

SINGLE AND COMPETITIVE HYDRODESULPHURIZATION OF THIOPHENE AND BENZO[b]THIOPHENE ON MOLYBDENUM CATALYSTS*

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The reactivity of benzo[b]thiophene and thiophene and the amount of 2,3-dihydrobenzo[b]thiophene and tetrahydrothiophene in the title reaction on sulphided Co-Mo-Al₂O₃ and MoS₂ catalysts has been determined at the temperature range 543–623 K and hydrogen pressures 0.5–2.0 MPa in a tubular flow integral reactor. Under above conditions, benzo[b]thiophene was more reactive than thiophene and the difference in their reactivities in the competitive reaction was substantially greater than in the single reaction. The selectivity to the intermediate 2,3-dihydrobenzo[b]thiophene and tetrahydrothiophene in the reaction of benzo[b]thiophene and thiophene respectively, was measured in the whole region of total conversion. Based on these and reported data, the mechanism of hydrodesulphurization is discussed.

In fundamental research of catalytic hydrodesulphurization, the importance of practical problems forces the researchers to pay increasing attention to higher molecular sulphur compounds, *i.e.* to benzo[b]thiophene and dibenzothiophene compared to thiophene. This tendency appears in the period where even the mechanism of hydrodesulphurization of the simplest sulphur-containing hetero compound, thiophene, is the matter of much dispute. Mechanistic schemes of hydrodesulphurization are constructed mostly on the basis of interpretation of reaction kinetic data. However, such schemes seem to be too speculative, because of complicated relation between kinetic data and mechanism of heterogeneous catalysed reactions. The character of sulphur bonding in the aromatic system changes relatively little with its size. Therefore, the mechanism by which a catalyst activates a sulphur compound and by which cleaves this substance in the presence of hydrogen to hydrogen sulphide and a hydrocarbon should be similar for different heterocycles. The size of the aromatic system, in which sulphur is incorporated, affects, of course, kinetic relations between the steps of catalytic cycle and this leads to changes in overall reaction rate and in the selectivity to intermediate products. If the assumption about the same mechanism for different sulphur heterocycles is accepted, then the response

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to the structural change in the substrate of the kinetic pattern of the reaction can provide valuable information about reaction mechanism. An example illustrating such reasoning is the confrontation of the proposed course of hydrodesulphurization of thiophene *via* the formation of diacetylene¹⁻³ with the fact that 3-alkylthiophenes, benzo[*b*]thiophenes and dibenzothiophenes undergo hydrodesulphurization, although they cannot form an acetylenic intermediate product^{4,5}.

In view of these relations we have compared hydrodesulphurization of thiophene and benzo[*b*]thiophene. Our attention was focused on the experimental comparison of the reactivities of thiophene and benzo[*b*]thiophene and on the role of saturated sulphur compounds in the reaction path of hydrodesulphurization. In discussion we made also use of some results of both theoretical and noncatalytic chemistry of sulphur compounds.

EXPERIMENTAL

Chemicals and reagents. Thiophene (T), tetrahydrothiophene (TT), benzo[*b*]thiophene (BT), diethyl sulphide (DS), decane (D) (all Fluka), decaline (DL) and ethylbenzene (EB) (Labora, Prague) were distilled before use and naphthalene (N) (Labora, Prague) was recrystallized from methanol. 2,3-Dihydrobenzo[*b*]thiophene (DHBT) was prepared by hydrogenation of benzo[*b*]thiophene on MoS₂ at a temperature of 500 K and a hydrogen pressure of 2 MPa; a solution of 10% mol of benzo[*b*]thiophene in cyclohexane was fed such that at the overall benzo[*b*]thiophene conversion *ca.* 60 per cent, the selectivity to 2,3-dihydrobenzo[*b*]thiophene exceeded 80 per cent. The reaction mixture was rectified *in vacuo*; the boiling point of the product was 378 K/12 kPa and its purity and identity was confirmed by gas chromatography and NMR spectroscopy. Hydrogen (H), (Technoplyn, Prague) was purified on a desoxidation palladium catalyst and dried over a molecular sieve. Hydrogen sulphide (S) (Matheson) was used without further purification.

