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Abstract

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On the Mechanism of Formation of Hydrocarbons with a Six-Membered Ring during the Catalytic Hydrocondensation of Carbon Monoxide with Cyclopentene

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The hydrocondensation reaction of carbon monoxide with olefins proceeds in the presence of hydrogen at 190–200° and atmospheric pressure over a precipitated cobalt catalyst. With cycloolefins the reaction proceeds selectively, although with low yields, forming higher homologues (*1*), which, apparently, is the result of interaction with the starting hydrocarbon of methylene radicals arising on the catalyst surface during incomplete reduction of carbon monoxide by hydrogen (*2*).

In the hydrocondensation of carbon monoxide with cyclopentene, a mixture of hydrocarbons was obtained with a number of carbon atoms greater than in cyclopentene, in a yield of 44% based on the CO that had reacted and 5% based on the cycloolefin passed through. After complete hydrogenation, it was found to contain 45% methylcyclopentane, 20% ethylcyclopentane, 8% propylcyclopentane, and 27% cyclohexane hydrocarbons, namely 10% cyclohexane, 10% methylcyclohexane, and 7% ethylcyclohexane. Thus, alongside homologues of the initial cyclopentene and their hydrogenation products, hydrocarbons with a six-membered ring were also formed (*3*). It was natural to assume that secondary isomerization with ring expansion of homologues of cyclopentene or cyclopentane formed as a result of hydrocondensation with CO occurs on the catalyst. However, a more detailed investigation showed that the catalyst is not active in isomeric transformations of this kind. Neither 1-methylcyclopentene-1 by itself and in a stream of nitrogen or hydrogen, nor methylcyclopentane in a stream of hydrogen or a mixture of hydrogen and carbon monoxide, underwent reactions with ring expansion under analogous conditions (*4*). This indicated that the formation of hydrocarbons containing a six-membered ring is directly connected with the hydrocondensation reaction of carbon monoxide with cyclopentene. It was proposed (*4*) that the methylene radical reacts with an adsorbed cyclopentene molecule to form, according to the Herington scheme (*5*), an adsorbed methylenecyclopentane molecule:

[scheme: adsorbed cyclopentene + CH_2 ⟶ adsorbed methylenecyclopentane]
(1)

which is then isomerized into 1-methylcyclopentene-1 with migration of the double bond or into cyclohexene; at the same time partially hydrogenated forms of these cycloolefins are formed as intermediates (*6*, *7*):

[scheme: adsorbed methylenecyclopentane + H ⇄ adsorbed methylcyclopentene species ⟶ adsorbed meth
(2)

[scheme: adsorbed cyclohexene species ⟶ adsorbed hydrogenated cyclohexene species]
(3)

Consequently, ring expansion was associated not with the stage of addition of the methylene radical to cyclopentene, but with the stage of isomerization of methylenecyclopentane.

In the present work the aim was an experimental verification of this mechanism. To this end, experiments were carried out to study, under analogous conditions, the behavior of methylenecyclopentane, its mixture with hydrogen, and with hydrogen and carbon monoxide.

The starting methylenecyclopentane (b.p. 74°/760 mm, n_D^{20} 1.4340, d_4^{20} 0.7800; literature data (^{7}): b.p. 73—73.2/750 mm, n_D^{20} 1.4342, d_4^{20} 0.7803) was synthesized by pyrolysis of cyclopentylcarbinol acetate (^{7}) and, after boiling over metallic sodium, was distilled on a column packed with triangular copper spirals, with an efficiency of 60 theoretical plates. The overall scheme of the synthesis was:

$HOOC(CH_2)_4COOH$ → cyclopentanone → cyclopentanol → cyclopentyl chloride → cyclopentylmagnesium ch

$\xrightarrow{HCHO}$ cyclopentylmethanol → cyclopentylmethyl acetate → methylenecyclopentane
(4)

The transformations of methylenecyclopentane were investigated in experiments with 0.1 g-mol of hydrocarbon passed over the catalyst at a space velocity of 0.08 h^{-1}, at 190° and atmospheric pressure, in a reaction glass tube 10 mm in diameter for 4 h. Thirty cm^3 of a Co—ThO_2—kieselguhr (Kisatibi) catalyst (100 : 18 : 100) were used, prepared by precipitation and reduced or regenerated with hydrogen at 375° for 3 h.

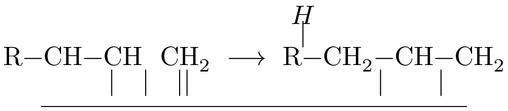
The liquid reaction products were analyzed by gas-liquid chromatography with triethylene glycol ester and *n*-butyric acid as the liquid phase, deposited in an amount of 7% on a solid support—INZ-600 diatomaceous brick with a grain size of 0.25—0.5 mm. Separation was carried out in a stream of carrier gas —helium—at a temperature 20—30° below the boiling point of the principal component of the catalyzate. The length of the separating column was 8 m, the internal diameter 5 mm. Hydrocarbons were identified with the aid of standards—pure individual hydrocarbons. When methylenecyclopentane alone was passed over the catalyst, a catalyzate was obtained in 95.5% yield (n_D^{20} 1.4322, d_4^{20} 0.7752), which was practically pure 1-methylcyclopentene-1. Thus, methylenecyclopentane was completely isomerized with migration of the double bond into the ring, which corresponds to reaction (2). In the experiment with a mixture of methylenecyclopentane and hydrogen in a molar ratio of 1 : 1, a catalyzate (n_D^{20} 1.4210) was obtained in 92.4% yield, with the following composition: 50.2 mol.% methylcyclopentane, 37.5% 1-methylcyclopentene-1, and 12.3% unreacted methylenecyclopentane.

