co-Mo/Al₂O₃ at 300°C. Steady-state conversion 8.3%. For symbols see Fig. 1

initial state; on the time scale, the moment of the perturbation is zero. The three types of perturbations were: pulse of thiophene or tetrahydrothiophene into a hydrogen stream, start of feeding, and stop of feeding. The fourth part of the figures sum-

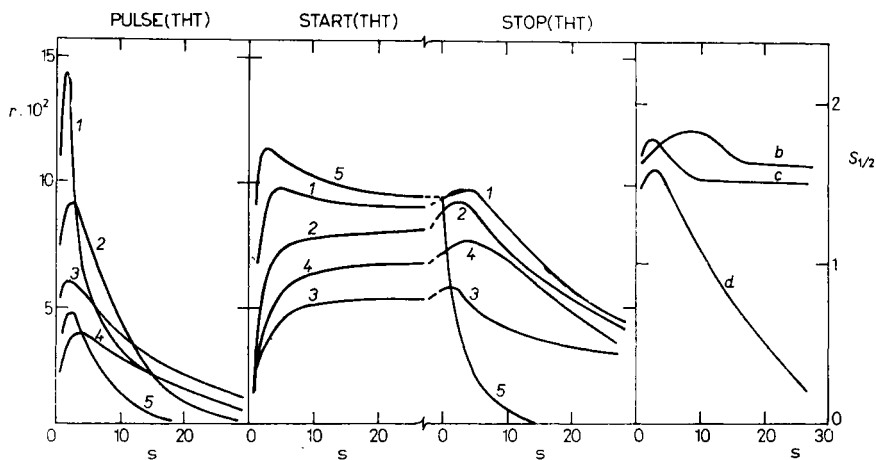


FIG. 3

Response curves of the products from tetrahydrothiophene (THT) on $\text{Mo}/\text{Al}_2\text{O}_3$ at 300°C . Steady-state conversion 2.2%. For symbols see Fig. 1

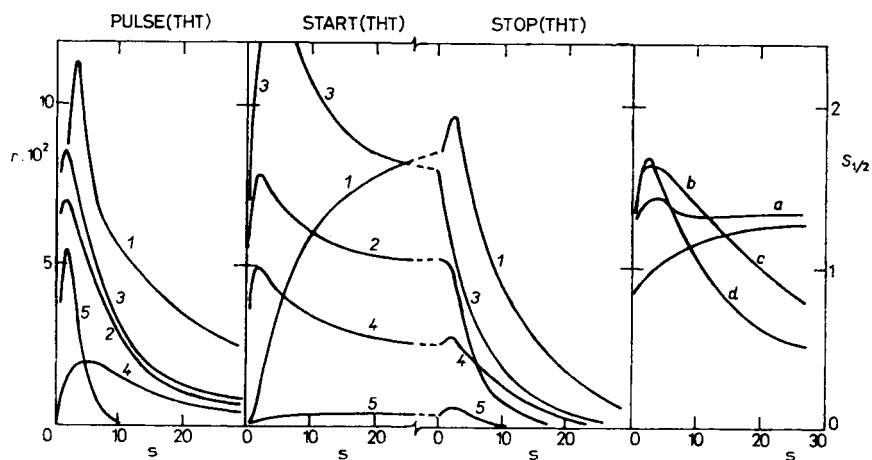


FIG. 4

Response curves of the products from tetrahydrothiophene (THT) on $\text{Ni-W}/\text{Al}_2\text{O}_3$ at 260°C . Steady-state conversion 1.1%. For symbols see Fig. 1

marizes the 1-butene/2-butene selectivities, calculated from the three types of non-stationary experiments and, in some instances, also the values obtained by perturbation of the steady-state by a pulse of H_2S . With Mo/Al_2O_3 which showed low activity, the measurements were possible only at $300^\circ C$, with the other two catalysts, two temperature levels have been used.

