

THE EFFECT OF Co IN HYDRODESULPHURIZATION OF 2,3-DIHYDROBENZO[b]THIOPHENE ON Co-Mo CATALYST

Rudolf PETER, Vlastimil MATĚJEC and Miroslav ZDRAŽIL

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 — Suchbát*

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Hydrodesulphurization of benzo[b]thiophene and 2,3-dihydrobenzo[b]thiophene on Mo/alumina and Co-Mo/alumina catalysts has been studied in a flow reactor at atmospheric pressure and temperature 543 K. The amount of dihydrobenzo[b]thiophene formed in hydrodesulphurization of benzo[b]thiophene and the amount of benzo[b]thiophene formed in hydrodesulphurization of dihydrobenzo[b]thiophene were much lower on Co-Mo catalyst than on Mo catalyst. The equilibrium constant of the hydrogenation of benzo[b]thiophene to dihydrobenzo[b]thiophene at 543 K was determined. This partial equilibrium was attained during hydrodesulphurization on Mo catalyst irrespectively of the fed sulphur compound but was not approached during hydrodesulphurization on Co-Mo catalyst. Kinetic equation describing simultaneously the reaction of both heterocycles was derived from consecutive "hydrogenation-elimination" scheme which does not contain step referred to as "direct hydrogenolysis of the thiophenic ring". It was concluded that the effect of Co in the reaction network is localized in the section between partially hydrogenated benzothiophene and hydrogen sulphide.

Benzo[b]thiophene (BT) is considered to be a proper model of sulphur compounds in heavier fractions of oil and in coal. Hydrodesulphurization (HDS) of it has been studied in the literature with the aim to elucidate the mechanism of the industrial HDS process. In our previous communication¹ it was found that promotion of the Mo/Al₂O₃ catalyst by Ni or Co diminishes substantially the amount of dihydrobenzothiophene (DHBT) during HDS of BT. We consider this phenomenon as important for the understanding of the role of Ni and Co in industrial Ni-Mo and Co-Mo HDS catalysts and this paper reports our new experimental material in this direction.

Previous studies by other authors on HDS of BT, giving DHBT concentrations in the reaction mixture, were all undertaken with Co promoted Mo catalysts²⁻⁷. The behaviour in this respect of Ni promoted and nonpromoted Mo catalysts has not been reported.

Literature data on the reaction of DHBT under HDS conditions are very scarce and are also limited only to Co-Mo catalysts. Simultaneous desulphurization to H₂S and dehydrogenation to BT was observed at atmospheric pressure of hydrogen^{3,8,9}. However, dehydrogenation was not found at pressure of hydrogen 5 MPa⁵.

The formation of DHBT during HDS of BT and the formation of BT during HDS of DHBT are mutually related by the principle of microscopic reversibility. The addition of Co or Ni to Mo catalysts suppresses the formation of DHBT in the former case¹ and consequently should also suppress the formation of BT in the latter case. The first purpose of this work was to verify experimentally this assumption.

The literature gives no quantitative data on the equilibrium BT-DHBT-H₂. (This is partial equilibrium in respect to the hydrodesulphurization reaction; the total equilibrium BT-DHBT-H₂-(H₂S + EB), where EB is ethylbenzene, is shifted entirely to the side of H₂S even at atmospheric pressure of hydrogen). Both the dehydrogenation of DHBT to BT and the hydrogenation of BT to DHBT was observed at atmospheric pressure of hydrogen and in the temperature range of 573–673 K^{3,8,9}. This suggests that partial equilibrium is strongly shifted neither to BT nor to DHBT side. However, without reliable equilibrium constant available, it is not clear whether the formation of DHBT and BT in HDS of BT and DHBT, respectively, is limited by equilibrium. The second aim of this work was to determine the partial equilibrium constant in the system BT-DHBT-H₂ at the temperature used in our studies.