Catalyst Co-Mo-Al₂O₃, G-35 (Girdler Südchemie, München) was crushed into 0.16–0.25 mm particles and activated by two procedures. The first one involved sulphidation by H₂S-H₂ mixture outside the pressure reactor, which was carried out as described earlier⁶, followed by transfer of the sample to the reactor in air and by heating it in a stream of hydrogen to the reaction temperature. The other procedure involved the sulphidation of the catalyst by thiophene directly in the pressure reactor. The catalyst was heated in hydrogen for 0.5 h, to reach 473 K, and during the feed of 20 mol.% of thiophene in decane the temperature was raised to the temperature of experiments. The conditions of feed were as follows: total pressure $P = 2.0$ MPa, initial partial pressure P^0 (T) = 14 kPa, P^0 (D) = 56 kPa and P^0 (H) = 1.93 MPa, and reciprocal space velocity $W/F(T) = 50$ g h mol⁻¹, where W is the weight of the catalyst and $F(T)$ is the feed of thiophene. MoS₂ catalyst was prepared from MoS₂ powder (Fluka, *purum*) by pelleting it (25 MPa) and crushing into 0.16–0.25 mm particles. It was activated by heating in the reactor under hydrogen at the temperature and pressure of experiment.

Reactor and procedure. Data were obtained in a flow tubular reactor described elsewhere^{7,8}. Under reaction conditions, the whole reaction mixture was in gas phase. The condensator of the reactor was cooled to 253 K, in experiments with naphthalene to 268 K. The composition of the condensate was analysed by gas chromatography under the following conditions: Apiezon L on Chromosorb P, 4 mm column (*i.d.*), a thermal conductivity detector, H₂ as carrier gas; de-

pending on the mixture to be analysed, the column was 1 or 2 m long, temperature was 423, 463 or 473 K and hydrogen flow rate was 40 or 50 cm³ (STP) min⁻¹. Hydrogen sulphide was absorbed in ammoniacal solution of CdCl₂ and determined by iodometric titration. These analyses were used to calculate conversions $x(S) = \text{mol}(S)/(\text{mol}(BT)^0 + \text{mol}(T)^0)$, $x(BT) = (\text{mol}(BT)^0 - \text{mol}(BT))/\text{mol}(BT)^0$, $x(T) = (\text{mol}(T)^0 - \text{mol}(T))/\text{mol}(T)^0$, $x(\text{DHBT}) = \text{mol}(\text{DHBT})/\text{mol}(BT)^0$, $x(\text{EB}) = \text{mol}(\text{EB})/\text{mol}(BT)^0$ and $x(\text{TT}) = \text{mol}(\text{TT})/\text{mol}(T)^0$. A good performance of a condensator was verified by blank experiments. Nevertheless, the balance of the reactor was not better than 90 per cent. Conversion $x(S)$ determined by titration was always smaller than $x(S)$ calculated from $x(\text{EB})$, $x(\text{BT})$, $x(\text{DHBT})$, $x(T)$ and $x(\text{TT})$ determined by gas chromatography. The analysis did not detect obviously some low molecular sulphur compounds which are present among the products of hydrodesulphurization carried out under higher hydrogen pressure⁹. The incompleteness of these analyses did not affect the interpretation of obtained results. Sulphur compounds were fed as solutions in decaline or decane; in single reactions the sulphur compound to hydrocarbon molar ratio was 1 : 9, 1 : 5 or 1 : 4, in the competitive reaction the molar ratio of thiophene to benzo[b]thiophene to hydrocarbon was 1 : 1 : 4 or 1 : 1 : 9. Hydrocarbons were used as internal standards for gas chromatographic analysis and their stability under experimental conditions was verified. For all the reaction conditions chosen, 4–10 samples were taken for analysis in 10 min intervals and all data reported are the average of the composition of at least 3 samples taken after the steady composition of the reactor outlet has been attained. The pairs of conversions compared were always measured in immediately successive runs. This eliminated irreproducibility and instability of catalyst activity which amounted to about ± 10 relative per cent.

