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Abstract

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KINETICS OF HYDRODESULFURIZATION REACTIONS

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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:

$$\text{(A)} \leq \text{(B)} \quad \text{(V)}; \quad \text{(G)};$$

$$\text{(D)} < \text{(E)} \leq \text{(Zh)} < \text{(thiophene structure)};$$

$$(CH_3 - CH(CH_3) - CH_2 - CH_2-)_2S < \text{(K)}; \quad \text{(L)}; \quad \text{(M)};$$

$$\text{(N)}; \quad \text{(O)} <$$

$< (P)$

where the structures shown in the source correspond to:

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

(V) C_4H_9-thiophene-C_4H_9; (G) thiophene-C_8H_{17};

(D) C_2H_5-thiophene-C_2H_5 $<$ (E) phenoxathiin-type sulfur heterocycle $\leq$ (Zh) diphenyl sulfide $<$ benzothiophe

(K) thiophene-C_3H_7; (L) thiophene-C_3H_6-C_6H_5; (M) diphenyl;

(N) $(CH_3 - CH(CH_3) - CH_2 - CH(CH_3)-)_2S$; (O) $C_6H_5 - S - CH(CH_3) - CH_2 - CH(CH_3) - CH_3$;

(P) $C_6H_5 - CH_2 - S - CH_2 - C_6H_5$.

Table 1

Parameters of the Frosta and Kazeev equations*

Compound	Temp., °C	P_{H2}, ata	β	α	a	b	D
Dibenzothiophene	325	33.3	1.0	0.62	0.31	0.69	76
Dibenzothiophene	375	9.4	1.0	0.32	0.10	0.66	70
Dibenzothiophene	375	19.9	1.0	1.14	0.23	0.65	79
Dibenzothiophene	375	33.5	1.0	1.34	0.44	0.65	91
Dibenzothiophene	375	36.5	1.0	1.05	0.50	0.64	94
Dibenzothiophene	425	33.3	1.0	2.29	0.61	0.62	95
Dibenzothiophene, $E_{app.} =$ 10.8 kcal/mol; $E =$ 4.6 kcal/mol							
Octahydrodibenzothiophene	325	33.3	1.0	0.94	0.32	0.79	83
Octahydrodibenzothiophene	375	9.5	1.1	0.51	0.14	0.71	68

Compound	Temp., °C	P_{H2}, ata	β	α	a	b	D
Octahydrodibenzothiophene	375	20.0	1.0	1.46	0.28	0.71	78
Octahydrodibenzothiophene	375	33.5	1.0	1.77	0.52	0.72	90
Octahydrodibenzothiophene	375	37.0	1.0	0.86	0.55	0.71	93
Octahydrodibenzothiophene	425	33.3	1.0	2.73	0.71	0.58	95
Octahydrodibenzothiophene, $E_{\text{app.}} =$ 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, $E_{\text{app.}} =$ 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, $E_{\text{app.}} =$ 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_{H2}, ata	β	α	a	b	D
Diphenyl sulfide	325	33.3	1.0	1.62	0.45	0.65	93
Diphenyl sulfide	375	15.0	1.0	2.29	0.25	0.66	92
Diphenyl sulfide	375	20.0	1.0	3.69	0.38	0.66	93
Diphenyl sulfide	375	33.3	1.0	3.25	0.73	0.66	94
Diphenyl sulfide	375	38.0	1.0	1.52	0.93	0.66	95
Diphenyl sulfide	425	33.3	1.0	4.65	0.95	0.64	95
Diphenyl sulfide, $E_{app.} = 8.6$ kcal/mol; $E = 5.4$ kcal/mol							
Thianthrene	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							
α-Propylthiophane	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_{H2}, 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 substituent	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 substituent	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 substituent	425	33.3	1.0	8.0	1.24	0.60	98

Compound	Temp., °C	P_{H2}, ata	β	α	a	b	D
2,8-Dimethyl-5-thianonane, $E_{\text{app.}} = 11.0$ kcal/mol; $E = 5.8$ kcal/mol							
Dibenzyl sulfide	325	33.3	1.36	4.7	1.32	0.58	92
Dibenzyl sulfide	375	33.3	1.50	9.4	2.2	0.42	93
Dibenzyl sulfide	425	33.3	1.50	18.2	2.9	0.37	95
Dibenzyl sulfide, $E_{\text{app.}} = 11.3$ kcal/mol; $E = 2.7$ kcal/mol							
Thianaphthene	375	33.3	1.0	3.8	0.78	0.70	93
2,4,6,8-Tetramethyl-5-thianonane $(CH_3{-}CH{-}CH_2{-}CH{-})_2S$, with CH_3 substituents	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_{H2}, 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 $\tau \to \infty$; 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:

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

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, $P_{H2} = 33.3$ 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, $P_{\text{H2}} = 33.3$ 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	Parameter h (average catalyst particle size 0.3 cm)	Parameter h (average catalyst particle size 0.06 cm)	Diffusion-inhibition factor f (average catalyst particle size 0.3 cm)	Diffusion-inhibition factor f (average catalyst particle size 0.06 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	10.8	16.6
375	2.35	0.47	0.42	0.93	1.34	3.19		
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 biphenyl[4], 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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