However, with $Co-Mo/Al_2O_3$ more information was obtained at $200^\circ C$ because at $300^\circ C$ the changes were too rapid for distinguishing minor differences in the shape of the response curves (Figs 1 and 2). The reaction mixture leaving the reactor contained the reactant (tetrahydrothiophene), which is omitted from the graphs for simplification, and the products of its transformation: hydrogen sulphide, 1-butene, 2-butene, butane; at $300^\circ C$ also thiophene and C_2 and C_3 hydrocarbons were formed. The rate of production of the lower hydrocarbons was small and their curves are therefore not given in Fig. 2. 1,3-Butadiene was not found in the products in contrast to the observation of Hargreaves and Ross⁶ who have studied the decomposition of tetrahydrothiophene in the presence and absence of hydrogen at $248^\circ C$. However, they have used very low hydrogen pressure (3 kPa).

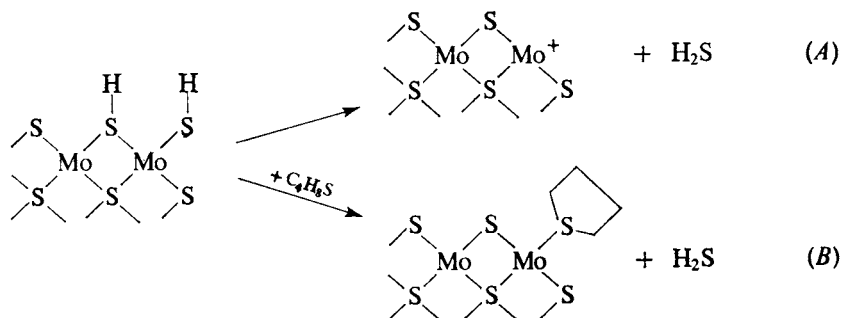
At $200^\circ C$ (Fig. 1), hydrogen sulphide is clearly the first product which leaves the reactor after a pulse of tetrahydrothiophene, in spite of the fact, shown by independent pulse experiments with pure compounds, that it is retained longer on the surface than the hydrocarbons. This is an evidence for the formation of the hydrocarbons from a strongly bonded surface precursor containing sulphur. This observation is supported further by the maximum on the curve for 1-butene in the stop(THT) experiment; the curve for hydrogen sulphide shows a monotonous decrease.

This behaviour of the pair tetrahydrothiophene-hydrogen sulphide resembles that of ethanol-water reported in our previous work^{3,5}, where replacement of surface hydroxyl groups by alkoxy groups under liberation of water was observed. The exchange of sulphur and oxygen in sulphide catalysts was observed by Mashkina⁷. It is known^{8,9} that the surface of sulphide catalysts contains sulphhydryl groups; two of these groups may form hydrogen sulphide (Eq. (A)) and after its desorption leave a Lewis site on the surface which serves then for adsorption of thiophene or tetrahydrothiophene. We suggest that direct replacement by tetrahydrothiophene is also possible (Eq. (B)) under liberation of hydrogen sulphide.

These two mechanisms may operate simultaneously, their ratio depending on the temperature, lower temperatures favouring the substitution mechanism.

The curves of 1-butene, 2-butene, and butane in all types of experiments indicate the formation of the 1-isomer as the principal primary product. Its relative concentration highly exceeds the thermodynamic equilibrium values ($S_{1/2}^{eq} \approx 0.25$) (ref.¹⁰). The (at least partly) consecutive character of 2-butene formation is clearly seen on the $S_{1/2}$ curve from the stop(THT) experiment. However, it is not necessary to assume the desorption of all 1-butene molecules into the gas phase and their

readsorption. The transformation of 1-butene to 2-butene and butane can proceed immediately in the adsorbed state. Moreover, a part of 2-butene may be produced directly from the sulphur species.