Most other authors assume that H₂S is formed during HDS of BT by two parallel ways, the first one going through DHBT as an intermediate and the second one being "direct hydrogenolysis" of BT (*e.g.*^{3,7,8}). We have concluded on the basis of chemical considerations that all available facts are consistent with hydrogenation-elimination mechanism which does not involve any "direct hydrogenolysis" step from BT to H₂S¹⁰. The third purpose of this work was to show that the kinetics in the system BT-DHBT-(H₂S + EB) conforms to this hydrogenation-elimination mechanism.

This work reports on effect of promotor in Co-Mo catalysts both in HDS of DHBT and in HDS of BT. Atmospheric pressure of hydrogen was used in order to allow dehydrogenation of DHBT. Our other publication¹¹ describes the effect of promoter in HDS of BT on Co-Mo, Ni-Mo, Co-W, and Ni-W catalysts at pressure 2.5 MPa.

EXPERIMENTAL

Catalysts are described in Table I. The laboratory catalysts were prepared by impregnation of commercial alumina CHEROX 33-00 (Chemical Works, Litvínov, Czechoslovakia). A slurry of alumina particles (0.16–0.25 mm) in a solution of ammonium heptamolybdate was dried in

TABLE I
Characterization of catalysts

Catalyst	Type	Origin	Content, % wt	
			MoO ₃	CoO
Mo	Mo/Al ₂ O ₃	laboratory	8.6	—
CoMo(I)	CoMo/Al ₂ O ₃	laboratory	8.6	2.5
CoMo(II)	CoMo/Al ₂ O ₃	CHEROX 36-01 ^a	13.0	3.5

^a Manufactured by coprecipitation technology by Chemical Works, Litvínov, Czechoslovakia.

a rotary evaporator under reduced pressure at 373 K. Cobalt was introduced by similar impregnation of dried Mo/Al₂O₃ catalyst by a solution of cobalt nitrate. Catalysts were calcined for 3 h at 823 K in a flow of air. The commercial catalyst CHEROX 36-01 was crushed to 0.16 to 0.25 mm particle size. All catalysts were presulphided by the mixture H₂S + H₂ (1 : 10) at 720 K by the procedure described elsewhere¹², and stored on air.

Benzo[*b*]thiophene (BT) was supplied by Fluka and was redistilled before use. 2,3-Dihydrobenzo[*b*]thiophene (DHBT) was prepared by hydrogenation of BT on Mo/C catalyst (10% wt MoO₃, presulphided) at 2.1 MPa and 543 K. BT was fed as a solution in decane, the molar ratio BT : decane : H₂ in the feed being 1 : 5 : 44. At optimum space time, the conversion of BT to DHBT was 65% and to H₂S 30%. DHBT was isolated by rectification, its purity was determined by GLC as better than 99% (the rest mostly BT) and its identity was confirmed by NMR spectroscopy.

A glass tubular flow reactor with i.d. 4 mm was used. The apparatus worked at atmospheric pressure and the mean pressure in the reactor was 100 kPa. The reaction temperature was 543 ± 1 K. The sulphur compound was fed as a solution in decane and the molar ratio sulphur compound : decane : H₂ in the feed was 1 : 5 : 44. It was calculated that no liquid phase was present in the reactor under these conditions. The catalyst charge *W* was 1–30 g and the lowest feed rate *F* was 0.01 mol (BT) h⁻¹. The condenser at the reactor outlet was cooled to 263 K and the liquid products were analyzed by GLC (1.7 m column packed with 20% Apiezon L on Rysorb BLK operating at 473 K). The composition of the liquid products was followed for 2 h at each space time *W/F* (kg (cat) h mol (BT)⁻¹) and was stable in this period. The data at each space time were obtained with a fresh catalyst charge.

The results were expressed in terms of molar fractions of BT, DHBT and H₂S in the reaction mixture *vs* space time. Molar fractions were defined: $a(\text{BT}) = n(\text{BT})/n^{\circ}(\text{SF})$, $a(\text{DHBT}) = n(\text{DHBT})/n^{\circ}(\text{SF})$ and $a(\text{HS}) = n(\text{HS})/n^{\circ}(\text{SF})$, where *n* and *n*[°] are moles in the products and feed, respectively, HS is H₂S and SF is the fed sulphur compound (*i.e.* BT or DHBT). The values of *a*(BT) and *a*(DHBT) were determined by GLC analysis and *a*(HS) was calculated from the balance $a(\text{BT}) + a(\text{DHBT}) + a(\text{HS}) = 1$.