RESULTS

The reactivity of thiophene and benzo[b]thiophene was compared on the basis of integral kinetic data for the whole region of conversions 0–1.0. Pairs of conversions $x(T) - x(BT)$ under the same kinetic conditions were obtained both for single and competitive reactions. Kinetic conditions of experiments were changed in the following range: Co–Mo–Al₂O₃ sulphided by hydrogen sulphide or by the feed, MoS₂, $T = 523$ to 623 K, $P^0(T) = P^0(BT) = 4.7$ to 14 kPa, $P^0(H) = 0.5$ to 2.0 MPa, $W/F(T) = W/F(BT) = 30$ to 1 300 g h mol⁻¹. Data obtained in a series of experiments carried out under higher pressure in the reactor (2 MPa) on Co–Mo–Al₂O₃ catalyst sulphided by thiophene are presented in the form of integral kinetic curves in Fig. 1. It is seen that in single reactions, benzo[b]thiophene is significantly more reactive than thiophene and that in the reaction of the mixture of both compounds, this difference in the reactivity is even more pronounced. Data obtained in another series of experiments, using lower pressure in the reactor (to 1 MPa) and Co–Mo–Al₂O₃ catalyst pre-sulphided by H₂S + H₂ and MoS₂ are shown in Fig. 2. In this case the conversions of benzo[b]thiophene are plotted against thiophene conversions obtained under the same conditions. It is seen that the higher reactivity of benzo[b]thiophene and the greater difference in reactivities in competitive reactions has been observed for the whole range of variables.

To clarify the nature of influencing the reaction of thiophene by benzo[b]thiophene, further experiments were made in which benzo[b]thiophene was replaced

in the feed by naphthalene, the latter compound being isoelectronic with benzo[*b*]-thiophene, and also by diethyl sulphide which is readily cleaved to hydrogen sulphide. The results of these experiments (Table I), along with data in Fig. 2, show that naphthalene does not affect the reaction of thiophene, but that diethyl sulphide retards the reaction to the same extent as does benzo[*b*]thiophene. If a thiophene–naphthalene–decane mixture is fed to the reactor under conditions specified in Table I, naphthalene is not hydrogenated.

The analysis of literature information and of preliminary experiments showed that in the course of hydrodesulphurization of benzo[*b*]thiophene, the gas phase contains substantially greater amount of a saturated sulphur compound compared to the reaction of thiophene. Some data on amounts of tetrahydrothiophene in the reaction of thiophene were obtained by us earlier¹⁰ and hence we centered in this work especially on 2,3-dihydrobenzo[*b*]thiophene formed in the reaction of benzo[*b*]thiophene. The integral dependences at two temperatures and the pressure 2 MPa are shown in Fig. 3. This figure includes also data obtained in another series of experiments and allows to compare the amount of 2,3-dihydrobenzo[*b*]thiophene and tetrahydrothiophene in the reaction of benzo[*b*]thiophene and thiophene under the same experimental conditions.

DISCUSSION

Of the products of hydrodesulphurization of thiophene and benzo[*b*]thiophene, a series of compounds can be isolated^{11–14} which are not thermodynamically stable

TABLE I

Effect of diethyl sulphide and naphthalene on hydrodesulphurization of thiophene^a

Feed ^b		Conversion	
<i>i</i>	<i>j</i>	<i>i</i>	<i>j</i>
Diethyl sulphide	—	0.82	—
Thiophene	—	0.64	—
Thiophene	diethyl sulphide	0.29	0.82
Thiophene	—	0.60	—
Thiophene	naphthalene	0.61	— ^c

^a A series of experiments immediately following each other on the same charge of the catalyst, Co–Mo–Al₂O₃ pre-sulphided by H₂S, $W/F(i) = W/F(j) = 40 \text{ g h mol}^{-1}$, $T = 573 \text{ K}$. ^b For the feed of one component *i*: $P^0(i) = 4.7 \text{ kPa}$, $P^0(\text{DL}) = 42.3 \text{ kPa}$, $p^0(\text{H}) = 953 \text{ kPa}$, for the feed of two components *i, j*: $P^0(i) = P^0(j) = 4.7 \text{ kPa}$, $P^0(\text{DL}) = 37.6 \text{ kPa}$, $P^0(\text{H}) = 953 \text{ kPa}$. ^c Conversion was not determined.