The change of the reaction temperature to 300°C (Fig. 2) increases, of course, the reaction rate but the over-all picture remains the same. The only exception is the appearance of small amounts of thiophene and C₂, C₃ hydrocarbons in the products.

However, thiophene is the main product of the reaction of tetrahydrothiophene on the Mo/Al₂O₃ catalyst (Fig. 3). The absence of cobalt causes a decrease of desulphurization activity, whereas the dehydrogenation activity is maintained. The content of butane in the C₄ fraction is higher than with the Co-Mo/Al₂O₃ catalyst and this is in agreement with the maxima or shoulders on the curves of the hydrocarbons in the stop experiment. Also the hydrogen sulphide curve shows a maximum which was not present in experiments with Co-Mo/Al₂O₃ and which indicates stronger retention of H₂S on the surface.

For the Ni-W/Al₂O₃, the data obtained at 260°C are shown here (Fig. 4) because the response curves were better resolved than at 300°C. The major change against Co-Mo/Al₂O₃ is the release of hydrogen sulphide later than of the C₄ hydrocarbons which makes the mechanism of tetrahydrothiophene adsorption according to Eq. (B) more probable. Smaller selectivity ratio $S_{1/2}$ was also observed but still higher than thermodynamic equilibrium value. Significant amount of thiophene were also formed. Like in case of Mo/Al₂O₃, this compound disappears from the products much more rapidly than other substances after stopping the feed. This indicates different reaction pathway and very probably different reaction sites for the dehydrogenation.

Large difference in dehydrogenation activity of sulphided unpromoted and nickel promoted molybdenum catalysts, measured by the reaction of isopropylbenzene, was observed by López and coworkers¹¹; the Mo/Al₂O₃ catalyst was by one order of magnitude more active.

Thiophene

Tetrahydrothiophene was not detected in the products of the reaction of thiophene. On all catalysts (Figs 5–7), hydrogen sulphide was released simultaneously or later

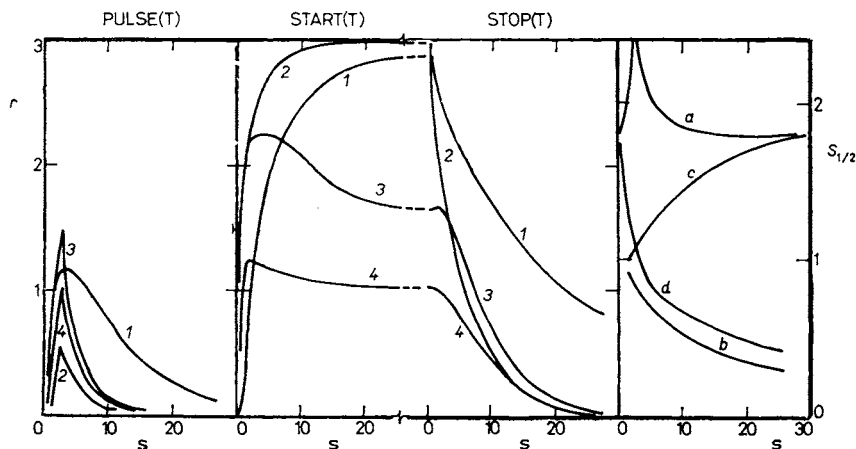


FIG. 5

Response curves of the products from thiophene (T) on Co-Mo/Al₂O₃ at 300°C. Steady-state conversion 7.3%. For symbols see Fig. 1