RESULTS AND DISCUSSION

Two integral curves of composition *vs* space time *W/F* were measured on each catalyst, one with BT and one with DHBT as the fed compound. The temperature, total pressure and ratio sulphur compound : decane : H₂ in the feed were the same in all runs. The obtained data of molar fractions *vs* *W/F* are shown in Figs 1 and 2. The molar fractions are further replotted in Fig. 3 according to the concept of Wei and Prater¹³ as reaction paths in the reaction triangle not containing space time.

Effect of Co on products distribution. The runs with BT as the starting compound confirmed that the promoter effect observed at 2.1 MPa^{1,11} manifests itself also at atmospheric pressure. The amount of DHBT on promoted catalysts was about three times lower than on nonpromoted one (Fig. 3).

In the runs with DHBT as the starting compound, much less BT was formed on promoted than on nonpromoted catalysts (Fig. 3). This fully confirmed our expectation based on the principle of microscopic reversibility in the system BT–DHBT–H₂–(H₂S + EB).

The two Co–Mo catalysts exhibited nearly identical curves in Fig. 3 even when one was prepared by coprecipitation and the second one by impregnation. This supports our opinion that the position of reaction paths in the reaction triangle in Fig. 3 is strongly influenced by the presence or absence of a promoter (Co or Ni) but is insensitive to the details of catalyst preparation.

Thermodynamics. The position of the total equilibrium in the system BT–DHBT– H_2 –(EB + H_2S) which corresponds to our initial composition is expressed in Fig. 3 by the vertex (H_2S + EB). This gives no limitation to the shape of the reaction paths from BT or DHBT to H_2S . The position of the partial equilibrium BT–DHBT– H_2 is expressed in Fig. 3 as a line going through the vertex (H_2S + EB) and intersecting

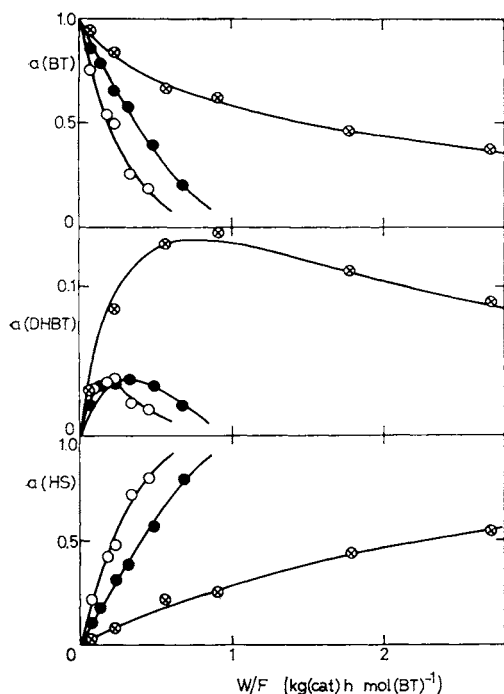


FIG. 1

Integral kinetic curves for HDS of BT at temperature 543 K and total pressure 100 kPa; the curves are calculated using constants in Table II. \otimes Mo, \circ CoMo(I), \bullet CoMo(II)

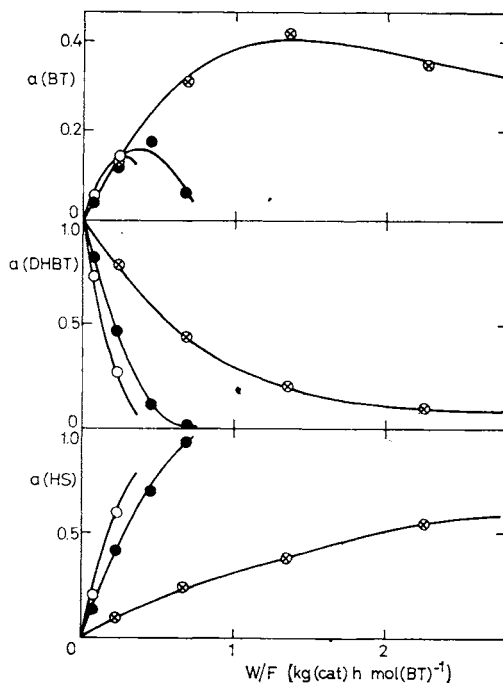


FIG. 2

Integral kinetic curves for HDS of DHBT at temperature 543 K and total pressure 100 kPa; the curves are calculated using constants in Table II. \otimes Mo, \circ CoMo(I), \bullet CoMo(II)

