

KINETICS OF THE CATALYTIC HYDRODESULPHURISATION REACTION SYSTEM; HYDROGENOLYSIS OF THIOPHENE

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Kinetics has been studied of the reaction system taking place during the reaction of thiophene on the cobalt-molybdenum catalyst in a gradientless circulation flow reactor at 360°C and atmospheric pressure. Butane has been found present in a small amount in the reaction products even at very low conversion. In view of this, consecutive and parallel-consecutive (triangular) reaction schemes have been proposed. In the former scheme the appearance of butane is accounted for by rate of desorption of butene being comparable with the rate of its hydrogenation. According to the latter scheme part of the butane originates from thiophene *via* a different route than through hydrogenation of butene. Analysis of the kinetic data has revealed that the reaction of thiophene should be considered to take place on other active sites than that of butene. Kinetic equations derived on this assumption for the consecutive and the triangular reaction schemes correlate experimental data with acceptable accuracy.

Catalytic hydrodesulphurisation of naphta fractions is an important process and as such has been studied systematically. Greatest attention has been paid to hydrodesulphurisation of aromatic heterocyclic compounds of sulphur, especially thiophene on a cobalt-molybdenum catalyst. The problem of hydrodesulphurisation of thiophene has been reviewed in several papers, *e.g.*^{1,2}. For the present work as substantial appear the following conclusions:

The reaction of thiophene with hydrogen under laboratory reaction conditions (250–400°C, atmospheric pressure) yields in substantial amounts 1-butene, *trans*-2-butene, *cis*-2-butene, butane and hydrogen sulphide. Butadiene is present in the gas phase only at very low conversions³; tetrahydrothiophene at an elevated pressure⁴. Generally it has been accepted that butane forms by hydrogenation of butene, which is an intermediate. Only Kolboe³ concluded that also butane is a primary product of hydrogenolysis of thiophene, for it is present in the reaction mixture even at very small conversion. As far as the mechanism of breaking the thiophene ring is concerned conflicting views have appeared in the literature. While Amberg and coworkers^{5,6}, Lipsch and Schuit⁷ have concluded that the first step of hydrodesulphurisation of thiophene is the rupture of the C—S bond giving rise to butadiene, other papers^{4,8} put forward evidence that the primary reaction is hydrogenation of the aromatic ring of thiophene to tetrahydrothiophene. Butadiene then forms after elimination of hydrogen sulphide. The absence of butadiene in the gas phase has been explained in both cases by its strong reactivity. Proposals that the initial step is intramolecular hydrodesulphurisation exist too^{9,10}.

The results of some kinetic studies^{11,12} have lead to the idea of different active sites for hydrodesulphurisation and hydrogenation; active sites differing by their acidity have been considered by Desikan and Amberg⁶. On the more acidic sites hydrogenation takes place and partly also

hydrodesulphurisation, while on less acidic sites only hydrodesulphurisation. Other authors have concluded^{7,13} that the sites for hydrodesulphurisation and hydrogenation are identical. In the study of the kinetics of hydrogenolysis of thiophene the majority of authors attempted only description of the rate of formation of hydrogen sulphide (rate of disappearance of thiophene)¹³⁻¹⁵. This rate is usually expressed by equations of the Langmuir-Hinshelwood type modified by incorporating terms for thiophene and hydrogen sulphide adsorption. Satterfield and Roberts¹¹ and recently also Lee and Butt¹² have presented kinetic equations for the rate of formation of hydrogen sulphide and butane. These equations reflect the concept that butane originates by hydrogenation of butene (intermediate of hydrogenolysis) and that the hydrodesulphurisation and hydrogenation sites are different.

The main aim of this paper has been to obtain a reliable and accurate kinetic description of reactions taking place during hydrogenolysis of thiophene on the Czechoslovak cobalt-molybdenum catalyst Cherox-3600 applicable in the region of internal diffusion. With this objective we have chosen the reactor (gradientless circulation flow reactor) and the concentration range (the inlet mole fraction of thiophene 0.025-0.2). In the process of fitting the data to equations we have preferred the approach based on the concept of reaction mechanism to the purely empirical approaches.

