

## INVESTIGATION OF THE MECHANISM OF THIOPHENE HYDRODESULPHURIZATION BY ISOTOPIC METHOD

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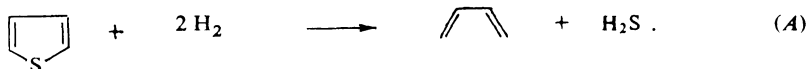
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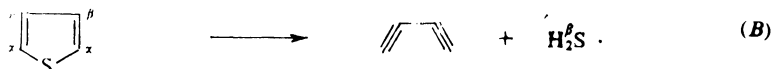
The reaction of thiophene with deuterium on alumina supported Ni-, Mo- and Ni-Mo-catalysts (laboratory samples) and Ni-W-, Ni-Mo- and Co-Mo-catalysts (commercial samples) was investigated at 150–455°C and different D<sub>2</sub>/C<sub>4</sub>H<sub>4</sub>S ratio in a closed system with internal circulation (total reactant pressure 3 kPa) and in a gradientless flow system (atmospheric pressure). Analysis of the deuterium distribution in thiophene and hydrogen sulphide and of its change in dependence on the extent of reaction revealed that thiophene hydrodesulphurization proceeds with participation of external hydrogen and not intramolecularly with participation of the β-hydrogen atoms of thiophene. This conclusion was checked also by the reaction of deuteriothiophene with light hydrogen. In the analysis of the results, the fast H<sub>2</sub>-D<sub>2</sub> exchange with thiophene was taken into account; exchange reaction of deuterium with hydrogen sulphide was not significant.

The mechanism of the catalytic thiophene hydrodesulphurization has been extensively discussed in the literature since this reaction is considered to be a model of the industrial process of the catalytic hydrodesulphurization of light petroleum fractions. An exhaustive survey of the chemical aspects of the problem has been published by Zdražil<sup>1</sup> recently. Without dealing here in detail with all the existing hypotheses, we are only going to show that all the known mechanistic schemes of the conversion of thiophene, and of its analogues, can be classified into three different types:

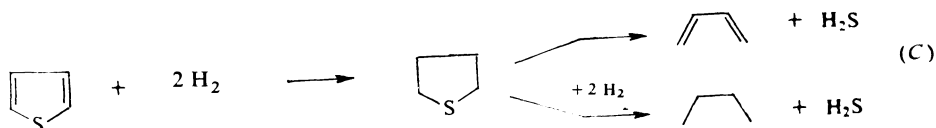
1. The reaction is effected by a direct splitting of the C—S bonds of thiophene by external hydrogen resulting in hydrogen sulphide formation, and the hydrocarbon intermediate is then partly or completely hydrogenated to the corresponding products which are desorbed into the gaseous phase<sup>2</sup>



2. The C—S bond splitting is an intramolecular process involving the  $\beta$ -hydrogen atoms of the thiophene molecule itself (so called dehydrosulphidation); the resulting hydrocarbon fragments are then hydrogenated with external hydrogen<sup>3-5</sup>



3. The first step of the reaction is a partial or complete hydrogenation of thiophene, followed by splitting of the C—S bonds and by the formation of hydrogen sulphide with the participation of either external hydrogen or of hydrogen from the hydrogenated intermediate itself; the reasons substantiating this scheme are best summarized in the above mentioned review<sup>1</sup>.



One of the efficient ways that can be used to investigate the mechanism of thiophene conversion is the method based on the analysis of the isotope distribution in the products formed if hydrogen is replaced by deuterium. However, relatively few studies using deuterium for this purpose can be found in the literature<sup>2,4-6</sup>, and with the only exception<sup>4</sup>, practically in none of them the change of the isotope distribution in the products was analyzed in dependence on the extent of reaction; such an analysis may play a decisive role in the elucidation of the reaction mechanism.

It is worth mentioning that in the presence of deuterium, an intensive deuterium-hydrogen exchange in the molecule of thiophene takes place simultaneously with hydrodesulphurization, the velocity of the former process being significantly higher than that of the latter<sup>5</sup>. The hydrogen atoms of thiophene are not equivalent with respect to their reactivity:  $\alpha$ -atoms are exchanged much faster than  $\beta$ -atoms<sup>8</sup>.