the line BT–DHBT in a point E. (The change of hydrogen pressure during the reaction was neglected). Any reaction path from BT to (H₂S + EB) must lie entirely inside the triangle BT, E, (H₂S + EB) and any path from DHBT to (H₂S + EB) must lie inside the triangle DHBT, E, (H₂S + EB).

It is seen in Fig. 3 that on the nonpromoted catalysts the reaction paths from BT and from DHBT to (H₂S + EB) asymptotically approach each other at desulphurization conversion $x(\text{HS})$ about 50% ($x(\text{HS}) = a(\text{HS})/100$) and merge at higher values of it. The partial equilibrium line must be asymptotic to both the reaction path BT–(H₂S + EB) and the path DHBT–(H₂S + EB) and in the region where they merge it must be identical with them. These requirements are fulfilled by the line (H₂S + EB)–E shown in Fig. 3. The equilibrium constant K_p at the temperature 543 K obtained from that line is 0.35 ($K_p = p^*(\text{DHBT})/p^*(\text{BT}) p^*(\text{H})$, where $p^*(I)$ is equilibrium pressure of the substance I expressed in relative units with reference pressure 0.1 MPa and H is hydrogen). An alternative determination of K_p from the data in Fig. 3 will be described below.

Kinetics. The possibility to determine the surface reaction network by the analysis of bulk phase kinetics is very limited in heterogeneous catalysis. If the surface reactions are not completely rate determining, the reaction sequence observed in the bulk phase might be completely different from the true surface reaction network. This effect has been referred to as “adsorption disguise”¹⁴ and was analyzed several times by other authors (e.g.^{13–16}).

In this situation the purpose of the following kinetic analysis was not to distinguish between alternative reaction schemes. The aim was only to confirm that observed kinetic data fit to the hydrogenation-elimination mechanism which follows from chemical considerations¹⁰.

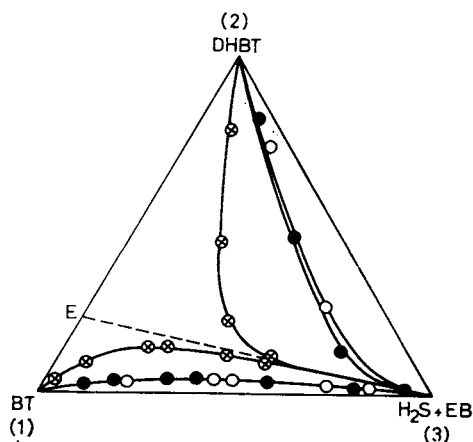


FIG. 3

Reaction paths in the system BT–DHBT–(H₂S + EB) at temperature 543 K and total pressure 100 kPa (the change of partial pressure of hydrogen during the reaction is neglected); the curves are calculated using constants in Table II. Reaction paths —, ⊙ Mo, ○ CoMo(I), ● CoMo(II), - - - partial equilibrium BT–DHBT–H₂

The kinetic theory used in this work is explained in detail in the classical paper by Wei and Prater¹³. Consequently, only a brief comment upon the procedure applied is presented below and the formalism introduced in the mentioned original paper is upheld.