EXPERIMENTAL

Kinetic measurements were carried out in a (differential) circulation flow reactor (CSTR). Gas recirculation was achieved by a magnetic piston pump¹⁶ located in an air thermostat. The pumping capacity of the pump, 1000 l/h enabled the ratio of the recycle to the feed to be maintained above 50 so that the reactor operated as an ideal mixer. Circulating mixture was brought from the pump into the reactor *via* a heating tube to be heated close to the reaction temperature. The catalyst (1-2.7 g) was placed in a glass tubular reactor on a fritted support. The reactor was heated by a resistor furnace; the temperature was measured by a thermocouple in a glass well reaching into the bed of catalyst. Gaseous components (hydrogen, 1-butene, eventually nitrogen and butane) entered the circulation loop *via* gas lines equipped with a manostat, a needle valve, desoxidation and drying columns, a capillary flow meter and a manometer. Thiophene was injected by a linear feeding device into the evaporator to be evaporated and mixed with the gaseous components. From here the gas mixture proceeded into the circulation loop.

Analysis of hydrocarbons in the reaction mixture was carried out by chromatography (flame ionisation detector). The gas sample of the reaction mixture (0.3 cm³) was drawn through a six way sampling valve; the sampling valve was thermostated to 100°C. The conditions of the analysis were: column (4 m long, 3 mm I.D.) with 25% dimethylsulpholane on Chromosorb P (80-100 mesh), the flow rate of the carrier gas (hydrogen) 25 cm³/min, temperature 30°C. The analyzed species were leaving the column in the sequence: Butane, 1-butene, *trans*-2-butene, *cis*-2-butene. Hydrogen sulphide was not detected by the employed detector. Thiophene, which would have an excessively long retention time, was flushed after completion of the analysis from the column by reversing the carrier gas flow. The calibration verified linearities of peak areas on concentration of the components in the injected sample and the proportionality constants have been found to be the same for all C₄ hydrocarbons. Hydrogen sulphide was trapped in an ammonia solution of cadmium chloride and the amount of sulphur was determined by iodometric titration. This way of analysis enables the rate of formation of hydrogen sulphide, R_S,

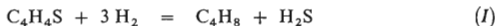
to be determined directly. From the chromatographic analysis we could determine the mole fraction of butane in C_4 fraction (butane + butene), \bar{y}_B , as the ratio of the area of the butane peak to the sum of peak areas of butane and butenes.

Cobalt-molybdenum commercial catalyst Cherox-3600 (chemical works, Litvínov) contained before use 2.6% of CoO, 11.9% of MoO₃ and Al₂O₃; the measurements were performed with the fraction 0.16 to 0.25 mm. Prior to the measurements the catalyst was activated directly in the apparatus by reduction and sulphidation under standard conditions: During two hours the catalyst was gradually heated to 360°C and reduced by hydrogen. (3 h). Sulphidation lasted four hours and the sulphidation mixture was that originated from the inlet mixture of hydrogen and thiophene (20 mol% of thiophene, $W/F_T = 100$ g h/mol; thiophene conversion $x = 35\%$). The content of hydrogen sulphide in the sulphidation mixture (10 mol.%) corresponded to its maximum content in the kinetic experiments.

Kinetic measurements were carried out at 360°C under atmospheric pressure and in the absence of transport effects (checked by calculations¹⁷). The insignificance of internal diffusion effects was also tested experimentally by comparing the results for the fractions 0.16—0.25 mm and 0.25—0.5 mm. Reaching the steady state was verified by repeated analyses. The constancy of catalyst activity and selectivity was checked by measurements under standard conditions: The deviations of individual measurements from the average were less than 5%. A single charge of catalyst was used roughly 40 hours.

