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Abstract

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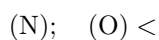
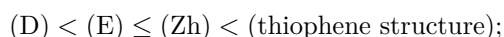
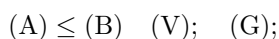
KINETICS OF HYDRODESULFURIZATION REACTIONS

(Presented by Academician A. V. Topchiev, 8 XII 1959)

The information available in the literature on the kinetics of hydrodesulfurization reactions of organosulfur compounds, which are of considerable technological importance, is limited to data on thiophene, dibenzothiophene, and octahydrodibenzothiophene (¹⁻⁴).

In the present work we report the results of a systematic study of the kinetics of hydrogenolysis, in the presence of an alumocobaltomolybdenum catalyst, of a series of sulfides and thiophenes. The method adopted in our laboratory for carrying out experiments, analyses, and kinetic treatment of the experimental results has already been reported (⁴). In Fig. 1, as an example, curves are given for the dependence of the depth of conversion on the conditional contact time for 2,4,6,8-tetramethyl-5-thianonane. The character of these curves is typical for all the organosulfur compounds studied by us.

The hydrogenolysis reactions were well described by equations proposed in general form by Frost and Kazeev. The parameters of these equations found by us are given in Table 1. From consideration of these parameters it follows that the organosulfur compounds, according to the rate of hydrogenolysis, can be arranged in the following series in order of increasing rates of their hydrogenolysis:



< (P)

where the structures shown in the source correspond to:

(A) dibenzothiophene $\leq$ (B) octahydrodibenzothiophene;

(V) C₄H₉-thiophene-C₄H₉; (G) thiophene-C₈H₁₇;

(D) C₂H₅-thiophene-C₂H₅ < (E) phenoxathiin-type sulfur heterocycle $\leq$ (Zh) diphenyl sulfide < benzothiophene

(K) thiophene-C₃H₇; (L) thiophene-C₃H₆-C₆H₅; (M) diphenyl;

(N) (CH₃ - CH(CH₃) - CH₂ - CH(CH₃)-)₂S; (O) C₆H₅ - S - CH(CH₃) - CH₂ - CH(CH₃) - CH₃;

(P) C₆H₅ - CH₂ - S - CH₂ - C₆H₅.

Table 1

Parameters of the Frost and Kazev equations*

Compound	Temp., °C	P_{H_2} , ata	β	α	a	b	D
Dibenzothiophene	125	33.3	1.0	0.62	0.31	0.69	76
Dibenzothiophene	175	9.4	1.0	0.32	0.10	0.66	70
Dibenzothiophene	175	19.9	1.0	1.14	0.23	0.65	79
Dibenzothiophene	175	33.5	1.0	1.34	0.44	0.65	91
Dibenzothiophene	175	36.5	1.0	1.05	0.50	0.64	94
Dibenzothiophene	125	33.3	1.0	2.29	0.61	0.62	95
Dibenzothiophene, $E_{app.} =$ 10.8 kcal/mol; $E =$ 4.6 kcal/mol							
Octahydrodibenzothiophene	125	33.3	1.0	0.94	0.32	0.79	83
Octahydrodibenzothiophene	175	36.5	1.1	0.51	0.14	0.71	68

Compound	Temp., °C	P_{H_2} , ata	β	α	a	b	D
Octahydrodibenzothio- phene	375	33.3	1.0	1.46	0.28	0.71	78
Octahydrodibenzothio- phene	375	33.3	1.0	1.77	0.52	0.72	90
Octahydrodibenzothio- phene	375	33.3	1.0	0.86	0.55	0.71	93
Octahydrodibenzothio- phene	425	33.3	1.0	2.73	0.71	0.58	95
Octahydrodibenzothio- phene, $E_{app.} =$ 8.9 kcal/mol; $E =$ 4.1 kcal/mol							
2,5-Dibutylthiophene	325	33.3	1.0	1.0	0.40	0.65	85
2,5-Dibutylthiophene	375	33.3	1.0	1.7	0.53	0.65	90
2,5-Dibutylthiophene	425	33.3	1.0	2.5	0.71	0.66	95
2,5-Dibutylthiophene, $E_{app.} =$ 7.6 kcal/mol; $E =$ 4.8 kcal/mol							
2-Octylthiophene	325	33.3	1.0	0.96	0.30	0.70	89
2-Octylthiophene	375	33.3	1.0	1.7	0.46	0.69	92
2-Octylthiophene	425	33.3	1.0	3.0	0.70	0.71	95
2-Octylthiophene, $E_{app.} =$ 9.8 kcal/mol; $E =$ 6.9 kcal/mol							
2,5-Diethylthiophene	375	33.3	1.0	1.8	0.58	0.66	90