The various possible representations of the hydrogenation-elimination mechanism of HDS of BT are shown in Fig. 4. The common feature of them, which is characteristic for the hydrogenation-elimination mechanism, is that the desorption of DHBT is a side branch of the chain from BT to H₂S; these schemes do not contain any "direct hydrogenolysis" step. Species \mathcal{U}_N are adsorbed intermediates with no corresponding free species. \mathcal{U}'_N is assumed to be BT with one hydrogen atom added to the thiophenic ring and \mathcal{U}''_N a compound with mercapto group (the desorption of a trace amount of the latter compounds was observed by Daly² but is neglected here). The schemes containing and not containing nondesorbed intermediates lead in the following kinetic analysis to the equations of the same structure and are thus indistinguishable. For this reason, only the simplest scheme shown in Fig. 4c is processed below. The change of hydrogen pressure during the reaction was neglected.

It was shown¹³ that, when the concentrations of adsorbed species are at steady state (the adsorption-desorption steps are not assumed to be in equilibrium), this reaction scheme is described by the equation

$$\frac{d\alpha}{d(W/F)} = \frac{1}{1 + w_1 a_1 + w_2 a_2} \Theta \alpha, \quad (1)$$

where α is the composition vector with elements $a_1 = a(\text{BT})$, $a_2 = a(\text{DHBT})$ and $a_3 = a(\text{HS})$, $(1 + w_1 a_1 + w_2 a_2)$ is the isotherm term, $\Theta \alpha$ is the mass action term, Θ is the pseudo monomolecular rate constants matrix and W/F is space time

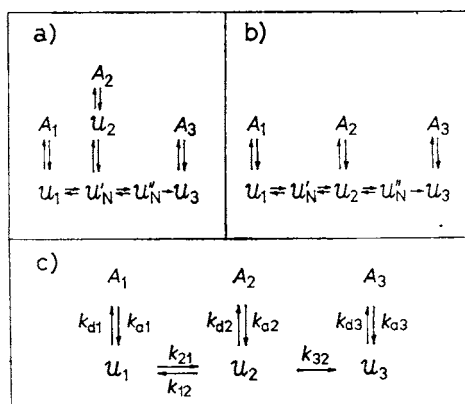


FIG. 4

The scheme of the hydrogenation-elimination mechanism of HDS of BT. a), b) Possible localization of nondesorbed intermediates, c) simplified presentation not showing nondesorbed intermediates. A₁ free species, \mathcal{U}_i adsorbed species, $i = 1$ BT, $i = 2$ DHBT, $i = 3$ (H₂S + EB), \mathcal{U}_N nondesorbed intermediates, k rate constants

(kg(cat) h mol⁻¹). The elements of the matrix Θ are composed from four nonzero pseudo monomolecular constants ϑ_{12} , ϑ_{21} , ϑ_{31} , ϑ_{32} (mol h⁻¹ (kg(cat))⁻¹). Constants w and ϑ (six altogether) are complex and are composed from constants k (nine altogether) from the scheme in Fig. 4c (for details see¹³). Eq. (1) can be transformed into the form

$$\frac{d\beta}{d(W/F)} = \frac{1}{1 + v_1 b_1 + v_2 b_2} A\beta, \quad (2)$$

where β is the composition vector expressed in terms of hypothetical species B_i , b_i are components of vector β , A is the diagonal matrix of characteristic constants λ_i ($\lambda_0 = 0$) and v are constants. Components b_i are given by

$$b_1 = a_1 + u_1 a_2 \quad (3)$$

$$b_2 = a_1 + u_2 a_2, \quad (4)$$

where u are constants, and $b_0 = 0$. Eqs (2)–(4) contain six constants v_1 , v_2 , λ_1 , λ_2 , u_1 and u_2 which are composed from nine constants k from the scheme in Fig. 4c.

Eqs (2)–(4) were applied to the data in two steps. The reaction paths in Fig. 3 which do not contain space time W/F were fitted firstly and then the curves $a = f(W/F)$ in Figs 1 and 2 were calculated.

