REACTIVITY OF C_6-C_8 ALKANES IN FORMING ALKYLTHIOPHENES AND AROMATIC HYDROCARBONS IN THE PRESENCE OF H_2S ON A Cr-CONTAINING CATALYST

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On interaction of n-hexane with H_2S on a Cr-containing catalyst, together with a heterocyclization reaction dehydrocyclization also occurs with the formation of alkylthiophenes and benzene, respectively [1]. In the absence of H_2S on such catalysts, more than two dozen hydrocarbons of different structure are formed from n-hexane. Even more complex catalyzates are obtained by catalytic conversion of C_7 and C_8 alkanes [2]. In the presence of H_2S the selectivity of the catalyst varies. The catalytic interaction or C_7-C_8 alkanes with H_2S has not previously been studied.

It was of interest to compare the heterocyclizing and dehydrocyclizing properties of a Cr-containing catalyst in the presence of H_2S in relation to the chain length of n-alkane containing 6-8 C atoms.

EXPERIMENTAL

Initial hydrocarbons were chromatographically pure n-hexane, n-heptane, and n-octane, H_2S contained 98-99% of principal substance. The experiments were conducted in a flow system at 450°C, $\nu_{\text{mass}} = 0.8\ h^{-1}$, and molar ratio H_2S:n-alkane = 2:1 over a catalyst of composition: Cr_2O_3 (5%), Polirit (5%), K_2O (1%), γ-Al_2O_3 (89%) [1]. The liquid reaction products were analyzed on an LKhM-80 chromatograph [katharometer, temperature programming in the region 60-160°C, heating rate 6 deg/min, stainless steel column 3 mm × 2.5 m packed with Chromosorb P-AW (0.16-0.2 mm) with 1% KOH and 10% polyethylene glycol 3000, and He carrier gas]. Calculation of the mixture composition was carried out using the data from the integrator. In addition, analysis was carried out on an LKhM-8MD chromatograph with a flame ionization detector, N_2 carrier gas, at 80°C on a capillary column on Pyrex glass 40 m × 0.25 mm, and Carbowax 40M/KF prepared according to method [3]. For proof of the structure of the alkylthiophenes, PMR spectra were recorded on a Bruker M-250 spectrometer. For recording the spectra, the catalyzates were diluted with acetone-d_6. TMS was used as the internal standard.

DISCUSSION OF RESULTS

Under the conditions chosen a high yield of liquid catalyzate is achieved (Table 1). Reactions of heterocyclization, dehydrocyclization, and dehydrogenation with slight cracking mainly occur. According to the GLC data, in the catalyzates obtained are small quantities of α- and β-alkenes, the total amount of whidh decreases from 8 to 4.5% with increase in molecular weight of the alkane, and alkadienes, the total amount of which increases from ~1 to 2.6%. The main products of the interaction of H_2S with n-hexane are 2-ethylthiophene and 2,5-dimethylthiophene; while interaction with n-heptane gives mainly 2-propylthiophene and 2-methyl-5-ethylthiophene, and with n-octane mainly 2-butylthiophene, 2,5-diethylthiophene, and 2-methyl-5-propylthiophene. As a result of dehydrocyclization, benzene and toluene respectively are formed from n-hexane and n-heptane, while ethylbenzene and o-xylene are formed from n-octane.

Alkylthiophenes may be formed from H_2S and n-hexane or n-heptane in a heterocyclization reaction by ring closure on sulfur of the C-1 and C-4 or C-2 and C-5 atoms with formation of a thiophene ring, and in the case of n-octane additionally by ring closure with the C-3 and C-6 atoms:

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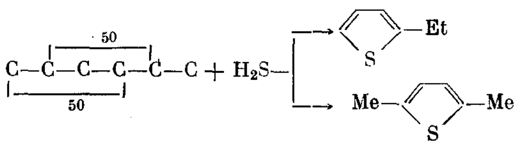
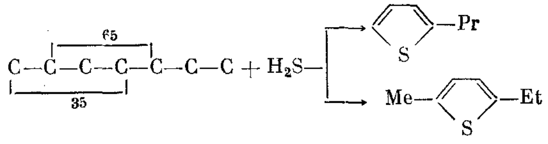
TABLE 1. Conversions of Normal C_6-C_8 Alkanes by Interaction with H_2S [450°C, $\nu_{mass} = 0.8\ h^{-1}$, H_2S:hydrocarbon = 2 (molar)]