RESULTS AND DISCUSSION

The kinetics of system of reactions taking place during hydrogenolysis of thiophene can be described quantitatively by the rates of formation of the key components (*e.g.* hydrogen sulphide and butane — R_S, R_B). The reaction system is one with two key components for from the possible stoichiometric equations containing only the reactants and products, only two equations are linearly independent, *e.g.*



Butenes may be looked upon as one component for under the reaction conditions their isomerisation is practically at equilibrium^{11,12}. The rate of formation of hydrogen sulphide, R_S , is available directly from experiments; the rate of formation of butane, R_B , can be computed from measured quantities using the following balance

$$R_B = \bar{y}_B(R_S + F_U/W), \quad (I)$$

where \bar{y}_B is the mole fraction of butane in the C_4 fraction. The partial pressures of components were computed from the primary data and the relationship following from the reactor material balance:

$$p_i = P(Fy_i^0 + WR_i)/(F + W \sum_j R_j). \quad (2)$$

The relationships between the rates of formation of the non-key components R_T , R_H , R_U and the rates of formation of the key components R_S , R_B are clear from the stoichiometric equations (I) and (II).

The experimentally obtained dependences of rates of formation R_S and R_B on thiophene conversion ($x = R_S W / F_T$) for various inlet compositions are given in Figs 1–4. Altogether 53 experimental points were obtained. The effect of butane on rates of formation R_S and R_B was examined on the set of experiments in which nitrogen in the inlet mixture was replaced by butane – this replacement did not show in the values of R_S and R_B .

An important information brings the dependence of selectivity of the thiophene reaction to butane ($S = R_B / R_S$) on the conversion of thiophene x (Fig. 5). From this figure it is apparent that butane is present in small amounts in the C_4 fraction even at the zero conversion when $P_U \rightarrow 0$ ($S^0 > 0$) which is in accord with the results of Kolboe and Amberg³. In contrast to earlier kinetics studies^{11,12}, we have set up the reaction scheme so as to admit the presence of butane in the hydrocarbon fraction already at small conversions. This fact can be interpreted by two types of reaction schemes:

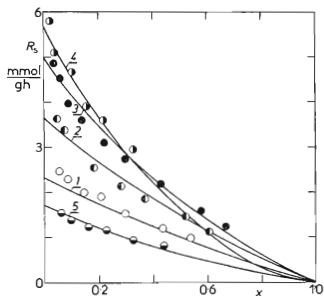


FIG. 1

Rate of Formation of Hydrogen Sulphide as a Function of Thiophene Conversion

Inlet mole fraction of thiophene, hydrogen and nitrogen: 1 0.025, 0.975, 0; 2 0.05, 0.95, 0; 3 0.10, 0.90, 0; 4 0.20, 0.80, 0; 5 0.05, 0.45, 0.50. The curves were computed for the B–2 model.

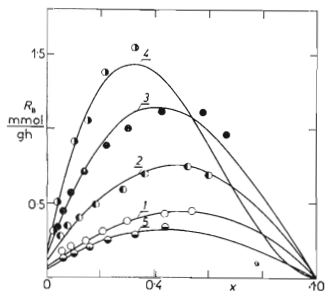


FIG. 2

Rate of Formation of Butane as a Function of Thiophene Conversion

Same caption as for Fig. 1.

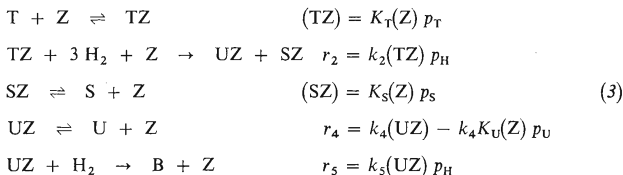
a) *The consecutive scheme.* Butane is formed only by hydrogenation of butene (intermediate product of hydrogenolysis), but the rate of desorption of butene from the surface of the catalyst is comparable with the rate of its hydrogenation to butene.

b) *Parallel-consecutive (triangular) scheme.* Part of butane originates from thiophene *via* another route than through hydrogenation of butene.

The Consecutive Scheme of the System (A)

In the case that the rates of surface reactions and adsorption or desorption steps are comparable one cannot use for the description of the reaction system the usual equations of the Langmuir-Hinshelwood type^{18,19}. In the derivation of the kinetic equations it is necessary to start from the scheme of the reaction system incorporating mutual arrangement of the elementary steps and solve the kinetic equations of individual steps together with the balance on the active sites. Explicit expressions for the rates of formation as functions of partial pressures of the components involved can be obtained, however, only in the simplest cases.