The aim of the present work was to elucidate, using the isotopic method, some mechanistic features of hydrodesulphurization on various catalysts; thiophene was used as model reactant.

## EXPERIMENTAL

*Catalysts.* The laboratory samples were prepared by impregnation of alumina CHEROX 33-00 (Chemical Works Litvínov, Czechoslovakia) with aqueous solutions of the corresponding salts (ammonium paramolybdate, and/or nickel nitrate), drying at 110°C and calcination at 550°C. Besides, three commercial catalysts were used: Co-Mo/Al<sub>2</sub>O<sub>3</sub> (CHEROX 36-01, Czechoslovakia), Ni-W/Al<sub>2</sub>O<sub>3</sub> (CHEROX 34-02) and Ni-Mo/Al<sub>2</sub>O<sub>3</sub> (USSR). The catalysts used are summarized in Table I.

<sup>1</sup>Collection Czechoslovak Chem. Commun. [Vol. 49] [1984]

*Apparatus.* Two types of experimental arrangements were used: *a*) closed (static) system with internal circulation, coupled with a mass spectrometer, for measurements at subatmospheric pressure, and *b*) gradientless flow system with a vibrating fluidized bed of catalyst, working at atmospheric pressure.

*In the static system* with circulation, the following experimental procedure was used. A 0.2 g sample of the catalyst in oxide form was evacuated at 723 K, then sulphided with reaction mixture thiophene + D<sub>2</sub> at the same temperature for 3 h and evacuated for 2 h at the temperature of the experiment up to the residual pressure of 10<sup>-5</sup> kPa. Then the circulation pump was put into operation and a mixture of thiophene and deuterium of a known composition was introduced at a total pressure of 3 kPa; the thiophene + D<sub>2</sub> mixture was prepared prior to the experiment outside the reactor. At defined time intervals, the gaseous reaction mixture was periodically analyzed by introducing samples directly from the circulating system through a sampling device into the mass spectrometer. From the results of the analysis, the percentage of thiophene and hydrogen sulphide of different isotope content (*d<sub>n</sub>*) was estimated, as well as the mean content of deuterium in thiophene (*x<sub>T</sub>*) and in hydrogen sulphide (*x<sub>S</sub>*). After the experiment, the gaseous mixture was pumped off from the reactor for 2 h. No additional sulphidation of the catalyst before the next experiment was carried out.

*In the gradientless flow system*, the catalyst was pre-reduced in a stream of hydrogen for 3 h at 723 K, then deuterium was introduced to displace hydrogen; completion of the displacement was checked by gas chromatography. After the desired temperature had been established in the reactor, a mixture of thiophene with deuterium was introduced. The mixture was prepared by passing a stream of deuterium through a saturator containing thiophene; the ratio of components was controlled by the temperature of the saturator. The catalyst was sulphided by the reaction mixture itself. The gas, leaving the reactor passed through a glass sampling ampoule, which was then transferred to the inlet system of the mass spectrometer in order to analyze the isotopic composition of thiophene and of the products formed.

TABLE I  
Catalysts used

Notation	Type	Composition	Note
AN	Ni/Al <sub>2</sub> O <sub>3</sub>	3% wt. NiO	<sup>a</sup>
AM	Mo/Al <sub>2</sub> O <sub>3</sub>	12% wt. MoO <sub>3</sub>	<sup>a</sup>
ANM I	Ni-Mo/Al <sub>2</sub> O <sub>3</sub>	3% wt. NiO, 12% wt. MoO <sub>3</sub>	<sup>a, b</sup>
AKM	Co-Mo/Al <sub>2</sub> O <sub>3</sub>	3.55% wt. CoO, 14.1% wt. MoO <sub>3</sub>	<sup>c</sup>
ANW	Ni-W/Al <sub>2</sub> O <sub>3</sub>	6% wt. NiO, 30% wt. WO <sub>3</sub>	<sup>c</sup>
ANM II	Ni-Mo/Al <sub>2</sub> O <sub>3</sub>	—	<sup>c</sup>

<sup>a</sup> Laboratory sample; <sup>b</sup> sequence of introducing active components: Mo, Ni; <sup>c</sup> commercial sample.