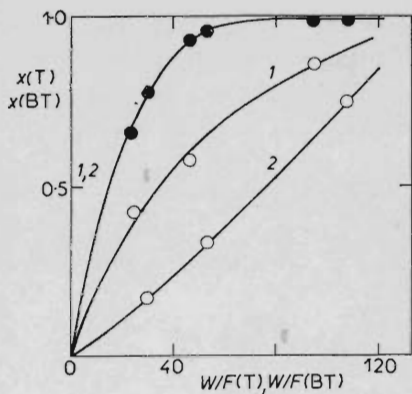


FIG. 1

Integral kinetic curves for hydrodesulphurization of benzo[*b*]thiophene and thiophene. Co-Mo-Al₂O₃ sulphided by thiophene, $T = 593$ K, (○) thiophene, (●) benzo[*b*]thiophene. 1 Single reactions, $P^0(T)$ or $P^0(BT) = 14$ kPa, $P^0(D) = 56$ kPa, $P^0(H) = 1.93$ MPa; 2 reaction in mixture, $P^0(T) = P^0(BT) = 14$ kPa, $P^0(D) = 56$ kPa, $P^0(H) = 1.92$ MPa

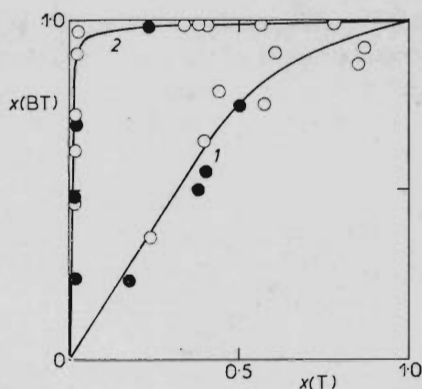


FIG. 2

Comparison of reactivities of benzo[*b*]thiophene and thiophene. 1 Conversion in single reactions, $P^0(T)$ or $P^0(BT) = 4.7$ kPa, $P^0(D) = 42.3$ kPa; 2 conversion for the reaction in mixture, $P^0(T) = P^0(BT) = 4.7$ kPa, $P^0(D) = 42.3$ kPa; (○) Co-Mo-Al₂O₃ pre-sulphided by H₂S, $T = 523$ or 573 K, $P^0(H) = 0.5$ or 1.0 MPa, $W/F(T)$ and $W/F(BT) = 34$ to 210 g h mol⁻¹; (●) MoS₂, $T = 573$ or 623 K, $P^0(H) = 1.0$ MPa, $W/F(T)$ and $W/F(BT) = 31$ to 1300 g h mol⁻¹

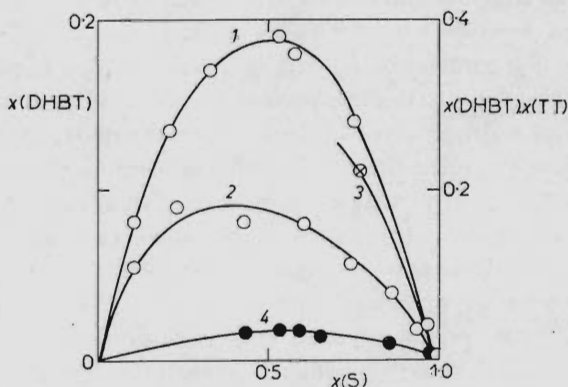
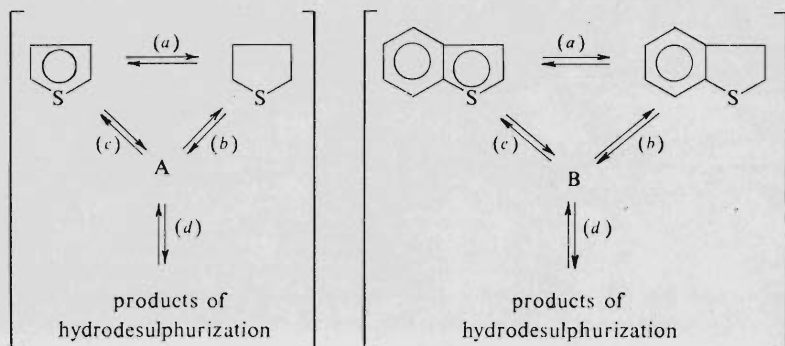