To derive the kinetic equations we shall consider the following scheme (double arrows indicate reversibility of the step; T thiophene, S hydrogen sulphide, U butene, B butane, Z active site; the symbols in the parentheses refer to the surface concentration)



On the right hand sides are the kinetic equations of the limiting (comparable) steps, or, equilibrium conditions of fast reversible steps. In order that we may explain the presence of butene even at conversion $x \rightarrow 0$ ($p_{\text{U}} \rightarrow 0$) the steps 2, 4 and 5 were considered as limiting ones. Adsorption of butane is not considered in the scheme (3) and it is assumed that hydrogen reacts directly from the gas phase or from independent centers where it adsorbs only weakly (ref.^{12,15,20}). The surface reaction² is not an elementary process and consists from a series of consecutive elementary steps. Unequivocal information about their sequence (mechanism of rupture of the thiophene ring) lacks in the literature⁴⁻¹⁰. In case that elimination of hydrogen sulphide precedes hydrogenation of thiophene^{4,8}, one can consider, for instance, the following sequence of steps: hydrogenation of thiophene to tetrahydrothiophene, elimination of hydrogen sulphide to butadiene and hydrogenation to butene. If the limiting step in this sequence is the interaction of adsorbed thiophene with hydrogen, which seems to suggest the forms of the published equations for $R_{\text{S}}^{11-15,20}$ (in the

numerator of these expressions appears the product $p_T p_H$ and if it is assumed that hydrogen reacts from the gas phase or from independent sites, it is possible to describe the rate of the surface reaction 2 in the scheme (3) as $r_2 = k(TZ) p_H$. This equation, however, can be used also for other sequences of elementary steps if the interaction of the adsorbed thiophene is the limiting step and hydrogen reacts from the gas phase.

From the scheme (3) it is apparent that $R_S = r_2$, $R_B = r_5$ and $r_2 = r_4 + r_5$; further we may write for the balance on the active sites that $(Z) + (TZ) + (SZ) + (UZ) = 1$. By solving these equations and the equations in the scheme (3), expressions for the rate of formation of hydrogen sulphide and butane are obtained, containing partial pressures of measurable components only.

$$R_S = \frac{k_2 K_T p_T p_H}{1 + K_T p_T + K_S p_S + [(k_2 K_T / k_4) p_T p_H + K_U p_U] / [1 + (k_5 / k_4) p_H]} \quad (4)$$

$$R_B = R_S \frac{(k_5 / k_4) p_H + (k_5 K_U / k_2 K_T) p_U / p_T}{1 + (k_5 / k_4) p_H} \quad (5)$$

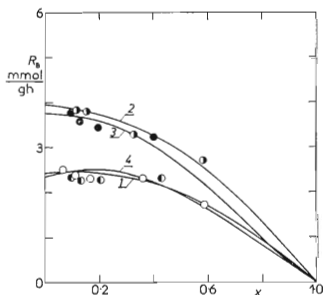


FIG. 3

Rate of Formation of Hydrogen Sulphide as a Function of Thiophene Conversion

Inlet mole fraction of thiophene, butene and hydrogen: 1 0.05, 0.05, 0.90; 2 0.05, 0.10, 0.85; 3 0.10, 0.10, 0.80; 4 0.10, 0.05, 0.85. The curves were computed for the model B—2.

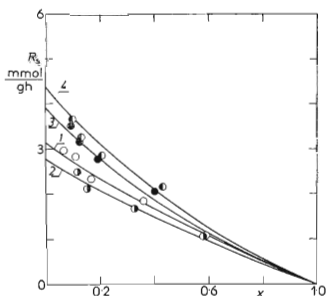


FIG. 4

Rate of Formation of Butane as a Function of Thiophene Conversion

Same caption as for Fig. 3.