The analysis was performed by mass spectrometer MI-1305 at an ionisation potential of 20 V. Under these conditions, thiophene did not practically form fragmentation ions in the range of the masses 34–36, which is most important for this study since it corresponds to the masses of hydrogen sulphide of different isotope content. In the calculations, correction was made for the content of heavy isotopes of sulphur and carbon.

The experimental procedure is described in greater detail in papers<sup>7,8</sup>.

## RESULTS AND DISCUSSION

Let us examine what the isotopic composition of the formed hydrogen sulphide should be like and in what direction it should change with time after the replacement of hydrogen by deuterium if we assume different reaction mechanisms.

1) If sulphur is eliminated from thiophene by external hydrogen, *i.e.* the first of the above mentioned mechanism is operating, the formed hydrogen sulphide will consist only of  $D_2S$  at the very beginning of the reaction. Simultaneously with hydrogenolysis, however, isotopic exchange of thiophene with deuterium occurs at a high rate, as a result of which the gaseous phase is gradually enriched with light hydrogen. Correspondingly to the extent of the reaction, the content of deuterium in hydrogen sulphide has to decrease continuously till it achieves an equilibrium value.

2) If the mechanism of the reaction is intramolecular, the primary sulphur containing reaction product will consist of  $H_2S$  only and this situation will not change until the less reactive  $\beta$ -atoms of thiophene following the  $\alpha$ -atoms, begin to be exchanged with deuterium. After that, according to the extent of isotopic exchange in thiophene, the deuterium content in hydrogen sulphide has to increase gradually till an equilibrium is attained.

3) In a mechanism assuming a primary hydrogenation step, sulphur is eliminated from a partly or completely deuterated molecule of thiophene which may contain as many as four deuterium atoms. If hydrogen sulphide is formed with the participation of external hydrogen it will contain only  $D_2S$ ; in the case of internal hydrogen participation it will consist mainly of  $HDS$ . In the former case, an increasing extent of reaction leads to a decrease of the deuterium content in hydrogen sulphide, in the latter case (and at an excess of deuterium with respect to thiophene), it leads to a certain increase.

Before comparing the results of our study with these preliminary considerations, we must be sure that the observed regularities are not influenced by an isotopic exchange of the formed hydrogen sulphide itself with deuterium under the reaction conditions used. To check the possibility of such an exchange, we prepared a mixture of hydrogen sulphide with deuterium in the ratio 1 : 4 and introduced it into a reactor with AKM catalyst at 455°C (the highest temperature used in the study) and a pressure of 6.6 kPa. The isotopic composition of hydrogen sulphide changed during 35 min

by less than 10%. Consequently, one can assume that the isotopic exchange in hydrogen sulphide does not virtually influence the results of our experiments.

In Table II, the data are presented on the isotopic composition of thiophene and hydrogen sulphide obtained in the static system at the initial stage of observation, *i.e.* in the first 3–10 min after the beginning of the reaction. During this time, the isotopic exchange in thiophene was able to proceed, in the majority of cases, to such an extent that the gaseous phase was substantially enriched with light hydrogen, especially at a not too large initial excess of deuterium. Nevertheless, at sufficiently high ratios  $D_2/C_4H_4S = r$ , the  $D_2S$  molecules prevailed in the mixture, as it can be seen in Table II. With the diminishing of the  $r$  value, the content of  $D_2S$  was decreasing. After the establishment of isotopic equilibrium,  $x_S$  was always lower than  $x_T$ , which obviously results from a difference of isotopic effects for hydrogen sulphide and thiophene.\* This circumstance has to be taken into consideration when we confront the isotopic composition of thiophene and of hydrogen sulphide in order to elucidate the mechanism of the process.

Similar results were also obtained in the gradientless system where the predominance of  $D_2S$  is still more pronounced, including the cases where the extent of exchange in thiophene is very low (Table III).

With all the six catalysts investigated, the mass spectra of the reaction products have the same character and were changing with time in the same way. The difference consisted essentially in the activity of the catalysts. This leads to the assumption that even the reaction mechanism remains unchanged.

