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Abstract

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On the Methylation of Cyclopentene by Methylene Radicals Formed by the Contact Reduction of Carbon Monoxide with Hydrogen

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It was shown earlier ([1]) that under the conditions of the reaction of catalytic hydrocondensation of carbon monoxide with olefins ([2]), cyclohexene is methylated by methylene radicals formed by the contact hydrogenation of carbon monoxide with hydrogen, as a result of which mono-methyl- and 1,2-dimethyl-substituted cyclohexenes are obtained. Prior to this, the intermediate formation of methylene radicals during the catalytic synthesis of hydrocarbons from CO and H_2 by the methylation of benzene to toluene had been demonstrated experimentally ([3]).

In the present work, the results obtained in studying the behavior, in the hydrocondensation reaction with carbon monoxide, of another cycloolefin—cyclopentene—are briefly set forth.

The apparatus and the procedure for carrying out the experiments remained the same as in the earlier works ([1,2]).

The starting cyclopentene was obtained from adipic acid through the stages of cyclopentanone, cyclopentanol, and dehydration of the latter over aluminum oxide, with a yield of 85% of theoretical, calculated for cyclopentanol ([4]). The cyclopentene was distilled on a column packed with copper triangular spirals, with an efficiency of 40 theoretical plates, and had the following constants: b.p. 43.3°/729 mm, d_4^{20} 0.7716, n_D^{20} 1.4221; found MR 22.44; calculated for C_5H_8F 22.62. Literature data: b.p. 44.2°/760 mm, d_4^{20} 0.7719, n_D^{20} 1.4224.

Cyclopentene was fed from an automatic burette into a glass reaction tube (diameter 12 mm) containing 30 ml (23 g) of the catalyst usually used in the hydrocondensation reaction of carbon monoxide with olefins. The catalyst bed length was 28–29 cm. The activity of the contacts was checked in the hydropolymerization reaction of ethylene under the action of small amounts of CO in the presence of H_2, and was sufficiently high: the yield of hydropolymerizate was 500-600 ml/m^3, calculated for the active gas ($CO + H_2 + C_2H_4$).

Before experiments with cyclopentene, the contact was regenerated in the usual way. Regeneration was also carried out after every 20–30 hours of operation of the contact. All experiments were carried out at 190° and atmospheric pressure. All liquid catalyzates obtained in the work were dried over anhydrous copper sulfate and fractionated on the above-mentioned column.

Before studying the behavior of cyclopentene in the hydrocondensation reaction with CO, the behavior of cyclopentene alone and of its mixture with hydrogen was studied under analogous conditions.

It turned out that cyclopentene, passed in an amount of 100 ml over the contact at a space velocity of 0.26 l/l • h, did not change. 98 ml of catalyzate was obtained, having d_4^{20} 0.7716, n_D^{20} 1.4221 and distilling at ···

44.2°/760 mm. Cyclopentene (200 ml) and hydrogen (27 l), passed together in a molar ratio of 65.4 : 34.6 over the same contact (after its regeneration) at a total space velocity of the vapor-gas phase of 113 l/l • h, gave 2.7 l of gas containing 99.3% H_2 and 185 ml of liquid catalyzate, which had d_4^{20} 0.7583, n_D^{20} 1.4150, and bromine number 119.1, corresponding to 51.4% unsaturated compounds, and boiled within the range 44–49.5°/760 mm. The catalyzate, in an amount of 125 ml, was hydrogenated at room temperature over platinized carbon (2.5 g) with addition of H_2PtCl_6. 16.6 l of H_2 was absorbed, corresponding to 50.5% unsaturated compounds. After hydrogenation the catalyzate had d_4^{20} 0.7454, n_D^{20} 1.4064, and almost all distilled at 49.2°/760 mm, i.e., it was pure cyclopentane (literature data: b.p. 49.26°/760 mm, d_4^{20} 0.7454, n_D^{20} 1.4065 (^{6})). Thus, the only reaction in the experiment with a mixture of cyclopentene and hydrogen was the hydrogenation reaction to cyclopentane to the extent of ~50%, calculated on the cycloolefin. Neither hydrocracking nor hydrogenolysis of the five-membered ring (^{7}) was observed.