For the limiting selectivity S^0 it follows from Eq. (5) ($p_U \rightarrow 0$) that

$$S^0 = \frac{(k_5/k_4) p_H}{1 + (k_5/k_4) p_H} \quad (6)$$

Since the experimentally found selectivity S^0 is considerably less than unity, we must have $(k_5/k_4) p_H \ll 1$. Eqs (4)–(6) then simplify to the form

$$R_S = \frac{k_2 K_T p_T p_H}{1 + K_T p_T + K_S p_S + K_U p_U + (k_2 K_T/k_4) p_T p_H} \quad (7)$$

$$R_B = R_S[(k_5/k_4) p_H + (k_5 K_U/k_2 K_T) p_U/p_T] \quad (8)$$

$$S^0 = (k_5/k_4) p_H \quad (9)$$

The last three equations (7)–(9) shall be referred to as the model A–1. In its derivation it was assumed that the hydrodesulphurisation and hydrogenation sites are identical. The following two models presume the existence of two kinds of sites: Z and Y.

In the model A–2 it is assumed that on the sites Z the reaction follows the scheme (3). Part of butene, though, is hydrogenated also on the other sites Y and the rate of this path may be described by the Langmuir–Hinshelwood equation. For the rate of formation of butane, with the assumption $(k_5/k_4) p_H \ll 1$, we obtain then

$$R_B = R_S[(k_5/k_4) p_H + (k_5 K_U/k_2 K_T) p_U/p_T] + \frac{k_6 K'_U p_U p_H}{1 + K'_U p_U} \quad (10)$$

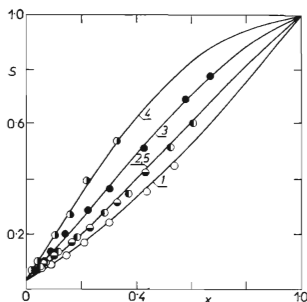
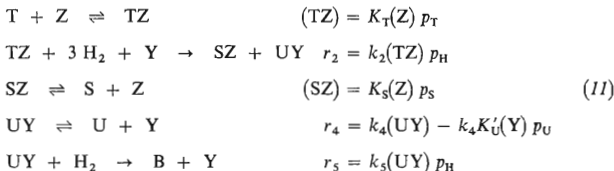


FIG. 5
Selectivity as a Function of Thiophene Conversion
Same caption as for Fig. 1.

where K'_U is the adsorption constant of butene on the sites Y. The equation for the rate of formation of hydrogen sulphide and for the limiting selectivity are the same as those for the model A-1 (Eqs (7), (9)).

For the model A-3 the reactions scheme (3) is modified by introducing additional sites Y. On the sites Z adsorbs hydrogen sulphide and thiophene which here reacts, and, eventually butene which does not react on the sites Z. On the hydrogenation sites Y adsorbs and reacts only butene. The reaction scheme and corresponding kinetic (equilibrium) relationships, may be written as follows:



The surface reaction 2 may be interpreted in such a way that the first intermediate product of hydrodesulphurisation not containing sulphur (*e.g.* butadiene), adsorbs on sites Y to be hydrogenated in a rapid step to butene. Equally as for the scheme (3) we may write relations: $R_S = r_2$, $R_B = r_5$, $r_2 = r_4 + r_5$ and the balance of the sites Z. In addition, one has to consider the balance on the sites Y, $1 = (Y) + (UY)$, and the equilibrium condition for the adsorption of butene on sites Z, $(UZ) = K_U(Z) p_U$. In a similar manner as that applied to the scheme (3), one can arrive at the resulting kinetic equation for the rate of formation of hydrogen sulphide

$$R_S = \frac{k_2 K_T p_T p_H}{1 + K_T p_T + K_S p_S + K_U p_U} \tag{12}$$

and for the rate of formation of butane (provided that $k_5 p_H / k_4 \ll 1$)

$$R_B = \frac{R_S (k_5 / k_4) p_H + k_5 K'_U p_U p_H}{1 + K'_U p_U}, \tag{13}$$

where K'_U is the adsorption constant of butene on sites Y. The expression for the limiting selectivity is the same as that for the model A-1 (Eq. (9)).