The data obtained are not in agreement with the dehydrosulphidation mechanism according to which the molecules  $H_2S$  should prevail among the products in the initial stage of the reaction. In order to verify this conclusion additionally, an experiment was performed in which a mixture of deuteriothiophene with light hydrogen was used as a starting material. Deuteriothiophene was obtained directly in the reaction circuit by an exchange reaction of normal thiophene with a large excess of deuterium at 190°C on the AM catalyst. The velocity of this exchange reaction was sufficiently high at this temperature whereas hydrogenolysis proceeded only to a small extent. After the achievement of isotopic equilibrium, deuteriothiophene was separated in a special trap by freezing it out with liquid nitrogen and gaseous deuterium was pumped off. Then, light hydrogen was introduced into the reactor, the temperature of which was increased to 230°C and deuteriothiophene was defrosted. After the beginning of the reaction, the reaction mixture was periodically analyzed by mass spectrometry. The ratio of deuteriothiophene to hydrogen in the starting mixture

\* It must be taken into account that the molecules  $D_2S$  formed in the very beginning, *i.e.* before the gaseous phase becomes enriched with light hydrogen, remain in the system and also contributed to the value of  $x_S$ . Consequently, the content of deuterium in hydrogen sulphide at equilibrium is actually still lower and the ratio  $(x_T/x_S)_\infty$  higher than shown in Table II.

was approximately 1 : 3, the initial isotopic composition of deuteriothiophene is shown in the first line of Table IV. In the course of the experiment, the temperature was raised to 430°C.

It is evident from Table IV that a predominant formation of D<sub>2</sub>S with a following decrease of the deuterium fraction in hydrogen sulphide was not observed in this

TABLE II

Initial isotopic composition of thiophene and hydrogen sulphide (closed system, initial pressure 3 kPa, 0.2 g of catalyst)

Catalyst	<i>r</i> <sup>a</sup>	Temperature °C	Isotopic composition, %									<i>x</i> <sub>T</sub> <sup>b</sup> %	<i>x</i> <sub>S</sub> <sup>c</sup> %	$(x_T/x_S)_\infty$
			of thiophene					of hydrogen sulphide						
			<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>				
ANM I	18 : 1	380	0.4	0.8	5.5	27.4	65.9	21.8	38.7	39.5	89.4	58.9	1.5	
AKM	16 : 1	150	82.3	16.1	1.4	0.2	—	13.0	34.8	52.2	4.9	69.6		
		290	7.3	13.2	42.9	28.7	8.0	17.1	37.1	45.7	54.3	64.3		
		340	4.6	7.4	20.9	34.6	32.5	16.0	36.0	48.0	70.8	66.0	1.3	
ANM II		190	46.6	34.1	18.4	0.6	0.3	16.3	37.2	46.5	18.5	65.1		
		280	60.5	29.9	9.3	0.2	—	21.5	41.7	36.8	12.3	57.6	1.5	
		350	9.8	7.7	23.0	33.8	25.6	22.6	39.6	37.7	64.4	57.5		
AN	4 : 1	340	5.2	17.9	33.0	32.1	11.7	21.6	46.6	31.7	56.8	55.0	1.4	
		380	1.6	9.2	27.6	40.5	21.2	27.0	45.3	27.7	67.7	50.3	1.4	
ANW		280	29.0	43.5	22.7	4.3	0.5	21.9	45.0	33.1	26.0	55.6	1.4	
		340	5.5	23.0	38.9	25.8	6.8	30.3	45.4	24.3	51.4	47.0	1.4	
		380	3.2	14.3	32.4	34.4	15.7	30.4	45.0	24.6	61.3	47.1	1.5	
AKM		340	1.7	10.0	31.1	39.0	18.2	27.3	45.5	27.3	65.5	50.0	1.5	
		420	0.9	7.3	25.1	41.7	25.0	26.7	46.7	26.7	70.7	50.0	1.4	
		455	1.1	7.9	28.5	41.1	73.4	26.7	46.7	26.7	69.5	50.0	1.4	
ANM II		280	5.5	25.2	49.5	17.9	2.0	25.0	45.0	30.0	46.5	52.5	1.5	
		340	1.9	12.3	33.6	37.0	15.2	33.3	41.7	25.0	62.8	45.8	1.5	
		380	1.0	7.9	26.8	41.2	23.2	28.6	42.9	28.6	69.5	50.0	1.5	
AM		280	1.3	9.6	29.0	40.2	20.0	25.8	48.5	25.8	67.1	50.0	1.5	
		340	1.0	7.5	28.1	41.5	23.9	27.7	43.6	28.7	70.0	50.5	1.4	
		380	1.5	9.1	27.6	40.5	21.3	33.3	46.7	20.0	67.8	43.3	1.6	
ANM I		280	1.0	7.4	25.7	39.3	28.6	30.9	43.9	25.2	70.8	47.1	1.6	
		340	1.6	9.2	27.5	40.0	21.7	33.7	42.9	19.6	67.8	41.1	1.6	
		380	1.6	7.8	25.5	40.8	24.3	27.5	45.5	27.0	69.6	49.8	1.4	
AKM	1 : 1	450	43.7	38.4	14.4	2.9	0.7	71.2	23.7	5.1	19.7	16.9		