FIG. 3

Dependence of $x(\text{DHBT})$ and $x(\text{TT})$ on $x(\text{S})$ for single reactions of benzo[*b*]thiophene and thiophene on pre-sulphided Co-Mo-Al₂O₃ catalyst. 1, 2 (○) $x(\text{DHBT})$, $P^0(BT) = 40$ kPa, $P^0(DL) = 200$ kPa, $P^0(H) = 1.76$ MPa, $W/F(BT) = 1$ to 100 g h mol⁻¹, 1 $T = 543$ K, 2 $T = 603$ K; 3, 4 (●) $x(\text{TT})$, (⊗) $x(\text{DHBT})$, $P^0(BT) = P^0(T) = 14$ kPa, $P^0(DL) = 56$ kPa, $P^0(H) = 1.93$ MPa, $T = 533$ K, $W/F(T) = W/F(BT) = 25$ to 100 g h mol⁻¹

under reaction conditions. Each of them may in principle be considered as an intermediate product of the reaction. This work is concerned mainly with the role of saturated sulphur compounds and therefore only simplified reaction mechanism presented in Scheme 1 is discussed. Intermediate products A and B do not contain



SCHEME 1

the sulphur bonded in the ring and their more detailed structure is not relevant to the discussion. (In the reaction of thiophene such compounds can be *e.g.* 1-butene-4-thiol, butanethiol or butadiene, in the reaction of benzo[*b*]thiophene, these can be *e.g.* *o*-vinylthiophenol, *o*-ethylthiophenol or styrene).

According to the Scheme, intermediates A and B arise from thiophene or from benzo[*b*]thiophene by two reaction paths which are still the matter of discussion^{5,8,10-15}. The first pathway, visualized by steps (a) and (b), involves the saturated sulphur compound as the intermediate product. The second path, step (c), is usually referred as the direct hydrogenolysis of the C—S bond without the preceding saturation of the thiophene ring. Kinetic data available in literature do not allow to decide whether (a), (b) and (c) form a triangle scheme and in what ratio the products A and B are formed by pathways (a)–(b) and (c), neither whether one of steps (a), (b) and (c) in the Scheme is redundant, does not correspond to any chemical reaction and the Scheme is consecutive or branched. The complexity of heterogeneous catalysed reactions, especially the presence of adsorption-desorption steps causes namely that without further, not readily verifiable assumptions, parallel and consecutive surface reactions cannot be distinguished by studying concentration changes in the gas phase¹⁶. Very illustrative example of the complexity of this problem can be found *e.g.* in the study concerned with the role of cyclohexene as the intermediate product in hydrogenation of benzene to cyclohexane¹⁷. Compared to this, kinetic analysis of the scheme of hydrodesulphurization is further complicated by a number of potential intermediate products and by diversity of their chemical properties.