The Triangular Scheme of the System (B)

In this case it is assumed that on the surface of the catalyst the following reactions take place: 1) adsorbed thiophene reacts with hydrogen to butene (the rate constant k_1);

2) on the same sites reacts part of thiophene in a different way to butane; the kinetic equation of this reaction has the form as that for reaction 1) except for the different reaction rate constant (k_2); 3) butene hydrogenates to butane either on the same sites (model B-1) or on different sites (model B-2) (rate constant k_3). Similarly as for the consecutive scheme it is assumed that hydrogen reacts from the gas phase or from independent sites where it is only weakly adsorbed. Among the rates of formation of the key components and the rates of surface reactions 1), 2), 3) the following relations hold: $R_S = r_1 + r_2$, $R_B = r_2 + r_3$. If it is assumed that the rates of the surface reactions are comparable (limiting), that the law of active mass may be applied and that the adsorbed components are in equilibrium with the gaseous components, the expressions of the Langmuir-Hinshelwood type result for the rates r_1 , r_2 , r_3 . For the rates of formation R_S , R_B and the limiting selectivity S^0 we then write

$$R_S = \frac{(k_1 + k_2) k_T p_T p_H}{1 + K_T p_T + K_S p_S + K_U p_U} \quad (14)$$

$$R_B = [k_2/(k_1 + k_2)] R_S + \frac{k_3 K'_U p_U p_H}{1 + K'_T p_T + K'_S p_S + K'_U p_U} \quad (15)$$

$$S^0 = k_2/(k_1 + k_2). \quad (16)$$

If the hydrogenation of butene takes place on the same sites as hydrodesulphurisation (Z), we have $K'_i = K_i$ (model B-1). If the hydrogenation sites (Y) are different (model B-2), we have $K'_i \neq K_i$ ($i = T, S, U$). A review of the expressions for the rates of formation of hydrogen sulphide and butane (R_S , R_B) and for the limiting selectivity (S^0) is presented in Table I.

TABLE I

Models of the Consecutive (A) and Triangular (B) Schemes

Model	Equation			Active sites	
	R_S	R_B	S^0	hydro-desulphurisation	hydro-generation
A-1	(7)	(8)	(9)	Z	Z
A-2	(7)	(10)	(9)	Z	Z, Y
A-3	(12)	(13)	(9)	Z	Y
B-1	(14) ^a	(15) ^a	(16)	Z	Z
B-2	(14)	(15)	(16)	Z	Y

^a $K'_i = K_i$.

The Selection of the Model and the Determination of Kinetic Constants

The constants of kinetic equations for the rate of formation of hydrogen sulphide and butane for models A and B were computed by minimizing the following objective function

$$Q_i = \sum_{j=1}^n (R_{i,\text{cal}}^j - R_{i,\text{exp}}^j)^2, \quad i = \text{S, B}, \quad (17)$$

where n is the number of experimental points ($n = 53$), subscripts "cal" and "exp" refer to calculated and experimental values. In the process of interpreting the triangular scheme (models B-1 and B-2) we have processed first Eq. (14) for R_S in a more general form with adjustable exponents over p_T and p_H as well as over the adsorption term in the denominator for R_S . Since all these exponents were found to fall into the region 0.8–1.1, their values were rounded to unity. The kinetic constants for this alternative are summarized in Table II. From this table it follows that the rate of formation of hydrogen sulphide is strongly influenced by the adsorption of hydrogen sulphide and thiophene; adsorption of butene exhibits only a small influence. In the processing of the rates of formation of butane (Eq. (15)) we have substituted for R_S expression (14) with the already computed constants. The constants of the kinetic equation (15) were computed in a similar way as before: the exponents over p_U , p_H and over the adsorption term were first taken to be adjustable. Their values, which had been found in the interval 0.95–1, were then rounded to unity. The resulting values of constants are given in Table II. The rate of formation of butane is not, in contrast to the rate of formation of hydrogen sulphide, affected by partial pressure of thiophene or hydrogen sulphide. Hence $K'_T = K'_S = 0$. The adsorption constants of thiophene and hydrogen sulphide are thus not the same ($K_T \neq K'_T$, $K_S \neq K'_S$). Accordingly, we cannot do with the idea of identical active sites for