Next, cyclopentene was passed over fresh portions of the contact in a stream of a gas mixture of CO and H_2. The space velocity of cyclopentene was 0.18–0.26 l/l • h, that of the initial gas 25–36 l/l • h, and that of the vapor-gas phase 71–102 l/l • h. The composition of the vapor-gas phase was 64.4–66.5% cyclopentene, 28.4–30.9% H_2, and 4.5–5.3% CO. Over 293.5 h, 1688 ml of cyclopentene and 236.5 l (NTP) of gas were passed; of these, 197.5 l were H_2 and 33.2 l CO. 1606.5 ml of liquid catalyzate (average yield 95 vol.%) and 83.1 l (NTP) of gas were obtained; of these, 66.5 l were H_2, 8.4 l CO, 0.7 l CO_2, and 1.8 l C H_2 . Entered into the reaction (NTP): 131.0 l of H_2 and 24.8 l of CO, which amounts, respectively, to 66.3 and 74.7%, calculated on the initial component. The content of unsaturated compounds in the catalyzate was 65–75% and increased as the space velocity of the starting substances decreased. During fractionation on a column, the catalyzate began to boil at 43.6°/760 mm, distilled by 2.5% within the range 43.6–44.2°, and by 93% within the range 43.6–49.3°. The residue boiling above 49.3° (i.e., above cyclopentane) amounted to 4.5 vol.%. The liquid catalyzate consisted mainly of a mixture of cyclopentene and cyclopentane. Hydrogenolysis of the five-membered ring with formation of pentane was not observed. The 43.6–44.2° fraction contained an insignificant amount of aliphatic hydrocarbons formed from CO and H_2.

Fig. 1

Figure 1: Fig. 1

Upon hydrogenation of 170 ml of liquid catalyzate obtained in one experiment and having d_4^{20} 0.7672, n_D^{20} 1.4203, and bromine number 176.2, over platinized carbon with addition of H_2PtCl_6 at room temperature, 31.5 l (NTP) of H_2 was absorbed. The hydrogenate had d_4^{20} 0.7467, n_D^{20} 1.4070, and bromine number 0.0; upon distillation on a column it began to boil at 48.5°/760 mm and 95% distilled at 49.1—49.3°/760 mm. Thus, the reaction products boiling above cyclopentane were present in the catalyzate in an amount of 4—4.5%.

For a more detailed investigation of these products, obtained from the ternary mixture C_5H_8—H_2—CO, the portion distilling up to 49.3° was distilled off from the entire catalyzate. From 1596 ml of liquid catalyzate, 65 ml of higher-boiling residue was obtained, amounting to 4.1 vol.%. After boiling for 6 h over metallic sodium and distillation, this residue had d_4^{20} 0.7745, n_D^{20} 1.4247, and bromine number 73.2; after hydrogenation in the presence of platinized carbon and H_2PtCl_6 at room temperature and subsequent passage through KSM silica gel ($a_1 = 14.7$), d_4^{20} 0.7587, n_D^{20} 1.4171, and bromine number 0.0. The hydrogenate, in an amount of 38 ml, was fractionated on a column. The distillation curve is shown in Fig. 1, and the fractions collected and their constants are given in Table 1.

As can be seen from Fig. 1, the curve has three broad plateaus with b.p. 71—72, 102—103, and 131—132°, corresponding to fractions II, IV, V (Table 1).

Fractions II-V were investigated by the method of combination light scattering*:

Fraction II, $\Delta\nu$: 312(0), 431(1), 532(3), 788(1), 802(3), 844(2), 890(8), 981(3), 1015(3), 1087(3), 1136(2), 1193(2), 1319(2), 1352(2), 1393(1), 1450(8); fraction III, $\Delta\nu$: 321(1), 382(2), 426(3), 480(0), 533(3), 802(8), 844(2), 891(4), 975(1), 1025(5), 1083(1), 1108(1), 1158(3), 1267(5), 1315(1), 1350(2), 1447(7); fraction IV, $\Delta\nu$: 387(2), 420(1), 444(2), 545(3), 769(6), 801(3), 844(3), 892(4), 934(1), 970(2), 1032(6), 1061(1), 1090(2), 1128(1), 1160(3), 1201(1), 1249(2), 1263(2), 1306(2), 1331(2), 1357(2), 1450(8); fraction V, $\Delta\nu$: 320(1), 364(2), 394(1), 422(1), 445(1), 458(1), 539(2), 574(0), 754(3), 770(1), 794(3), 841(3), 895(5), 975(1), 1012(2), 1032(5), 1062(1), 1093(2), 1134(2), 1161(2), 1187(2), 1261(3), 1303(2), 1349(2), 1451(9).