Compound	Temp., °C	P_{H_2} , ata	β	α	a	b	D
Diphenyl sul- fide	325	33.3	1.0	1.62	0.45	0.65	93
Diphenyl sul- fide	375	15.0	1.0	2.29	0.25	0.66	92
Diphenyl sul- fide	375	20.0	1.0	3.69	0.38	0.66	93
Diphenyl sul- fide	375	33.3	1.0	3.25	0.73	0.66	94
Diphenyl sul- fide	375	38.0	1.0	1.52	0.93	0.66	95
Diphenyl sul- fide	425	33.3	1.0	4.65	0.95	0.64	95
Diphenyl sul- fide, $E_{app.} =$ 8.6 kcal/mol; $E =$ 5.4 kcal/mol	325	33.3	1.0	1.22	0.38	0.73	91
Thianthrene	375	33.3	1.0	2.27	0.54	0.73	94
Thianthrene	425	33.3	1.0	3.16	0.69	0.73	96
Thianthrene, $E_{app.} =$ 8.3 kcal/mol; $E =$ 4.9 kcal/mol	325	33.3	1.0	2.84	0.58	0.71	96
α - Propylthiophane	375	33.3	1.0	5.23	0.96	0.60	97
α - Propylthiophane	426	33.3	1.0	8.25	1.35	0.49	98

Compound	Temp., °C	P_{H_2} , ata	β	α	a	b	D
α - Propylthiophane, $E_{app.} =$ 8.5 kcal/mol; $E =$ 4.0 kcal/mol 2,8- Dimethyl- 5- thianonane $(CH_3-CH-CH_2-CH_2-)_2S$, with CH_3 sub- stituent	325	33.3	1.0	2.2	0.47	0.79	92
2,8- Dimethyl- 5- thianonane $(CH_3-CH-CH_2-CH_2-)_2S$, with CH_3 sub- stituent	375	33.3	1.0	4.3	0.78	0.65	94
2,8- Dimethyl- 5- thianonane $(CH_3-CH-CH_2-CH_2-)_2S$, with CH_3 sub- stituent	425	33.3	1.0	8.0	1.24	0.60	98

Compound	Temp., °C	P_{H_2} , ata	β	α	a	b	D
2,8-Dimethyl-5-thianonane, $E_{app.} = 11.0$ kcal/mol; $E = 5.8$ kcal/mol	325	33.3	1.36	4.7	1.32	0.58	92
Dibenzyl sul- fide	375	33.3	1.50	9.4	2.2	0.42	93
Dibenzyl sul- fide	425	33.3	1.50	18.2	2.9	0.37	95
Dibenzyl sul- fide, $E_{app.} = 11.3$ kcal/mol; $E = 2.7$ kcal/mol	375	33.3	1.0	3.8	0.78	0.70	93
Thianaphthe- 2,4,6,8-Tetramethyl- 5-thianonane ($CH_3-CH-CH_2-CH-$) ₂ S, with CH ₃ sub- stituents	375	33.3	1.0	5.81	1.05	0.57	97
1,3-Dimethyl- 1-(phenylthio)butane	375	33.3	1.0	5.88	1.11	0.58	96

Fig. 1

Figure 1: Fig. 1

Compound	Temp., °C	P_{H_2} , ata	β	α	a	b	D
α -(1-Phenyl)-propylthiophane	375	33.3	1.0	5.14	1.01	0.52	96

* General form of the Frost equation:

$$v_0 \ln \frac{1}{1-y} = \alpha + \beta v_0 y,$$

where v_0 is the average feed rate of the initial compound to the reactor per gram of catalyst per hour; y is the extent of hydrogenolysis in fractions of unity; α and β are parameters.

General form of the Kazeev equation:

$$\ln \frac{D}{D-M} = a\tau^b,$$

where τ is the conditional contact time in seconds, M is the extent of hydrogenolysis in percent, D is the limiting value of M as $\tau \rightarrow \infty$; a and b are parameters.

The values of the parameter α , proportional to the rate constants of the hydrogenolysis reaction of these compounds at a temperature of 375°C, which is of practical interest, are related to one another as follows:

$$(A, B, V, G, D) : (E, Zh) : (Z, K) : (L, M, N, O) : P = 1 : 2 : 3 : 4 : 7.$$

This dependence theoretically substantiates the possibility of selective hydrodesulfurization of petroleum products on an alumina-cobalt-molybdenum catalyst, as well as the use of this catalyst for group analysis of organosulfur compounds. In addition, it gives a quantitative characterization of the possibility of preferential cleavage of the bond between the sulfur atom and carbon atoms, which makes it possible to predict the nature of the products formed as a result of hydrogenolysis.