<sup>a</sup> Initial molar ratio of deuterium to thiophene; <sup>b</sup> mean content of deuterium in thiophene; <sup>c</sup> in hydrogen sulphide.

TABLE III

Isotopic composition of thiophene and hydrogen sulphide (gradientless flow system, atmospheric pressure, flow rate of D<sub>2</sub>: 4 l/h)

Catalyst		<i>r</i> <sup>a</sup>	Temperature °C	Isotopic composition, %									<i>x</i> <sub>T</sub> <sup>b</sup> %	<i>x</i> <sub>S</sub> <sup>c</sup> %
type	amount g			of thiophene					of hydrogen sulphide					
				<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>			
ANM II	4.0	9.7 : 1	310	95.8	4.2	0.3	0.2	0.1	12.3	28.1	59.6	1.5	73.7	
			420	96.3	3.4	0.3	0.1	—	7.5	30.2	62.3	1.2	77.4	
			435	93.7	5.8	0.3	0.2	0.1	7.7	26.4	65.9	1.9	79.1	
AM	2.8		450	16.5	30.3	28.1	16.1	9.1	8.7	34.6	56.7	42.8	74.0	
ANM I	2.7		270	94.3	4.7	0.5	0.4	0.2	7.2	30.3	62.6	2.0	77.8	
			308	89.3	8.0	1.5	0.9	0.4	8.5	27.7	63.8	3.8	77.7	
			410	78.8	14.1	4.1	2.2	0.9	8.5	23.9	67.6	8.1	79.6	
ANM II	4.0	18 : 1	450	63.1	30.2	6.0	0.5	0.3	4.4	15.0	80.6	11.2	88.1	

<sup>a,b,c</sup> See footnotes in Table II.

TABLE IV

Isotopic composition of thiophene and hydrogen sulphide in the reaction of deuteriothiophene with hydrogen (closed system, catalyst AM, initial pressure approximately 6 kPa, H<sub>2</sub>/C<sub>4</sub>D<sub>4</sub>S approx. 3 : 1)

Temperature °C	Time min	Isotopic composition, %									<i>x</i> <sub>T</sub> <sup>b</sup> %	<i>x</i> <sub>S</sub> <sup>c</sup> %
		of thiophene					of hydrogen sulphide					
		<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>			
230	0	0.0	0.3	1.8	16.9	81.0					94.7	
	2	0.0	0.2	2.4	17.5	79.9	40.0	44.9	15.1	94.3	37.5	
	7	0.3	2.4	16.2	36.8	44.4	34.1	45.5	20.5	80.7	43.2	
	19	0.4	4.5	23.4	44.8	26.9	34.3	45.1	20.6	73.3	43.1	
	63	0.8	6.8	25.0	43.2	24.2	32.4	46.5	21.1	70.8	44.3	
430	87	1.3	9.1	27.9	40.2	21.5	32.5	46.2	21.3	67.9	44.4	
	121	1.9	11.6	30.5	38.7	17.4	33.4	44.9	21.8	64.6	44.2	
	137	1.8	11.3	31.1	38.4	17.4	33.6	44.4	21.9	64.6	44.1	

<sup>b,c</sup> See footnotes in Table II.

experiment, which should have been expected in the case of the dehydro sulphidation mechanism. On the contrary, more  $H_2S$  molecules than  $D_2S$  were formed, and as the reaction was proceeding,  $x_S$  was increasing to a small but observable extent as a result of an enrichment of the gaseous phase with deuterium due to the isotopic exchange.

