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Abstract

Full Text

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HYDROGENATION OF ETHYLCYCLOBUTANE AND 1,1,2-TRIMETHYLCYCLOPROPANE IN THE PRESENCE OF PALLADIZED CARBON

In the presence of platinized carbon, cyclopentane (1), cyclobutane (2,3), and cyclopropane (2,4) hydrocarbons are capable, under comparatively mild conditions, of adding hydrogen with cleavage of the ring (hydrogenolysis). Alkylcyclopropanes, in addition to this reaction, which is common to all lower cycloparaffins, are capable of undergoing yet another hydrogenation reaction with opening of the ring. This reaction proceeds through intermediate isomerization of alkylcyclopropanes to olefins, which are then hydrogenated to paraffins (5). As is seen from the scheme given below, the final products of the two reactions are different.

Hydrogenolysis:

$$\text{1,1,2-trimethylcyclopropane} \longrightarrow CH_3{-}C(CH_3)_2{-}CH_2{-}CH_3 \quad 100\%.$$

Isomerization followed by hydrogenation:

$$\text{1,1,2-trimethylcyclopropane} \longrightarrow \text{(olefins)} \longrightarrow \begin{cases} CH_3{-}CH(CH_3){-}CH(CH_3){-}CH_3, & 80\%, \\ CH_3{-}CH(CH_3){-}CH_2{-}CH_2{-}CH_3, & 20\%. \end{cases}$$

Despite the fact that activated carbon is an active isomerizing agent for alkylcyclopropanes (5), hydrogenation in the presence of platinized activated carbon proceeds only in the direction of hydrogenolysis. This may be explained by the fact that, owing to the special activity of platinum as a hydrogenolysis catalyst, the rate of this reaction considerably exceeds the rate of isomerization, as a result of which the latter does not take place.

Earlier, Kazanskii and co-workers found that, in contrast to platinized carbon, palladized carbon is not capable of catalyzing the hydrogenolysis of cyclopentane (6) and its homologues (7). There are no data on the hydrogenolysis of alkylcyclobutanes in the presence of palladium catalysts. Cyclopropane, according to the work of Bond and Sheridan (^{8}), is capable of adding hydrogen in the presence of palladium deposited on pumice, but at temperatures higher than in the case of the analogous platinum catalyst. In the present work we studied the hydrogenolysis of ethylcyclobutane and 1,1,2-trimethylcyclopropane in the presence of one

and of the same sample of palladized carbon. These data are readily comparable with hydrogenolysis in the presence of platinized carbon, studied with the same hydrocarbons (^{3,4}). It should be noted that, on the sample of palladized carbon used by us, hydrogenolysis of cyclopentane proceeded only to the most insignificant extent ($\sim 3\%$) at temperatures above 300°.

Experiments showed that ethylcyclobutane, in the presence of this catalyst, underwent hydrogenolysis, but this required a somewhat higher temperature than in the case of platinized carbon. In this process both possible bonds of the four-membered ring were also cleaved; however, the branched isomer was obtained in a somewhat larger amount (about 60%).

More substantial differences from platinized carbon were observed in the case of 1,1,2-trimethylcyclopropane. It was found that at temperatures of 100 and 120°, in the presence of palladized carbon, both possible reactions of hydrogenation of alkylcyclopropanes took place—hydrogenolysis and isomerization followed by hydrogenation—as a result of which the catalyzate contained all three possible products of cleavage of the three-membered ring:

$$\text{1,1,2-trimethylcyclopropane} \xrightarrow[\mathrm{H_2;\ 120^\circ}]{\mathrm{Pd/C}} \begin{cases} CH_3-C(CH_3)_2-CH_2-CH_3 & \sim 80\% \\ CH_3-CH(CH_3)-CH(CH_3)-CH_3 & \\ CH_3-CH(CH_3)-CH_2-CH_2-CH_3 & \sim 20\% \end{cases}$$

When the reaction temperature was raised to 220°, the side reaction proceeded to a greater extent, and the mixture of 2,3-dimethylbutane and 2-methylpentane already amounted to 40% of the total mixture.

The results obtained show that palladized carbon is not as specific a catalyst for the hydrogenolysis of lower cycloparaffins as platinized carbon. Only with respect to alkylcyclobutane are the results of the hydrogenation reactions in the presence of these two catalysts close.

Table 1

Hydrocarbon	B.p., °C (760 mm Hg)	n_D^{20}	d_4^{20}
Cyclopentane	49.4	1.4062	0.7453
n-Pentane	36.0	1.35745	0.62619
Ethylcyclobutane	70.4	1.4021	0.7270

Fig. 1

Figure 1: Fig. 1

Hydrocarbon	B.p., °C (760 mm Hg)	n_D^{20}	d_4^{20}
n-Hexane	68.740	1.37486	0.65937
3-Methylpentane	63.282	1.37652	0.66431
1,1,2-Trimethylcyclopropane	52.6	1.3862	0.6948
2-Methylpentane	60.271	1.37145	0.65315
2,3-Dimethylbutane	57.988	1.37495	0.66164
2,2-Dimethylbutane	49.741	1.36876	0.64916

In the case of alkylcyclopropane, the lower activity of palladium as a hydrogenolysis agent leads to the fact that the rate of the hydrogenolysis reaction competes with the rate of the isomerization reaction of the alkylcyclopropane into an open-chain hydrocarbon, proceeding at the expense of the support—activated carbon; as a result, both reactions take place at temperatures of 100–200°.