TABLE II
Kinetic Constants for the Triangular Scheme (models B-1, B-2)

Rate of formation of hydrogen sulphide, R_S , Eq. (14)		Rate of formation of butane, R_B , Eq. (15)	
$(k_1 + k_2) K_T$	12.27 $\mu\text{mol/g h kPa}^2$	$k_3 K'_U$	5.99 $\mu\text{mol/g h kPa}^2$
K_T	0.125 kPa^{-1}	K'_T	0(10 ⁻³) kPa^{-1}
K_S	0.249 kPa^{-1}	K'_S	0(10 ⁻³) kPa^{-1}
K_U	0.031 kPa^{-1}	K'_U	0.035 kPa^{-1}
Q_S	1.43 (mmol/g h) ²	$k_2/(k_1 + k_2)$	0.030 —
		Q_B	0.82 (mmol/g h) ²

hydrodesulphurisation and hydrogenation as assumed in the model B-1. The model B-2 appears from this point of view as satisfactory. On the sites Z adsorbs hydrogen sulphide, thiophene and weakly butene; on the sites Y adsorbs butene; hydrogen sulphide and thiophene do not adsorb. The fact that unity exponents have been found confirms the assumption that the limiting step are reactions of the adsorbed thiophene and butene with hydrogen, which reacts from the gas phase or from independent centers. The goodness of fit of experimental data by the kinetic equations (14) and (15) is evidenced by the mean relative deviations 5 and 6% for R_S and R_B .

The results of processing of experimental data for the consecutive schemes (models A-1, A-2, A-3) are shown in Table III. Similarly as for the triangular scheme in the processing of the rates of formation of butene (Eq. (8), (10), (13)) we have substituted for R_S the expression (12) with the already evaluated constants. It is seen that for the correlation of the rate formation of hydrogen sulphide all three models are satisfactory (the mean relative deviation of R_S is 5%). For the sake of distinguishing between individual models as more important appears the rate of formation of butane. Model A-1 (Eq. (10)) does not fit sufficiently closely the obtained data (the mean relative deviation of R_B is 28% by contrast to 7% for models A-2 and A-3). For the models A-2, which presumes hydrogenation of butene on both

TABLE III
Kinetic Constants for the Consecutive Scheme (models A-1, A-2, A-3)

Rate of formation of hydrogen sulphide, R_S			Rate of formation of butane, R_B			
Kinetic constants	A-1, A-2 Eq. (7)	A-3 Eq. (12)	Kinetic constants	A-1 Eq. (8)	A-2 Eq. (10)	A-3 Eq. (13)
$k_2 K_T$ ($\mu\text{mol/g h kPa}^2$)	12.60	12.27	$k_6 K'_U$ ($\mu\text{mol/g h kPa}^2$)	—	6.52	—
K_T (kPa^{-1})	0.100	0.125	$k_5 K'_U$ ($\mu\text{mol/g h kPa}^2$)	—	—	5.98
K_S (kPa^{-1})	0.262	0.249	$k_5 K_U$ ($\mu\text{mol/g h kPa}^2$)	10.49	—1.33	—
K_U (kPa^{-1})	0.033	0.031	K'_U (kPa^{-1})	—	0.032	0.035
$k_2 K_T / k_4$ (kPa^{-2})	0.359	—	$k_5 / k_4 \cdot 10^3$ (kPa^{-1})	1.02	0.310	0.342
Q_S (mmol/g h^2)	1.40	1.43	Q_B (mmol/g h^2)	7.36	0.76	0.82

the sites Z and Y, the term $R_S(k_5K_U/k_2K_T) p_U/p_H$ in Eq. (10) characterizes the rate of hydrogenation of butene on the hydrodesulphurisation sites Z. The obtained negative value of k_5K_U is therefore inadmissible. The only satisfactory model for the consecutive scheme is therefore the model A-3 based on the assumption of different active sites for hydrodesulphurisation and hydrogenation.