Fig. 1. Kinetics of hydrogenolysis of 2,4,6,8-tetramethyl-5-thianonane at $T = 375^\circ$, $P_{\text{total}} = 40$ atm, $P_{H_2} = 33.3$ atm.
I—hydrogen sulfide sulfur, *II*—sulfide sulfur, *III*—mercaptan sulfur.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

The rate of hydrogenolysis of a mixture of organosulfur compounds was found to obey the additivity rule, which is confirmed by the curves in Fig. 2. This circumstance makes it possible to predict changes in the composition of organosulfur compounds during hydrotreating of petroleum products.

To study the influence of reaction products on the rate of hydrogenolysis, we carried out experiments on the hydrogenolysis of dibenzothiophene dissolved in cetane, with additions of biphenyl and hydrogen sulfide. It was shown that the limiting conversion and the rate of hydrogenolysis decrease sharply when biphenyl is added to the initial dibenzothiophene solution, but are practically independent of the addition of hydrogen sulfide (Fig. 3). Dibenzothiophene and its derivatives const—

Fig. 2. Kinetics of hydrogenolysis of a mixture of α -propylthiophane (0.51%), α -hexylthiophane (0.46%), 2,4,6,8-tetramethyl-5-thianonane (0.46%), and 1,3-dimethyl-1-(phenylthio)butane (0.46%) and dibenzothiophene (0.81%), dissolved in cetane, at $T = 375^\circ$, $P_{\text{total}} = 40$ atm, $P_{\text{H}_2} = 33.3$ atm.

I—calculated kinetic curves for hydrogenolysis of the sulfide mixture; *II*—same for hydrogenolysis of dibenzothiophene; *III*—same for hydrogenolysis of the mixture of sulfides and dibenzothiophene; *IV*—yield of mercaptan sulfur.

Fig. 3. Calculated dependences of the depth of hydrogenolysis: *I*—dibenzothiophene (a); same with addition of hydrogen sulfide (b), *II*—same with addition of biphenyl, *III-IV*—corresponding rates of hydrogenolysis for *I* and *II*.

constitute a considerable mass of the so-called “residual sulfur.” Therefore, the data obtained are of interest for petroleum-refining practice, since fuels subjected to hydrotreating contain aromatic hydrocarbons in variable amounts.

By specially designed experiments we established that, in the presence of an alumina-cobalt-molybdenum catalyst, at the temperatures and pressures used in industry, hydrogenolysis proceeds in the intradiffusion region; it was also shown that, upon comminution of the catalyst, the reaction shifts into the transition region (Table 2). These data to a certain extent provide a theoretical basis for the advisability of carrying out the hydrotreating process in a suspended bed. In addition, the data obtained may find practical application in the development of new formulations for the preparation of hydrotreating catalysts.

Table 2

Temp., °C	Diffusion-inhibition				Diffusion-inhibition			
	Parameter h (average catalyst particle size cm)	Parameter h (average catalyst particle size cm)	Parameter f (average catalyst particle size cm)	Parameter f (average catalyst particle size cm)	Reaction rate constant, mol/g·h (observed)	Reaction rate constant, mol/g·h (corrected)	Apparent activation energy, kcal/mol (observed)	Apparent activation energy, kcal/mol (corrected)
325	1.65	0.33	0.56	0.965	0.62	1.10		
375	2.35	0.47	0.42	0.93	1.34	3.19	10.8	16.6
425	3.60	0.72	0.28	0.86	2.29	8.18		

A detailed analysis of the catalysts showed that the principal products of hydrogenolysis of all the organosulfur compounds studied by us are hydrogen sulfide and the corresponding hydrocarbon. Monocyclic aromatic hydrocarbons, as well as biphenyl⁴, under the conditions studied by us are practically not hydrogenated.

These observations substantiate the possibility of using an alumina-cobalt-molybdenum catalyst for the analysis and identification of organosulfur compounds contained in petroleum products by the products of their hydrogenolysis, analogously to how this is done using Raney nickel.

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CITED LITERATURE

- ¹ C. G. B. Hammar, 3rd. World Petrol. Congr., **4**, 295 (1951).
- ² W. R. Wilson, W. E. Voreck, R. V. Malo, Ind. and Eng. Chem., **49**, 657 (1957).
- ³ R. D. Obolentsev, A. V. Mashkina, DAN, **119**, 1187 (1958).
- ⁴ R. D. Obolentsev, A. V. Mashkina, in: *Collected Volume. Chemistry of Organosulfur Compounds Contained in Petroleum and Petroleum Products*, **2**, Publishing House of the Academy of Sciences of the USSR, 1959, p. 228.

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