However, valuable arguments for distinguishing the alternative routes in Scheme 1 can be obtained by application of the results of the chemistry of sulphur compounds. Some relations for thiophene were already discussed in literature^{4,5,18,19}. The electronic structure of aromatic sulphur heterocyclic compounds is analogous to that of aromatic hydrocarbons and the chemical behaviour in both series is determined to a great extent by their π -electron configuration. Three highest occupied orbitals of benzo[b]thiophene have π -character and their energies are essentially identical with the energies of the corresponding naphthalene orbitals. Also two highest occupied orbitals of thiophene have π -character and the average of their energies is the same as the energy of degenerated benzene π -orbitals. Only the orbital next in energy to the above orbitals has σ -character, is localized at sulphur and can be identified as the free electron pair at sulphur^{20,21}. This orbital has essentially spherical symmetry and its interaction with the surface does not require the perpendicular position of the thiophene ring to the surface, as has been usually assumed in interpreting adsorption related to hydrodesulphurization. Quantum chemical modelling of the protonation of thiophene has revealed that this orbital can participate in the formation of the surface π -complex^{19,22}. The chemical behaviour of thiophene and benzo[b]thiophene clearly demonstrates the aromatic character of these compounds^{23,24}. The degree of their aromaticity can be quantitatively described by different indices of aromaticity, obtained by quantum chemical or by physicochemical measurements. Also these parameters, characterizing the aromaticity on the level of electronic structure, confirm the great similarity between benzene and thiophene molecule and between naphthalene and benzo[b]thiophene molecule²⁵. The measure of π -electron distribution in sulphur-containing aromatic compounds is the π -electron density at atoms and bond orders calculated by quantum chemical methods. The results of earlier calculations made for thiophene were related to hydrodesulphurization by Gates and coworkers⁵. The survey of more recent literature on calculations of the electronic structure of benzo[b]thiophene and thiophene can be found *e.g.* in the work of Palmer and Kennedy²⁶. For purposes of this discussion, Table II presents only bond orders and π -electron densities at sulphur, both parameters describing the extent of delocalization of sulphur electrons, calculated for different sulphur compounds by Dewar and Trinajstić²⁷. All literature data mentioned show convincingly that thiophene and benzo[b]thiophene are aromatic, their electronic structure is analogous to that of benzene and naphthalene, and in both compounds the sulphur is bonded in a similar way.

The similarity of the electronic structure of aromatic carbon and sulphur compounds reflects in their similar chemical properties. Both series form charge-transfer π -complexes with various acceptors, thiophene behaves as benzene and benzo[b]thiophene as naphthalene^{28,29}. Also in the formation of π -complexes with surface hydroxyl groups of solid oxides, benzene and thiophene exhibit similar properties³⁰ and the same analogy was observed also for the adsorption of alkylbenzenes and

alkylthiophenes on hydrodesulphurization catalysts¹⁸. The presence of π -complexes has been proposed also for hydrogenation of aromatic hydrocarbons on a sulphided Co-Mo-Al₂O₃ catalyst³¹. It is evident that the same behaviour under hydrogenation conditions can be expected also for sulphur-containing aromatic derivatives. However, the products of their hydrogenation, saturated cyclic sulphur compounds, are, in contradistinction to saturated hydrocarbons, very unstable under reaction conditions. They can be detected as the main product of the reaction only under very limited range of conditions, otherwise they are readily cleaved to the final product, hydrogen sulphide. In principle, this cleavage can take place already in the stage of the partially saturated ring.

The assumption about hydrogenolytic reaction step (c), involving the cleavage of the aromatic bond having, according to Table II, a certain double bond character, is not in accord with the above results of the chemistry of sulphur-containing heterocyclic compounds. On the other hand, the presumed hydrogenation in step (a) is logical extrapolation of these results and can be used to interpret the relative reactivity of benzo[*b*]thiophene and thiophene and the amount of saturated sulphur compound in their reactions.

The higher reactivity of benzo[*b*]thiophene compared to thiophene in single reactions, which is evident from the results in Fig. 1 and 2, has been observed under different conditions also by other authors^{32,33}. This agrees well with the reactivity of aromatic hydrocarbons, since naphthalene exhibits higher reactivity than benzene on sulphide catalysts³⁴. Data about the relative reactivity of thiophene and benzo[*b*]thiophene in mixture are scarce. Kilanowski and coworkers³² determined it by pulse technique and did not observe any great difference from the reactivity in single reactions. Our results, obtained in the reactor operating under steady state conditions, indicate the strong mutual influencing of the reactions of both heterocyclic

TABLE II

π -Electron distribution in the vicinity of sulphur for some sulphur compounds, obtained by quantum chemical calculations²⁷

Molecule	π -Electron density at sulphur ^a	C-S bond order ^b
Thiophene	1.85	0.35
Benzo[<i>b</i>]thiophene	1.88	0.30 ^c
Dibenzothiophene	1.90	0.26
Thiophenol	1.96	0.22

^a The density at the sulphur not interacting with the π -system equals to 2. ^b The bond order of the aromatic bond in benzene is 0.67. ^c Bond orders of both C-S bonds are nearly identical.