As mentioned above, the trend of the change of  $x_S$  with time is important for determining the mechanism. Unfortunately, the velocity of the exchange reaction of thiophene at hydrogenolysis conditions is so high that the isotopic composition of hydrogen rapidly achieves the equilibrium level. Consequently, also the isotopic composition of hydrogen sulphide becomes constant shortly after the beginning of the experiment, especially on the most active catalysts as it can be seen from Fig. 1 (curves 3 and 3'). However, we were able to monitor the changes of the hydrogen sulphide composition on the less active catalysts and at not too high temperature.

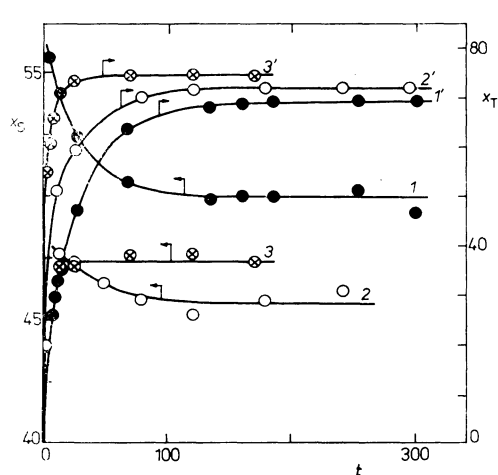


FIG. 1

Dependence of the deuterium content (%) in hydrogen sulphide ( $x_S$ ) and thiophene ( $x_T$ ), resp., on the time of reaction  $t$  (min). 1, 1' Catalyst ANW, 280°C; 2, 2' catalyst AM, 240°C; 3, 3' catalyst ANM I, 280°C. Initial ratio  $D_2/C_4H_4S = 4$

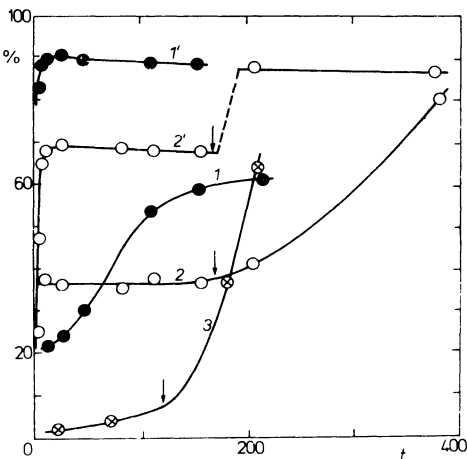


FIG. 2

Dependence of the relative height (arbitrary units) of the peak  $m/e = 34$  (curves 1–3) and of the deuterium content (%) in thiophene (curve 1', 2') on the time of reaction  $t$  (min). 1, 1'  $r (=D_2/C_4H_4S) = 18$ , catalyst ANM I, 380°C; 2, 2'  $r = 4$ , catalyst ANM I, 340°C; 3  $m (=D_2/C_4H_8) = 10$ , catalyst ANM II, 320°C. The arrows denote the points of an additional introduction of 12 kPa (curves 2, 2') and 18 kPa (curve 3), resp., of deuterium



The curves 1 and 2 in Fig. 1 demonstrate that  $x_s$  has a decreasing trend with an increasing extent of the reaction, which should be observed if the elimination of sulphur occurred with the participation of external hydrogen.

Thus, all the results obtained testify against the intramolecular mechanism of hydrodesulphurization (mechanism 2) and provide evidence in favour of one of the mechanisms with the participation of external hydrogen (mechanism 1 or 3).