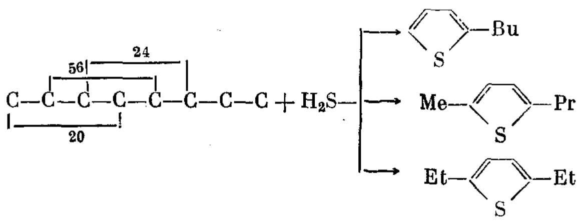
Catalyzate composition, mass %	Initial hydrocarbon		
	n-hexane	n-heptane	n-octane
Liquid catalyzate	91,30	98,80	100,00
Initial hydrocarbon	81,37	79,70	74,77
Isoalkane	0,26	0,15	0,90
Σ α, β - Alkenes	7,69	7,18	4,50
Σ Alkadienes	0,76	0,80	2,60
Σ Alkatrienes	0,59	0,72	0,39
Thiophene	0,32	0,14	–
2-Methylthiophene	0,73	0,78	0,60
2-Ethylthiophene	3,50	0,30	0,17
2,5-Dimethylthiophene	3,50	0,30	0,17
2-Propylthiophene	–	1,86	0,30
2-Methyl-5-ethylthiophene	–	3,46	0,44
2-Butylthiophene	–	–	1,11
2,5-Diethylthiophene	–	–	1,30
2-Methyl-5-Propylthiophene	–	–	3,02
Benzene	1,28	0,18	0,56
Toluene	–	4,33	0,26
Ethylbenzene	–	–	2,86
o-Xylene	–	–	5,22



(1)



(2)



(3)

In reactions (1)-(3) the total ratios of alkylthiophenes to benzene, toluene, and the sum of o-xylene and ethylbenzene are equal to 5.5, 1.25, and 0.7 to 1, respectively.

Among the other sulfur compounds found in small quantities in the catalyzates are thiophene (up to 0.3%) and, for all three alkanes studied, 2-methylthiophene (up to 0.8%). The formation of thiophene and 2-methylthiophene, as shown in [4, 5], occurs mainly by interaction of H_2S with the products formed by cracking and dehydrogenation – alkanes, alkenes, and alkadienes of lower molecular weight – instead of initial alkane.

Qualitative and quantitative analyses for content of 2-alkyl- and 2,5-dialkylthiophenes in the catalyzates obtained were carried out using PMR. For identification, the available data of PMR spectra for 2-methylthiophene [6, 7] and 2,5-dimethylthiophene[7] were taken into account. Spectral properties for the other 2-alkyl- and 2,5-dialkylthiophenes were not known. In the catalyzate of n-hexane with H_2S were identified 2-ethylthiophene, 2,5-dimethylthiophene, and 2-methylthiophene. For 2-ethylthiophene there is correspondence with a typical spectrum of an ABX spin system ($\delta H^3 = 6.87$, $\delta H^4 = 6.95$, $\delta H^5 = 7.08$ ppm; $J_{3,4} = 3.4$, $J_{3,5} = 0.7$ Hz and $J_{4,5} = 5.7$, $J_{3,CH_2} = 1.1$ Hz; the doublet of a quarter $\delta = 2.93$ ppm with $J_{CH_2,CH_3} = 7.4$, $J_{H^3,CH_2} = 1.1$ Hz*.) Assignment of the signals was confirmed using double

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*The signals from the CH_3 protons in ethyl, n-propyl, and n-butyl groups, and also from the CH_2 protons in propyl and n-butyl groups not connected to a double bond, overlap with the signals from initial alkanes.

resonance by irradiation at the frequencies of the H^3 and CH_2 group protons. For 2,5-dimethylthiophene there is correspondence with a broad singlet with $\delta = 6.54$ ppm from the β-protons, and a doublet from the CH_3 protons with $\delta = 2.46$ ppm, $J_{H,CH_3} = 0.8$ Hz. On irradiation at the frequency of the β-protons, the doublet from the CH_3 protons collapses. For 2-methylthiophene: $\delta H^3 = 6.81$, $\delta H^5 = 7.09$, $\delta Me = 2.55$ ppm; J_{Me,H^3}, 1.0 Hz and $J_{Me,H^5} \sim 0.3$ Hz. The results obtained were confirmed by addition to the solution of previously determined samples. Integration of the spectrum gave the following product composition, incorporating the three identified thiophene derivatives: 2,5-dimethylthiophene (43%), 2-ethylthiophene (43%), and 2-methylthiophene (14%).

The PMR spectrum from the catalyzate of n-heptane with H_2S was analyzed in a similar manner. Besides 2-methylthiophene, also identified were 2-propylthiophene [$\delta H^3 = 6.68$, $\delta H^4 = 6.79$, $\delta H^5 = 6.99$ ppm, $J_{3,4} = J_{3,5} = 1.3$, $J_{4,5} = 5.2$ Hz; $\delta CH_2 = 2.74$ ppm (triplet), $J_{CH_2,3} = 1.0$ Hz] and 2-methyl-5-ethylthiophene [$\delta H^3 = 6.50$, $\delta H^4 = 6.40$ ppm, $J_{3,4} = 3.3$ Hz; $\delta 5\text{-}CH_3 = 2.34$ ppm, $J_{5\text{-}CH_3,4} = 0.9$ Hz; $\delta 2\text{-}CH_2 = 2.68$ ppm, $J_{CH_2,3} = 0.9$ Hz and $J_{5\text{-}CH_3,2\text{-}CH_2} \sim 0.3$ Hz.

Integration of the spectrum not including 2-methylthiophene gave the following correlation: 2-propylthiophene (35%); 2-methyl-5-ethylthiopehene (65%). This was also confirmed by chromatographic analysis.