Experimental Part

Hydrocarbons: ethylcyclobutane, 1,1,2-trimethylcyclopropane, and cyclopentane were obtained by previously described methods (^{3,4,9}). The constants of these hydrocarbons, as well as the constants of the paraffinic hydrocarbons (^{11}) that may be formed upon their hydrogenation, are given in Table 1.

Catalyst—palladized charcoal (20% Pd)—was prepared according to Zelinsky (^{10}).

Hydrogenation was carried out by the previously described method (^{2}). In all cases the hydrocarbons, in a mixture with hydrogen, were passed over the previously reduced catalyst at a space velocity of 0.2 h^{-1}. In the distillation of the catalyzates, a column with a copper packing and an efficiency of 35 theoretical plates was used; toward the end of the distillation, 10 ml of *n*-heptane was added to the distillation flask as a chaser.

Fig. 1

I. Cyclopentane. In experiments on the hydrogenation of cyclopentane at temperatures of 310 and 320°, a catalyzate was collected with the following constants: n_D^{20} 1.4050; d_4^{20} 0.7430. Judging from the specific volumes of the catalyzates, it contains about 3% *n*-heptane.

II. Ethylcyclobutane. Hydrogenation of ethylcyclobutane at temperatures of 260, 270, and 280° gave catalyzates with refractive indices in the range from 1.3800 to 1.3775. Raising the reaction temperature to 290° gave a catalyzate with n_D^{20} 1.3770. Repeated passage of the catalyzate over palladized charcoal at

290° made it possible to obtain 12.8 g (18 ml) of catalyzate with n_D^{20} 1.3764 and d_4^{20} 0.6634. The results of the distillation of the catalyzate are given in Table 2 and in Fig. 1.

Table 2

Fraction No.	B.p., °C (760 mm Hg)	Amount, ml	n_D^{20}	d_4^{20}
I	63.1—63.6	5.0	1.3762	0.6641
II	63.6—64.6	3.0	1.3760	0.6643
III	64.6—68.0	4.0	1.3758	0.6624
IV	68.2—69.2	4.5	1.3762	0.6628
V	69.2—85.2	0.5	—	—
Losses		1.0		

From a comparison of the data in Tables 1 and 2, fractions I and II are 3-methylpentane; fraction IV is *n*-hexane, the constants of which are somewhat high because of an impurity of ethylcyclobutane; fraction III is transitional. Judging from the distillation curve, 3-methylpentane constitutes approximately 60% of the mixture.

Table 3

Fraction No.	B.p., °C (760 mm Hg)	Amount, ml	n_D^{20}	d_4^{20}
I	50.0	6.0	1.3690	0.6492
II	50.0	4.0	1.3690	0.6495
III	50.0—57.0	4.5	1.3710	0.6539
IV	57.0—61.2	1.5	1.3748	0.6595
Losses		1.5		

Table 4

Fraction No.	B.p., °C (760 mm Hg)	Amount, ml	n_D^{20}	d_4^{20}
I	49.3—50.1	5.5	1.3688	0.6490
II	50.1	7.0	1.3688	0.6492
III	50.1—57.4	4.0	1.3708	0.6535
IV	57.4—58.4	2.5	1.3743	0.6609
V	58.5—59.5	2.5	1.3745	0.6608
Losses		1.5		

III. 1,1,2-Trimethylcyclopropane. In the hydrogenation of 1,1,2-trimethylcyclopropane at temperatures from 60 to 220°, the index···

Fig. 2

Figure 2: Fig. 2

the refractive index of the catalyzate changed only slightly and was within the range from 1.3698 to 1.3710. The 17.5 ml of catalyzate collected at 120° had n_D^{20} 1.3710 and d_4^{20} 0.6510. The results of the fractionation of the catalyzate are given in Table 3 and in Fig. 2 (curve *a*).

Fig. 2

From comparison of the data of Tables 1 and 3 it may be concluded that fractions I and II are 2,2-dimethylbutane, while fractions III and IV are a mixture of 2,2-dimethylbutane with 2,3-dimethylbutane and 2-methylpentane. Judging from the fractionation curve, 2,2-dimethylbutane constitutes approximately 70–80% of the total mixture.

The hydrogenation catalyzate collected at 220° (23 ml) had n_D^{20} 1.3708 and d_4^{20} 0.6520. The results of its fractionation are given in Table 4 and in Fig. 2 (curve *b*). Comparison of the data of Tables 1 and 4 shows that fractions I and II are 2,2-dimethylbutane, fractions IV and V are a mixture of 2,3-dimethylbutane with 2-methylpentane, and fraction III is transitional. Judging from the fractionation curve, in this case the content of 2,2-dimethylbutane in the catalyzate is approximately 60%.

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