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## Abstract

## Full Text

## Chemistry

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# CATALYTIC TRANSFORMATIONS OF 2-METHYLTHIOPHENE UNDER THE INFLUENCE OF WATER VAPOR

It was natural to suppose that the reaction of catalytic demethylation with the participation of water vapor, common to a whole series of classes of chemical compounds ([1-5]), also extends to thiophene derivatives. Of course, in studying this question difficulties were bound to arise in connection with the specific behavior of thiophene derivatives on metallic catalysts in the presence of hydrogen ([6-11]), which is one of the products of the demethylation reaction.

The work was carried out by us on $Ni/Al_2O_3$ and $Co/Al_2O_3$ catalysts. The temperature limits and the values of the molar ratio of water to the substance under study ($\omega$) were chosen in accordance with these limits for the demethylation reaction in other classes of chemical compounds (temperature from 200 to 425°; $\omega$ from 27 to 177).

When thiophene was passed over the catalyst under these conditions at temperatures up to 425°, it was collected entirely unchanged. No gas evolution was observed; the catalyst remained capable of dehydrogenating cyclohexane. Under these conditions 2-methylthiophene splits off the methyl group and, to a lesser extent, undergoes ring cleavage, which corresponds to the conclusion that, in comparison with benzene and pyridine, toluene and 2-picoline have higher activity in reactions involving cleavage of the benzene and pyridine rings ([2, 5]). The presence of side methyl groups makes the ring system more reactive.

(Figure: Figure 1: two plots showing gas-evolution rate and thiophene content versus catalyst operating time.)

**Fig. 1.** Rate of gas evolution and thiophene content in the reaction products as functions of the catalyst operating time. **a** —experiment No. 59, **b** —experiment No. 60. Black points —thiophene; open points —gas.

The rate and composition of the reaction products of 2-methylthiophene with water, when their vapors are passed over a fresh catalyst, change with time (see Fig. 1 and Table 1). The rate of gas evolution at first falls and then reaches a constant value, the magnitude of which, other conditions being equal, is determined by the temperature and by the molar ratio water : 2-methylthiophene. In the first minutes of the experiment the liquid condensate contains thiophene, but the amount of the latter decreases to zero when the rate of gas evolution assumes a constant value. In the initial period of the reaction the gas contains carbon dioxide in an amount predominating over the amount of saturated hy-

drocarbons. When the rate of gas evolution becomes constant, the amount of carbon dioxide falls practically to zero, while the amount of saturated hydrocarbons becomes significant; above 400° unsaturated hydrocarbons and hydrogen sulfide appear.

The amount of thiophene formed in one and the same time from the start of the reaction on the nickel catalyst increases with temperature and decreases with an increase in the amount of water. The cobalt catalyst acts, in general, analogously to the nickel catalyst.

Table 1

| Experiment No. | Catalyst | $\omega$ | Temperature (°C) | Average sample during the time from the start of the experiment (min.) | $CO_2$ | Saturated hydrocarbons | Unsaturated hydrocarbons | $H_2S$ | $H_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 62 | $Ni/Al_2O_3$ (1 : 2) | 48 | 359 | 10 | 3.1 | 1.3 | 0.0 | 0.0 | 95.6 |
| 60 | $Ni/Al_2O_3$ (1 : 2) | 48 | 355 | 60 | 0.7 | 3.1 | 0.0 | 0.0 | 96.2 |

An increase in the reaction temperature increases the rate of gas evolution, while an increase in the amount of water decreases it. At the same time, an increase in the amount of water ($\omega = 177$ as against 48) entails an increase in the relative content of carbon dioxide in the gaseous products—evidently at the expense of the secondary reaction of saturated hydrocarbons with water.

Table 2

| Experiment No. | Catalyst | Regeneration time | $\omega$ | Temperature (°C) | Thiophene content, % | CO + $CO_2$ | Saturated hydrocarbons | Unsaturated hydrocarbons | $H_2S$ | $H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 47 | $Ni/Al_2O_3$ (1 : 2) | 3.0 | 177 | 200 | 0 | 25 | 50 | 0.0 | 0.0 | 25 |
| 48 | Same | 1.0 | 177 | 328 | 2 | 21 | 30.5 | 0.0 | 0.0 | 48.5 |
| 50 | Same | 1.0 | 48 | 255 | 5.6 | 3.6 | 6.1 | 0.0 | 0.0 | 90.3 |
| 52 | Same | 1.0 | 48 | 365 | 30 | 4.3 | 6.7 | 0.0 | 0.0 | 89.0 |
| 53 | Same | 1.0 | 48 | 411 | 39 | 11.8 | 0.85 | 2.8 | 4.7 | 79.85 |
| 56 | Same | 1.0 | 48 | 393.5 | 38 | 9.6 | 3.0 | 0.0 | 0.0 | 87.4 |
| 63 | Same | 1.0 | 48 | 361 | 30 | — | — | — | — | — |
| 54 | Same | 3.0 | 48 | 285 | 35 | 3.2 | 4.5 | 0.0 | 0.0 | 92.3 |
| 55 | Same | 3.0 | 48 | 334 | 53 | 3.2 | 5.5 | 0.8 | 0.0 | 90.5 |
| 58 | $Ni/Al_2O_3$ (1 : 1) | 3.0 | 48 | 250 | 56 | — | — | — | — | — |
| 65 | $Co/Al_2O_3$ (1 : 1) | 3.0 | 27.3 | 364 | — | 5.8 | 0.9 | 1.7 | 0.0 | 91.6 |