In the PMR spectrum of the catalyzate of n-octane with H_2S the following were found: 2,5-diethylthiophene with $\delta\beta\text{-H} = 6.44$ ppm, a broad singlet which became sharper on irradiation at the frequency of the CH_2 group protons ($\delta CH_2 = 2.70$ ppm, $J = 7.4$ Hz); 2-methyl-5-propylthiophene ($\delta H^3 = 6.40$, $\delta H^4 = 6.42$ ppm, $J_{3,4} = 3.5$, $J_{2\text{-}CH_2} = 1.0$, $J_{5\text{-}CH_3,4} = 1.0$ Hz; $\delta 5\text{-Me} = 2.32$, $\delta 2\text{-}CH_2 = 2.63$ ppm); 2-butylthiophene (the spectrum of the ring protons was different from the spectra of the previously identified 2-ethyl- and 2-propylthiophenes) with $\delta H^3 = 6.65$, $\delta H^4 = 6.77$, $\delta H^5 = 6.93$ ppm, $J_{3,4} = 3.4$, $J_{4,5} = 5.2$, $J_{2,5} = 1.2$ Hz, $\delta CH_2 = 2.78$ ppm, $J_{CH_2,3} = 1.0$ Hz; and also 2-methylthiophene. The composition of the interpreted alkylthiophenes proved to be the following: 2-methylthiophene (8.5%), 2,5-diethylthiophene (18.5%), 2-butylthiophene (30%), and 2-methyl-5-propylthiophene (43%). The presence of 5% 2-ethyl- and 2-propylthiophenes in the mixture was also possible.

The total amount of data from the GLC and PMR analysis of the catalyzates made it possible to calculate the participation of the different carbon atoms of n-alkanes in the formation of alkylthiophenes. By comparing the ratios of alkylthiophenes formed, it is evident that for an increase in carbon chain of the alkane the fraction of heterocyclization products with formation of a C—S bond on the C-2 and C-5 atoms increases. Thus, the ratio of yields of 2-ethylthiophene and 2,5-dimethylthiophene equals 1:1, that of 2-methyl-5-ethylthiophene and 2-propylthiophene is 1.8:1, and that of 2-methyl-5-propylthiophene and 2-butylthiophene is 2.8:1. In the case of n-octane the heterocyclization products are also formed by ring closure of the C-3 and C-6 atoms on sulfur. For an increase in length of carbon chain of the alkane the yield of heterocyclization products decreases; and for n-hexane, n-heptane, and n-octane, the reactivity towards formation of a C—S bond on the C-1 and C-4 atoms varies according to the relationship 1:0.5:0.35; at the same time, the share of heterocyclization proceeding via the C-2 and C-5 atoms increases according to 1:1.8:2.8. For an increase in chain length of alkane, the yield of heterocyclization products falls slightly, and the yield of dehydrocyclization products rises substantially.

In [8] it is shown that 41.8% o-xylene and 25.2% ethylbenzene is formed from n-octane on an Al—Cr—K catalyst at 535°C. As is evident from the data obtained, in the presence of H_2S under milder conditions (450°C) the yields of o-xylene and ethylbenzene were considerably lower, being equal to 5.2 and 2.8%, respectively. However, the ratio of yields of these products remained the same (∿ 1.8%). The formation of o-xylene and ethylbenzene from n-octane on a Cr-containing catalyst proceeds by a consecutive route through the formation of octanes, octadienes, 2,4,6-octatriene, and 1,3,5-octatriene accordingly [9]. The presence of alkenes, alkadienes, and alkatrienes in the catalyzate (see Table 1) makes it possible to assume that the formation of o-xylene and ethylbenzene in the presence of H_2S occurs by the same route.

A consecutive route for formation of alkylthiophenes via alkenes and alkadienes was also demonstrated in the case of the reaction of H_2S with n-butane and n-pentane leading to thiophene [4] and 2-methylthiophene [5], respectively.

Thus, on a Cr-containing catalyst the formation of aromatic hydrocarbons and alkylthiophenes proceeds via a common dehydrogenation stage. The longer the n-alkane chain, the more easily trienes form an aromatic ring, but not a thiophene ring by closure of C-1 and C-4 or C-2 and C-5 atoms on sulfur. As confirmation of this there is the presence of a small quantity of trienes (∿0.4%) in the catalyzate of n-octane with H_2S and the eightfold increase in ratio of amount of aromatic hydrocarbons formed in comparison with the composition of the catalyzate from n-hexane.

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CONCLUSIONS

1. In the presence of a chromium-containing catalyst, 2-ethylthiophene and 2,5-dimethylthiophene are formed from hydrogen sulfide and n-hexane; 2-propylthiophene and 2-methyl-5-ethylthiophene are formed from n-heptane; and 2-butylthiophene, 2-methyl-5-propylthiophene, and 2,5-diethylthiophene are formed from n-octane. With an increase in length of carbon chain of the alkane, heterocyclization occurs to a greater degree with the formation of a sulfur—carbon bond on the C-2 and C-5 atoms.

2. Together with heterocyclization, dehydrocyclization also occurs. On changing from n-hexane to n-heptane and to n-octane the yield of dehydrocyclization products increases.

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