In order to avoid incorrect interpretation of the results obtained, attention should be drawn to the phenomenon observed at higher degrees of thiophene conversion, namely to the trend to an increase of relative height of the peak with  $m/e = 34$ , which formally corresponds to light hydrogen sulphide  $H_2S$  (Fig. 2, curves 1 and 2). Since during the period of a remarkable increase of the height of peak 34, the isotopic composition of thiophene and consequently also that of hydrogen in the gaseous phase were already approaching an equilibrium value (Fig. 2, curves 1' and 2'), this increase cannot be related to a change of the isotopic composition of the formed hydrogen sulphide. This might be caused by a secondary process of hydrogenolysis of the thiophene decomposition products leading to the appearance of ions with the mass of 34 (e.g.  $C_2D_4H_2^+$  or  $C_2D_5^+$ ) in the mass spectrum. The introduction of an additional amount of deuterium into the reaction mixture not only left the relative height of peak 34 unchanged (which should diminish if this peak corresponded only to hydrogen sulphide  $H_2S$ ) but it even led to its increase, obviously due to a more intensive hydrogenolysis (Fig. 2, curve 2). The results

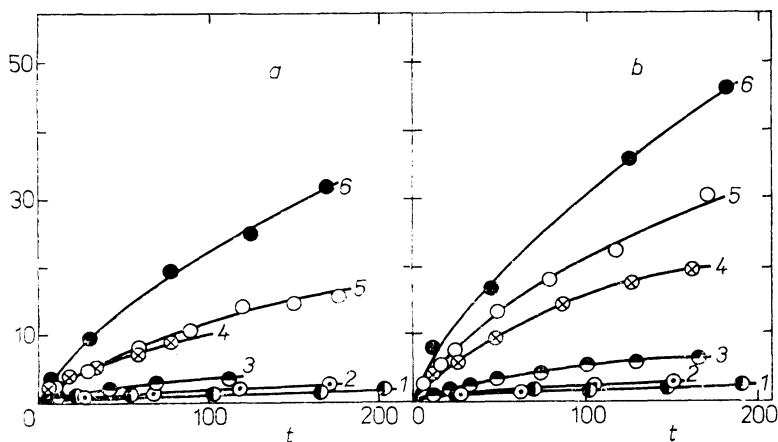
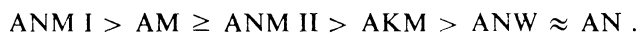


FIG. 3

Rate of accumulation of the products of thiophene hydrogenolysis [dependence on time of the sum of the heights of peaks  $m/e = 61$  to  $64$  (arbitrary units) corresponding to  $d_5$ - to  $d_8$ -butenes] at  $340^\circ C$  (a) and  $380^\circ C$  (b) on the catalysts: 1 AN, 2 ANW, 3 AKM, 4 ANM II, 5 AM, 6 ANM I; initial ratio  $D_2/C_4H_4S = 4$

of an experiment in which a mixture of butene — a product of thiophene hydrogenolysis — with deuterium was allowed to react, can serve as indirect evidence of a complex character of peak 34 at higher conversions. As can be seen from Fig. 2 (curve 3), a gradual increase of the height of peak 34 was also observed in this case although hydrogen sulphide could not be formed here. A similar phenomenon may have been the reason for the conclusion of thiophene hydrogenolysis proceeding according to a dehydrosulphidation mechanism<sup>4,5,9</sup>. In any case, the high degrees of thiophene conversion (amounting *e.g.* in the study<sup>4</sup> to 16–76%) substantiate such a suspicion.

It was not the object of the present study to determine the activity of the catalysts used. Nevertheless, the data obtained allow the relative activity to be estimated from butene accumulation. Since the molecular peaks of butene with  $m/e$  from 56 to 60 are superposed by fragmentation peaks of thiophene and its deuterioisomers, the amount of butene was estimated only from the peaks with  $m/e = 61$  to 64 ( $d_5$ - to  $d_8$ -butenes) free of such a superposition. It may be seen from a comparison of the curves in Fig. 3 representing the time dependence of the sum of the peak heights  $m/e = 61$ –64 that the catalysts used are ranged according to their activity in the same order at 340 as well as at 380°C, namely



Concluding, we may state that the results of the present study allow us to assume that thiophene hydrogenolysis on hydrodesulphurization catalysts proceeds either according to one of the above mentioned mechanisms with the participation of external hydrogen or according to both such mechanisms simultaneously.

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