From the analysis of the rates of formation of hydrogen sulphide and butane one can conclude that the data are acceptably correlated both by the model A-3, based on the consecutive scheme, and the model B-2 based on the triangular scheme. In both cases the kinetic equations presume the existence of different active sites for hydrodesulphurisation and hydrogenation. The decision which of the presented scheme is more plausible, is difficult to make for the kinetic equations for the rate of formation of hydrogen sulphide are formally identical (Eq. (12) and (14)) for both cases and the equations for the rate of formation of butane (13) and (15) differ only in the first term. Over a greater portion of the experimentally investigated region the partial pressure of butene remains relatively high and this term has thus little effect. On the contrary, in the region of low conversions ($p_U \rightarrow 0$) this term is dominant. This offers the possibility of distinguishing between models A-3 and B-2 on the basis of data on limiting selectivity; for the model A-3 $S^0 \approx p_H$ (Eq. (9)), for the model B-2 $S^0 = \text{constant}$ (Eq. (16)).

Fig. 5 plots the dependences of selectivity S on conversion of thiophene ($x = WR_S/F_T$) for various inlet mixtures. Limiting selectivities found by numerical extrapolation for $x \rightarrow 0$ are summarized in Table IV showing also values of S^0 computed from models A-3 and B-2. For the extrapolated points a correlation with the partial pressure of hydrogen cannot be proven, which seems to justify the triangular scheme B-2. The confidence interval of the extrapolated data S^0 (0.01–0.07) thus encompasses the value 0.03 predicted by the model B-2.

TABLE IV
Comparison of Limiting Selectivities S^0

Inlet composition			$S^0 \cdot 10^2$ extrapolated	$S^0 \cdot 10^2$, computed	
T, %	H ₂ , %	N ₂ , %		model B-2	model A-3
2.5	97.5	0	4.6	3.0	3.3
5	95	0	4.7	3.0	3.2
10	90	0	2.5	3.0	3.1
20	80	0	2.9	3.0	2.7
5	45	50	4.9	3.0	1.5

In order to illustrate the fit of the experimental data by the model B—2 Figs 1—5 show the curves computed from Eqs (14) and (15). The calculation represents numerical solution of the set of two nonlinear algebraic equations, obtained by combining Eqs (14) and (15) with the expression (2), by the Newton–Raphson method. Considering the fact that the experimental error of R_i may reach up to 5%, the agreement between the computed and experimental values is acceptable.

Conformation of the resulting kinetic equations for the rate of formation of hydrogen sulphide and butane (Eq. (14), (15)) with the literature may be summarized as follows: By an equation similar to Eq. (14) described the rate of formation of hydrogen sulphide also Lee and Butt¹², Massoth¹⁵ and Kawaguchi²⁰; while Satterfield and Roberts¹¹, Vyskočil and Kraus¹³ and Marooka and Harmin¹⁴ prefer equation with the denominator raised to the second power. For the rate of formation of butane Satterfield and Roberts¹¹ and Lee and Butt¹² found a relation corresponding to Eq. (15) but they do not consider the appearance of butane at low conversion. These authors^{11,12} also presume the existence of different sites for hydrogesulphurisation of thiophene and hydrogenation of butene. The appearance of butane at low conversions ($p_U \rightarrow 0$), to which attention has been drawn also by Kolboe and Amberg³, has not been so far considered in the kinetic studies.

In the following paper the results of this work shall be extended by including another reaction — hydrogenation of ethylene taking place simultaneously with hydrodesulphurisation of thiophene.

LIST OF SYMBOLS

F_i, F	molar feed rates of component i and inlet mixture
k, K_i	rate constant, adsorption equilibrium constant of component i
P, p_i	pressure, partial pressure of component i
Q	objective function
r_j, R_i	rate of reaction step j , rate of formation of component i
S, S^0	selectivity ($S = R_B/R_S$), limiting selectivity ($p_U \rightarrow 0$)
T, S, U, B	thiophene, hydrogen sulphide, butene, butane
W	mass of catalyst
x	conversion of thiophene
y_i, y_i^0	mole fraction of component i in the reactor and in the feed
Z, Y	active sites
(Z), (TZ), etc.	relative concentration of free sites Z, of adsorbed thiophene on sites Z etc.

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