Fig. 1

The results of the optical analysis showed that fraction II is almost pure methylcyclopentane (literature data: b.p. 71.81°/760 mm, d_4^{20} 0.7486; n_D^{20} 1.4098 (6)) with traces of cyclohexane. Fraction III contains 60% methylcyclopentane and 40% cyclohexane (literature data for cyclohexane: b.p. 80.75°/760 mm, d_4^{20} 0.7786; n_D^{20} 1.4262 (6)). Fraction IV consists of 10% cyclohexane, 35% methylcyclohexane (literature data: b.p. 100.93°; d_4^{20} 0.7694, n_D^{20} 1.4231 (6)) and 55%

ethylcyclopentane (literature data: b.p. 103.47°; d_4^{20} 0.7665; n_D^{20} 1.4198 (6)). In fraction V, which was not investigated quantitatively, considerable amounts of ethylcyclohexane were found (literature data: b.p. 131.78°; d_4^{20} 0.7879; n_D^{20} 1.4320 (6)), ethylcyclopentane and propylcyclopentane (literature data: b.p. 130.95°; d_4^{20} 0.7763; n_D^{20} 1.4263 (6)) and small amounts of methylcyclohexane. In all fractions, the presence of small amounts of paraffin hydrocarbons is possible. The latter could have been formed from CO and H_2.

Table 1

Fraction No.	Boiling range, °C	Yield on starting hydrogenate, vol. %	d_4^{20}	n_D^{20}
I	55—70	2.5	–	–
II	70—72	30.8	0.7443	1.4080
III	72—94	13.3	0.7585	1.4146
IV	94—105	21.1	0.7631	1.4188
V	105—132	21.1	0.7714	1.4258
Residue	–	7.9	–	–
Losses	–	3.3	–	–

Since, in the reaction of cyclopentene with CO and H_2, as we have seen, no hydrocracking of the cycloolefin or of the cycloparaffin, all hydrocarbons with a side chain on a five-membered ring, as well as all hydrocarbons with a six-membered ring, which could have arisen only by isomerization of a five-membered ring with a side chain, were formed as a result of the hydrocondensation reaction of cyclopentene with CO. The yield of these cyclic hydrocarbons, containing more than five carbon atoms in the molecule, was ~33% based on the initial CO and 44% based on the CO that had reacted, if it is assumed that each carbon atom of the side chains of the five-membered and six-membered rings, and also one carbon atom of the six-membered ring, came from the CO molecule. About 3% of the CO entering into the reaction was converted into CO_2, and the remaining ~53% into aliphatic hydrocarbons by the Orlov—Fischer—Tropsch reaction. In this reaction no more than 6-7 ml of hydrocarbons could have been formed; these were distributed throughout the entire volume of the hydrocondensate and, upon distillation, also entered different fractions (Table 1), and to a certain extent lowered the values of d_4^{20} and n_D^{20} of these fractions.

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* The spectra were recorded and studied in the laboratory of the Commission on Spectroscopy of the Academy of Sciences of the USSR by V. T. Aleksanyan and Kh. E. Sternin, to whom the authors express their gratitude.

Thus, as a result of the hydrocondensation of cyclopentene with CO in the presence of H_2, a side chain appears on the five-membered ring: methyl, ethyl, and propyl radicals. Simultaneously, expansion of the five-membered ring occurs with formation of the corresponding hydrocarbons with a six-membered ring, with a side chain consisting of a methyl or ethyl radical, or with no side chain. The greater part of the initial cyclopentene is hydrogenated to cyclopentane.

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