Reaction paths. Eq. (1) was transformed into

$$\frac{d\beta}{d\tau} = A\beta, \quad (5)$$

where τ is a new time scale given by $d\tau = d(W/F)/(1 + v_1 a_1 + v_2 a_2)$, ($a_1 = f(W/F)$ and $a_2 = f'(W/F)$). Time was eliminated by dividing the second equation from the set forming the matrix form (5) by the third one. This gives

$$\frac{db_1}{db_2} = \frac{\lambda_1 b_1}{\lambda_2 b_2} \quad (6)$$

and after integration

$$\frac{b_1}{b_1^0} = \left(\frac{b_2}{b_2^0} \right)^{\lambda_1/\lambda_2}, \quad (7)$$

where b_1^0 and b_2^0 are values of b_i 's for the feed. The function $F(a_1, a_2) = 0$ is then defined by Eqs (3), (4) and (7) and contains three constants, u_1 , u_2 and λ_1/λ_2 ; u_1 and u_2

must have opposite signs and λ_1/λ_2 must be positive. These constants were obtained for each catalyst by a nonlinear fitting procedure processing simultaneously the data from BT and DHBT runs. Their values are given in Table II and the reaction paths calculated using them are compared with the data in Fig. 3 (a_3 is given by $a_3 = 1 - a_1 - a_2$).

Time dependence of composition. The integration of Eq. (2) (using Eq. (7)) gives

$$\lambda_1(W/F) = \ln \left| \frac{b_1}{b_1^0} \right| + v_1(b_1 - b_1^0) + v_2 b_2^0 \frac{\lambda_1}{\lambda_2} \left(\left(\frac{b_1}{b_1^0} \right)^{\lambda_2/\lambda_1} - 1 \right). \quad (8)$$

This expression together with Eqs (7), (3) and (4) defines the functions $G(a_1, (W/F)) = 0$ and $H(a_2, (W/F)) = 0$; a_3 is given by $a_3 = 1 - a_1 - a_2$. The constants λ_1 , v_1 and v_2 were again obtained by a nonlinear fitting procedure using the values of constants u_1 , u_2 and λ_1/λ_2 obtained from fitting the reaction paths. The constant λ_1 must be negative and the signs of the constants v are not restricted. The calculated constants are given in Table II and the curves $a_i = f(t)$ obtained using them are compared with data in Figs 1 and 2.

Conclusions from kinetic analysis. The calculated curves in Figs 1–3 fit the data quite well. The observed kinetics thus agrees well with the hydrogenation-elimination mechanism of HDS which is characterized by the linear (not triangular) surface sequence as shown in Fig. 4. The necessary condition of the validity of this mechanism is thus fulfilled. However, this agreement is not a sufficient condition and cannot be taken as an evidence for the hydrogenation-elimination mechanism. The scheme

TABLE II

Kinetic parameters of hydrodesulphurization of benzo[b]thiophene and dihydrobenzo[b]thiophene at temperature 543 K and pressure of hydrogen 88 kPa

Constant	Catalyst		
	Mo	CoMo(I)	CoMo(II)
u_1 [—]	—4.105	—10.521	—9.576
u_2 [—]	0.749	0.376	0.440
λ_1/λ_2 [—]	7.465	3.029	2.899
λ_1 [mol (kg(cat)) ⁻¹ h ⁻¹]	—1.445	—15.241	—25.424
v_1 [—]	—0.139	—0.216	—0.610
v_2 [—]	—0.540	0.808	5.814
$a^*(\text{DHBT})/a^*(\text{BT})^a$	0.325	0.253	0.237

^a Equilibrium ratio given by $-1/u_1 u_2$ (see text).

0.37 (the change of hydrogen partial pressure during the reaction was neglected). This is practically the same value as obtained above from geometrical considerations. The constants u for CoMo(I) and CoMo(II) provide $K_p = 0.29$ and 0.27 , respectively, which is also reasonably close to this value.

The effect of Co in the reaction network. The reaction network of HDS of BT can be divided into two segments as shown in Fig. 5. The segment I covers all steps of the hydrogenation-dehydrogenation reaction between BT and DHBT. The segment II leading to ($H_2S + EB$) branches of the segment I in the point of the intermediate IN which cannot be unambiguously determined from our data. This intermediate can be referred to as "an intermediate with partially hydrogenated thiophenic ring". The existence of such intermediate is assumed also by other authors in the HDS of thiophene^{17,18}, benzothiophene^{5,6} and dibenzothiophene¹⁹.