In the experiment with a mixture of methylenecyclopentane, hydrogen, and carbon monoxide in a molar ratio of 59 : 36 : 5, the liquid catalyzate obtained in 90.0% yield (n_D^{20} 1.4275) contained (mol.%): 66.6 1-methylcyclopentene-1, 21.5 methylcyclopentane, 2.7 dimethylcyclopentane and ethylcyclopentane, 3.6 cyclopentene, 0.8 cyclopentane, and 5.4 unreacted methylenecyclopentane. In this experiment, the main reaction is likewise isomerization with migration of the double bond into the ring. Hydrogenation proceeds in parallel, and, to a small extent, demethylation and hydrocondensation with carbon monoxide take place, with the formation of higher homologues.

It is evident from the results obtained that in none of the experiments with methylenecyclopentane is its isomerization with expansion of the five-membered ring to a six-membered ring observed. This indicates that the assumption made earlier (4), that in the hydrocondensation of cyclopentene with carbon monoxide the formation of hydrocarbons with a six-membered ring proceeds through the intermediate formation of methylenecyclopentane by reaction (3), has not been confirmed. It follows from this that the formation of the six-membered ring from the five-membered ring is not connected with isomerization of the methylenecyclopentane molecule with migra-

···of the double bond into the ring, but with an earlier stage, i.e., with the stage of addition of the methylene radical to the cyclopentene molecule.

This conclusion gives grounds for assuming that the Herington scheme, which in general form may be expressed as follows:



$$\mathrm{R{-}CH{-}CH\;\;CH_2} \longrightarrow \mathrm{\overset{H}{R}{-}CH_2{-}CH{-}CH_2} \qquad (5)$$

\end{equation}

is not the only one in the mechanism of addition of a surface methylene radical to an olefin. The methylene radical on the surface behaves like the CH_2 radical in the liquid phase and can insert both into the C—H bond and into the unsaturated C—C bond. This proposition can not only be postulated (^{8}), in particular for the present case, but is also confirmed by other experimental data. In the hydrocondensation of carbon monoxide in the presence of hydrogen with benzene under analogous conditions over a Co catalyst, it proved possible to demonstrate the formation of toluene (^{9}), which was the first experimental confirmation of the reduction of carbon monoxide by hydrogen to a methylene radical on the catalyst surface. It has recently been shown (^{10}) that, together with toluene, cycloheptatriene is also formed, i.e., expansion of the six-membered ring to a seven-membered ring occurs. These processes are represented by the scheme:

$$\text{benzene} \xrightarrow{CH_2} \begin{array}{c}\text{toluene}\\ [\text{norcaradiene structure with } CH_2]\end{array} \longrightarrow \text{cycloheptatriene} \tag{6}$$

An intermediate norcaradiene structure with a three-membered ring arises as a result of addition of methylene at the C—C bond of the benzene molecule.

It may be assumed that, in the same way, CH_2 can add to a multiple bond and, in particular, to the multiple bond of cyclopentene, with formation of the bicyclo$(3,0,1)$-hexane structure, from which cyclohexene or cyclohexane readily arises:

$$\text{cyclopentene} \xrightarrow{CH_2} \text{methylenecyclopentane} \longrightarrow \text{methylcyclopentene} \tag{7}$$

$$\text{cyclopentene} \xrightarrow{CH_2} [\text{bicyclo}(3,0,1)\text{-hexane structure with } CH_2] \longrightarrow \text{cyclohexene} \tag{8}$$

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CITED LITERATURE

1. Ya. T. Eidus, N. I. Ershov, DAN, **87**, 433 (1952); Izv. AN SSSR, OKhN, 704; K. V. Ruzichkin, E. M. Terent' eva, Ya. T. Eidus, Izv. AN SSSR, OKhN, **1959**, 1318.

2. Ya. T. Eidus, Izv. AN SSSR, OKhN, **1961**, 336; *Kinetics and Catalysis*, **1**, 117 (1960); Ya. T. Eidus, *Actes du deuxième congrès international de Catalyse*, Paris, 1960, 1961, **1**, p. 659.
3. Ya. T. Eidus, M. B. Ordyan, DAN, **116**, 101 (1957).
4. Ya. T. Eidus, M. B. Ordyan, Izv. AN SSSR, OKhN, **1959**, 1458.
5. E. F. G. Herington, *Trans. Farad. Soc.*, **37**, 361 (1941).
6. J. Horiuti, G. Ogden, M. Polanyi, *Trans. Farad. Soc.*, **30**, 663 (1934); G. H. Twigg, E. K. Rideal, *Proc. Roy. Soc.*, A, **171**, 55 (1939); G. H. Twigg, *Trans. Farad. Soc.*, **35**, 934 (1939).
7. R. Ya. Levina, N. N. Mezentseva, *Uch. zap. Moskovsk. univ.*, issue 132, book VII, 241 (1950).
8. I. F. Bogdanov, *Tr. Inst. goryuchikh iskop. AN SSSR*, **18**, 34 (1962).
9. Ya. T. Eidus, N. D. Zelinsky, Izv. AN SSSR, OKhN, **1940**, 289; Dai Hang, Wang Hsien-ching, *Acta focalia sinica*, **3**, 214 (1958); RZhKhim, No. 23, 77858 (1959).
10. Ya. T. Eidus, B. K. Nefedov, M. E. Vol' pin, Izv. AN SSSR, OKhN, **1963**, 548.

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