The dependence of the composition of the liquid and gaseous reaction products on the temperature, the amount of water, and the composition of the catalyst in carrying out the reaction of methylthiophene is presented in Table 2 (for analysis, the average liquid sample during the first 4–6 min of the experiment and the gas sample during the first 10–15 min of the experiment were taken). The thiophene content in the catalyzate denotes its percentage in the resulting mixture of thiophene and unreacted methylthiophene.

The activity of the catalyst with respect to the demethylation reaction, unless it has been completely lost, is restored after one hour of heating the catalyst in hydrogen. More prolonged heating increases the activity of the catalyst in this reaction (Table 3).

The foregoing makes it possible to conclude that methylthiophene, like methylpyridines, toluene, and xylenes, undergoes a demethylation reaction (1) in the presence of water over a $Ni/Al_2O_3$ or $Co/Al_2O_3$ catalyst.

The simultaneous complete cleavage of the methylthiophene molecule may proceed both with the participation of water and with the participation of hydrogen (3), which is a product of the first two reactions.

Table 3

| Experiment No. | Catalyst | Regeneration time (hr.) | $\omega$ | Temperature (°C) | Thiophene content during the first 6 min of the experiment (%) |
|---|---|---|---|---|---|
| 57 | $Ni/Al_2O_3$ (1 : 1) after operation | 0.5 | 48 | 250 | 49 |
| 58 | $Ni/Al_2O_3$ (1 : 1) after operation | 1.0 | 48 | 250 | 56 |
| 59 | $Ni/Al_2O_3$ (1 : 1) after operation | 2.0 | 48 | 250 | 65 |

If the radical

(Figure: thiophene radical)

is denoted by T, then the reactions taking place will be represented as follows:

$$TCH_3 + 2H_2O = TH + CO_2 + 5H_2, \tag{1}$$

$$TCH_3 + 10H_2O = 5CO_2 + 12H_2 + H_2S, \tag{2}$$

$$\left.\begin{aligned} TCH_3 + 4H_2 &= C_5H_{12} + H_2S, \\ TCH_3 + H_2 &= TH + CH_4, \\ TH + 4H_2 &= C_4H_{10} + H_2S. \end{aligned}\right\} \tag{3}$$

Reactions (1) and (2) proceed on the active centers of the metallic catalyst (Ni, Co). The hydrogen sulfide formed by reaction (2) is not at first evolved into the bulk phase; instead, forming sulfides, it poisons the surface of the catalyst. Therefore the rates of reactions (1) and (2) decrease continuously. At the same time, as the fraction of the active catalyst surface occupied by the metal sulfide increases, the relative weight of reactions (3), proceeding under the action of hydrogen, increases. Finally, when the surface is completely covered by sulfides, a constant rate of the process is established. The composition of the products in

this part of the reaction differs from the composition of the products in the first stage. $H_2S$ appears in the gas, i.e., the demethylation reaction on the metallic surface is replaced by a desulfurization reaction on sulfides.

The amount of 2-methylthiophene that has reacted according to reactions (3) increases with increasing temperature, as is evidenced by the increase in the concentration of hydrocarbon gases and hydrogen sulfide in the products. Increasing the amount of water has the opposite effect. At the same time, raising the temperature and increasing the amount of water promote the occurrence of the secondary reaction

$$C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (3n + 1)H_2, \quad (4)$$

as a result of which, with the growth of the indicated parameters, the content of carbon monoxide and dioxide in the gas increases and the content of saturated hydrocarbons decreases.

The values of the activation energies found by us—for the first section of the reaction, where demethylation of 2-methylthiophene to thiophene predominates, 9750 cal/mole, and for the section with a constant rate, where, as we assume, the desulfurization reaction of methylthiophene on Ni or Co sulfide proceeds, 21200 cal/mole—are close to the data available in the literature.