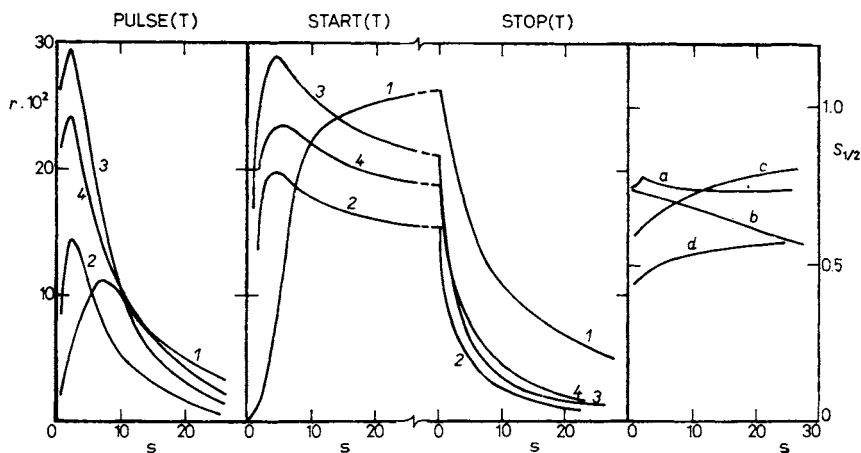


FIG. 6

Response curves of the products from thiophene (T) on Mo/Al₂O₃ at 300°C. Steady-state conversion 1.4%. For symbols see Fig. 1

than the C_4 hydrocarbons in the pulse(T) experiment, in contrast to molybdenum catalysts in the pulse(THT) experiment. Also the curve of H_2S in the start(T) experiment showed a delay against the C_4 hydrocarbons. This behaviour indicates that the

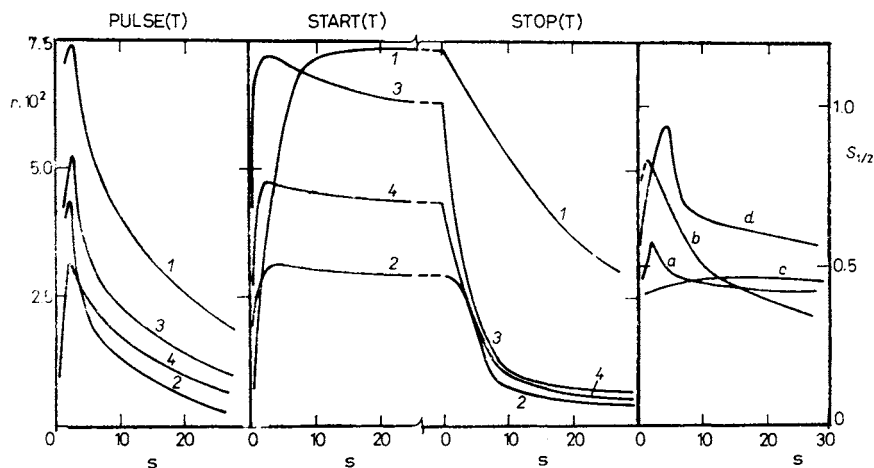


FIG. 7

Response curves of the products from thiophene (T) on Ni-W/ Al_2O_3 at 260°C. Steady-state conversion 0.23%. For symbols see Fig. 1

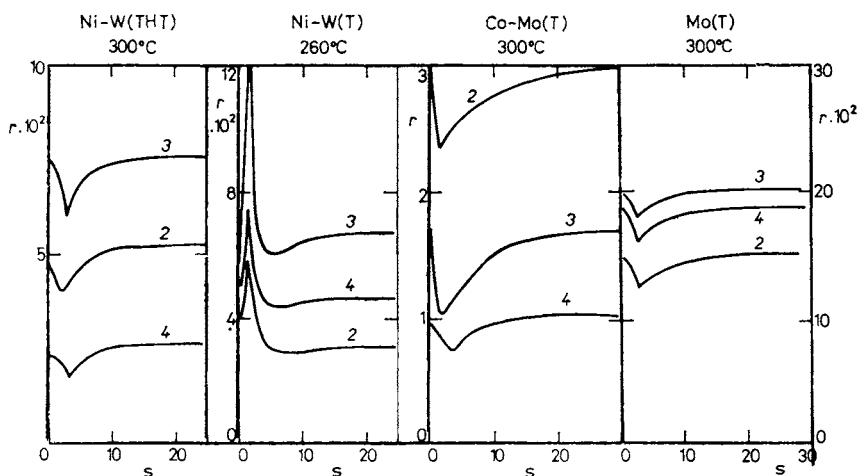


FIG. 8

Response curves of the products from the steady-state reactions of tetrahydrothiophene (THT) or thiophene (T) on different catalysts perturbed by a pulse of hydrogen sulphide

suggested substitution mechanism (B) is not operating with thiophene. The reason may be the decreased basicity of sulphur in thiophene compared with tetrahydrothiophene.