On the nonpromoted catalyst, the reaction steps in segment I are faster than those in segment II. The partial equilibrium BT-DHBT- H_2 is approached soon and the rate of H_2S formation is limited by an unspecified step or steps in segment II.

On the promoted catalysts, the action of Co is localized in the segment II where it accelerates the slow step or steps. The rate of disappearance of IN in the direction to H_2S becomes competitive to the rates in segment I (rate $IN \rightarrow DHBT$ when BT is starting compound and rate $IN \rightarrow BT$ when DHBT is fed) and partial equilibrium is not attained. The rates of steps in segment I are influenced by the promoter only indirectly. The increase with promotion of the rate of disappearance of starting compound (BT or DHBT) is lower than that of H_2S formation (Figs 1 and 2) and is a consequence of lower concentration of IN caused by the faster reaction $IN \rightarrow H_2S$.

The addition of Co to Mo is assumed either to enlarge and stabilize the active surface or to change also its quality (for review see *e.g.*²⁰). Our results provide a strong evidence for the latter effect. If the nonpromoted and promoted catalysts would differ only in quantity and not also in quality of the active surface the reaction paths for them in Fig. 3 have had to be identical.

Conclusions. *i* The addition of Co to Mo catalyst suppresses the formation of DHBT in HDS of BT and also the formation of BT in HDS of DHBT. *ii* The partial equilibrium constant of hydrogenation of BT to DHBT at 543 K was determined to be $K_p = 0.35$. *iii* The kinetic data fit the hydrogenation-elimination mechanism of HDS and the reaction of BT and of DHBT was described simultaneously by a single set of kinetic constants. *iv* Cobalt directly influences only a part of the reaction network, namely the section between partially hydrogenated BT and H_2S .

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REFERENCES

1. López R., Peter R., Zdražil M.: *J. Catal.* 73, 406 (1982).
2. Daly F. P.: *J. Catal.* 51, 221 (1978).
3. Givens E. N., Venuto P. B.: *Amer. Chem. Soc. Div. Petrol., Chem. Prepr.* 15 (4), 183 (1970).
4. de Beer V. H. J., Dahlmans J. G. J., Smeets J. G. M.: *J. Catal.* 42, 467 (1976).
5. Geneste P., Amblard P., Bonnet M., Graffin P.: *J. Catal.* 61, 115 (1980).
6. Pokorný P., Zdražil M.: *This Journal* 46, 2185 (1981).
7. Devanneaux J., Maurin J.: *J. Catal.* 69, 202 (1981).
8. Furimsky E., Amberg C. H.: *Can. J. Chem.* 54, 1507 (1976).
9. Kilanowski D. R., Teeuwen H., de Beer V. H. J., Gates B. C., Schuit G. C. A., Kwart H.: *J. Catal.* 55, 129 (1978).
10. Zdražil M.: *Appl. Catal.* 4, 107 (1982).
11. Peter R., Zdražil M.: *This Journal* 51, 327 (1986).
12. Zdražil M.: *J. Catal.* 58, 436 (1979).
13. Wei J., Prater C. D.: *Advances in Catalysis and Related Subjects*, Vol. 13, p. 203. Academic Press, New York 1962.
14. Smith R. L., Prater C. D.: *Chem. Eng. Prog. Symp., Ser.* 63, 105 (1967).
15. Beránek L.: *Advances in Catalysis and Related Subjects*, Vol. 24, p. 1. Academic Press, New York 1975.
16. de Boer D. H., van de Borg R. J. A. M.: *Actes du Deuxième Congrès International de Catalyse*, Paris 1960, Vol. 1, p. 919. Technip, Paris 1961.
17. Maternová J., Zdražil M.: *This Journal* 45, 2532 (1980).
18. Kwart H., Schuit G. C. A., Gates B. C.: *J. Catal.* 61, 128 (1980).
19. Singhal G. H., Espino R. L., Sobel J. E.: *J. Catal.* 67, 446 (1981).
20. Massoth F. E.: *Advances in Catalysis and Related Subjects*, Vol. 27, p. 265. Academic Press, New York 1978.

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