compounds (Figs 1 and 2). However, naphthalene does not affect the reactivity of thiophene (Table I). Therefore, benzo[*b*]thiophene does not retard the reaction of thiophene by competitive adsorption *via* π -complex, but participates in the later stage of the reaction where its aromaticity is already cancelled. On the other hand, the effect of diethyl sulphide in the feed (Table I) indicates that the compound which shows rate-retarding effect is either a saturated sulphur compounds or hydrogen sulphide, both being formed from benzo[*b*]thiophene. The retardation of the reaction of thiophene in the presence of diethyl sulphide has been observed by us earlier⁸ and the effect of hydrogen sulphide has been reported by a number of authors (*e.g.*^{35,36}). In principle, the relative reactivity of both heterocyclic compounds may depend upon reaction conditions³⁶. Nevertheless, it seems likely that under typical hydrodesulphurization conditions, especially in the case of the reaction in mixture, benzo[*b*]thiophene is always more reactive than thiophene. The reverse reactivity observed under industrial or similar conditions (*e.g.*³⁷) is obviously the result of influencing the reaction by diffusion.

It was observed that in hydrodesulphurization of benzo[*b*]thiophene the saturated sulphur compound is formed in greater amounts than in hydrodesulphurization of thiophene^{14,38}. Our results shown in Fig. 3 allow to compare the amount of both intermediate products under identical conditions. The different amounts of the saturated intermediate product in the reactions of thiophene and benzo[*b*]thiophene cannot be interpreted as arising from the different importance of path (a)–(b) in Scheme 1, since the amount of an intermediate product in a complex reaction cannot be simply related to the importance of the corresponding reaction path¹⁶. Kinetic behaviour of saturated sulphur intermediate products has as yet been investigated only scarcely Daly¹⁴ reported the integral dependence $x(\text{DHBT}) - x(\text{BT})$ for *ca.* 0–0.65 and our results in Fig. 3 cover the whole region of $x(\text{BT})$ 0–1.0. Based on the analysis of these data the question about the real or formal nature of step (c) in Scheme 1 cannot be answered. In principle, the dependence $x(\text{DHBT}) - x(\text{BT})$ could be the same in both cases¹⁶.

In previous work¹⁰ we reported on the effects of hydrogen pressure, temperature and catalyst on the amount of tetrahydrothiophene detectable in the reaction of thiophene. The amount of 2,3-dihydrobenzo[*b*]thiophene detectable in the reaction of benzo[*b*]thiophene changes in the same way. According to the results shown in Fig. 1 the maximal conversion $x(\text{DHBT})$ determined in the course of the reaction on Co–Mo–Al₂O₃ catalyst at 543 K and hydrogen pressure 2 MPa equals to approx. 0.2. The results reported by Daly¹⁴ and obtained with the catalyst of the same provenience and at a similar temperature (523 K) indicate that at the higher hydrogen pressure (8.5 MPa) the maximal $x(\text{DHBT})$ equals to 0.5, *i.e.* is substantially greater. On the other hand, at atmospheric hydrogen pressure (0.1 MPa) the amounts of 2,3-dihydrobenzo[*b*]thiophene are low and have been usually neglected (*e.g.*^{36,39}). The effect of temperature is illustrated in Fig. 3. At higher temperature, 2,3-dihydro-

benzo[*b*]thiophene is less stable, which was observed also by *e.g.* Givens and Venu-to³⁰. At low temperature and high hydrogen pressure, one can obtain tetrahydrothiophene and 2,3-dihydrobenzo[*b*]thiophene by hydrogenation of thiophene or benzo[*b*]thiophene in preparative yields, using PdS as the catalyst¹². Our experience with the preparation of 2,3-dihydrobenzo[*b*]thiophene described in Experimental shows that for this purpose one can use also hydrogenation of benzo[*b*]thiophene on MoS₂ catalyst.