Effect of Hydrogen Sulphide

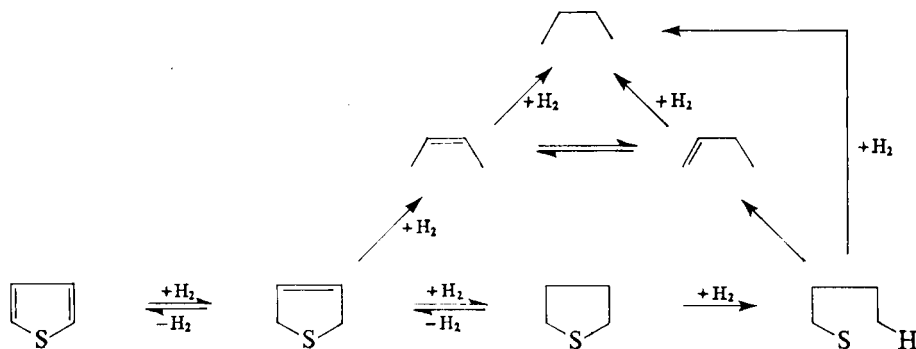
A series of experiments was made in which a pulse of hydrogen sulphide was introduced into the feed of thiophene or tetrahydrothiophene during a steady-state reaction. In all cases with one exception, hydrogen sulphide inhibited the formation of C₄ hydrocarbons; only in the reaction of thiophene on Ni-W/Al₂O₃, the rate was increased. Fig. 8 shows three examples of inhibition and the situation with Ni-W/Al₂O₃.

The Role of Hydrogen

The necessity of hydrogen presence for the splitting of the heterocyclic ring was confirmed by the experiment in which the activated Co-Mo/Al₂O₃ catalyst was heated in a stream of nitrogen to 500°C for 8 h. The resulting sample showed no activity for the reaction of tetrahydrothiophene at 250°C using the pulse(THT) technique. Even replacement of nitrogen by hydrogen as the carrier gas caused no change. However, the activity was restored when the catalyst was heated for a short time to 500°C in hydrogen.

Hargreaves and Ross⁶ were able to obtain C₄ hydrocarbons from tetrahydrothiophene in the absence of hydrogen on a Co-Mo/Al₂O₃ which was treated in hydrogen before the experiment.

These results confirm the direct role of adsorbed hydrogen in splitting of the saturated ring by hydrogenolysis. In the same time, the impossibility of elimination reaction is manifested which is caused very probably by the arrangement of the



SCHEME 1

five-membered ring containing sulphur. For a β -elimination the antiperiplanar confirmation of the C-S and C-H bonds leads to lowest activation energy^{12,13} which is difficult to achieve in tetrahydrothiophene without introducing considerable ring strain. This restriction doesn't influence the splitting of the second C-S bond where free rotation is possible.

The question remains open whether full or partial saturation of the thiophene ring is necessary before hydrogenolysis the first C-S bond. At present, we assume that both reaction path-ways, over tetrahydrothiophene and over dihydrothiophene operate simultaneously; this leads to the reaction network presented in Scheme 1. Whereas thiophene or tetrahydrothiophene may desorb (tetrahydrothiophene can be obtained as the product at higher hydrogen pressures, e. g.¹⁴), as well as the C₄ hydrocarbons, dihydrothiophene remains in the adsorbed state.

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