The observed dealkylation of methylthiophene is a model reaction for obtaining thiophene from its alkyl-substituted derivatives; therefore the present work shows the fundamental possibility of obtaining an accessible starting material for syntheses based on thiophene from sulfur-containing petroleums and shale tars ([12]). In view of the fact that the main reaction proceeds on the first section of the curve (see Fig. 1), it can be carried out in moving contact with continuous regeneration of the circulating catalyst.

## Experimental Part

The experiments were carried out in a catalytic apparatus with an insert reactor, described previously ([13]). Catalysts of the composition $Ni/Al_2O_3$, 1 : 1 and 1 : 2, and $Co/Al_2O_3$, 1 : 1, prepared by Zelinskii' s method ([14]), were used in the work. The catalyst was reduced before the experiment for one hour at the temperature of the experiment and was stored during idle time as indicated in ([9]).

The starting substances—thiophene and 2-methylthiophene—were purified by the formation and subsequent decomposition of their mercuric acetates ([15]).

The substances had the following constants. Thiophene: $d_4^{20}$ 1.0640, $n_D^{20}$ 1.5275, b.p. 82-83°/744 mm; 2-methylthiophene: $d_4^{20}$ 1.0200, $n_D^{20}$ 1.5190, b.p. 110-111°/752 mm (according to the literature data, respectively: $d_4^{20}$ 1.0644 and 1.0194; $n_D^{20}$ 1.5287 and 1.5203, b.p. 84.12°/760 mm and 112.5°/760 mm).

2-Methylthiophene and water were fed into the apparatus at a constant rate equal, respectively, to 0.078 ml/min for the organic substance and 0.70 ml/min for water ($\omega = 48$) and 2.70 ml/min ($\omega = 177$).

The gas was collected, and the rate of its evolution was recorded with a UGSP gasometer. The gas was analyzed on a VTI apparatus. Hydrogen sulfide was absorbed by an acidic solution of cadmium chloride ([16]). The percentage of unsaturated hydrocarbons was calculated on the assumption that their principal mass was pentane.

(Figure: Fig. 2. Absorption curves of aqueous solutions of thiophene (a) and 2-methylthiophene (b))

**Fig. 2.** Absorption curves of aqueous solutions of thiophene (**a**) and 2-methylthiophene (**b**)

The content of thiophene and 2-methylthiophene was determined from the absorption spectra of aqueous solutions in the ultraviolet region.

Although the literature contains data on the ultraviolet spectra of thiophene derivatives ([17]), analysis of small amounts of them is recommended to be carried out by the more characteristic infrared spectra ([18]), or by color reactions with cerium nitrate (it is indicated that for mixtures only qualitative determination is possible ([19])).

We recorded the ultraviolet absorption spectra of aqueous solutions of thiophene, 2-methylthiophene, and their mixtures of various composition. The absorption maxima found—230 m$\mu$ for thiophene and 234 m$\mu$ for methylthiophene (see Fig. 2)—coincide with those reported in the literature ([17]). We have shown that the Lambert–Beer law is applicable to these solutions and that determination of the concentrations of thiophene and 2-methylthiophene in their mixtures is possible. In view of the shallow form of the curves and the close position of the maxima, the absolute errors lie within $\pm 5\%$ (see Table 4). The data of Tables 2, 3, and 4 are average values from a series of determinations.

**Table 4**

| | Content of thiophene (%) | Content of thiophene (%) | Content of thiophene (%) | Content of thiophene (%) | Content of thiophene (%) | Content of thiophene (%) | Content of thiophene (%) |
|---|---|---|---|---|---|---|---|
| Actual | 8.3 | 15.4 | 30.1 | 41.7 | 10.6 | 10.6 | 30.1 |
| From spectrum | 11.9 | 9.9 | 25.2 | 38.0 | 6.1 | 7.3 | 33.3 |
| Absolute error | +3.6 | −5.5 | −4.9 | −3.7 | −4.5 | −3.3 | +2.9 |

In the combined catalyst from several experiments in which thiophene was detected, the organic layer was separated, dried, purified by formation and decomposition of the mercuracetate, and then distilled from a small flask with a dephlegmator (2 ml). The purified product had the following constants. Experiments Nos. 62–64: $d_4^{20}$ 1.0215, $n_D^{20}$ 1.5210, initial b.p. 65°, up to 109° 10% of the substance distilled over. Experiment No. 65: $d_4^{20}$ 1.0210, $n_D^{20}$ 1.5205, initial b.p. 72°, up to 109° 20% of the substance distilled over.

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*Note: Figure translations are in progress. See original paper for figures.*