The strong dependence of the concentration of the saturated intermediate product in the reaction of thiophene or benzo[*b*]thiophene on hydrogen pressure is manifestation of the different reaction order with respect to hydrogen of steps (*a*) and (*b*) and indicates that hydrogen operates differently in both steps. It is even possible to assume that step (*b*) in the reaction of thiophene involves elimination without direct participation of hydrogen and that hydrodesulphurization is the case of bifunctional catalysis in which the catalyst exhibits both hydrogenation and elimination activity^{8,10,15}. Based on this concept, no hydrogenolytic step would be involved in hydrodesulphurization. Consequently, the aromatic ring would be hydrogenated, the formed saturated sulphur bonds would be cleaved by elimination mechanism without direct participation of hydrogen and the unsaturated carbon bonds formed by this elimination would be than hydrogenated. The cleavage of saturated mercaptanes and saturated sulphides to olefins and hydrogen sulphide without direct participation of hydrogen, the process analogous to dehydration of alcohols and ethers, has been observed by a number of authors^{12,15,40,41}.

The simple application of the above concept to the reaction of benzo[*b*]thiophene is made difficult by the fact that one of the C—S bonds in 2,3-dihydrobenzo[*b*]thiophene, *i.e.* the bond adjacent to the benzene ring, cannot undergo cleavage by elimination mechanism. Hence, the hydrogenolysis of this bond seems to be the only possible mechanism of cleavage. However, even in 2,3-dihydrobenzo[*b*]thiophene the sulphur interacts with aromatic system. The extent of this interaction is demonstrated by C—S bond order and π -electron density at sulphur, reported for thiophenol in Table II. It is smaller than in the case where the sulphur atom is constituent of the ring, such as in thiophene, benzo[*b*]thiophene or dibenzothiophene. Nevertheless, this fact can be taken as support for the assumption that even the cleavage of the (C₆H₅)—S bond in 2,3-dihydrobenzo[*b*]thiophene or in thiophenol is not one-step hydrogenolysis but that it involves separate processes, *i.e.* at least partial saturation of benzene π -system and subsequent elimination cleavage of the so formed saturated C—S bond without participation of hydrogen. The results of the study of hydrogenative cleavage of phenols on sulphide catalysts⁴² may be related to this problem. Many authors either do not include the direct hydrogenolysis into this reaction at all or they regard it as only one of parallel paths, assuming that the reaction takes place *via* formation of cyclohexanol and cyclohexene. Whether cyclohexene is further hydrogenated to cyclohexane or dehydrogenated to benzene

depends at temperatures 623–673 on hydrogen pressure, due to thermodynamic reasons⁴³. In other words, the re-formation of the aromatic ring from cyclohexene formed in elimination step is possible even under hydrogenation conditions. Formation of benzene from cyclohexene at 623 K and a hydrogen pressure of 0.1 MPa on a sulphided Co–Mo–Al₂O₃ catalyst was observed *e.g.* by Vyskočil and Kraus⁴⁴. This is difference from butadiene or butenes, the products of elimination cleavage in the reaction of thiophene where the equilibrium of their hydrogenation is shifted to butane even at low hydrogen pressure⁴³.

Some of arguments presented in this discussion can be used also to analyse the mechanism of hydrodesulphurization of dibenzothiophene, which was not studied experimentally in this work. Judging from chemical properties⁴⁵, aromaticity indices²⁵ and from data in Table II, the sulphur is bonded in this heterocyclic compound similarly as is in benzo[b]thiophene and thiophene. However, in any saturated sulphur intermediate product, in the hydrodesulphurization of dibenzothiophene, the aromaticity of not only the sulphur-containing ring, but also of the adjacent benzene ring should be destroyed. Such saturated sulphur substances were, in fact, detected in the reaction mixture produced by hydrodesulphurization and many authors assume that these are intermediates of one of parallel hydrodesulphurization pathways^{11,12,46}.

We believe, therefore, that the mechanism of hydrodesulphurization of all aromatic sulphur-containing heterocyclic compounds is similar to each other and that it involves a partial cancellation of the aromaticity of the molecule, prior to subsequent cleavage of the saturated C–S bond. The concept of the one step hydrogenolytic cleavage of the aromatic C–S bond is likely only formal simplification of the multi-step course of the release of the sulphur from aromatic sulphur-containing heterocyclic compounds.

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