ISSN 1070-4272, Russian Journal of Applied Chemistry, 2015, Vol. 88, No. 4, pp. 585−589. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © M.M. El'chaninov, E.V. Pyatnitsyna, I.M. El'chaninov, 2015, published in Zhurnal Prikladnoi Khimii, 2015, Vol. 88, No. 4, pp. 553−557.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Step Mechanism of 1-Butanol Formation in the Course of Liquid-Phase Catalytic Hydrogenation of 2-Butyne-1,4-diol

M. M. El'chaninov, E. V. Pyatnitsyna, and I. M. El'chaninov

Platov South-Russian State Polytechnic University (Novocherkassk Polytechnic Institute),
ul. Procveshcheniya 132, Novocherkassk, Rostov oblast, 346428 Russia
e-mail: elchaninov-43@mail.ru

Received February 3, 2015

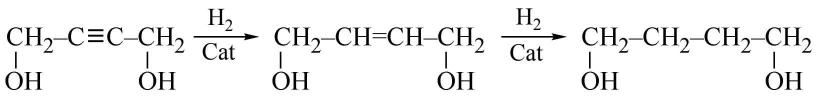
Abstract—Exhaustive hydrogenation of 2-butyne-1,4-diol to 1,4-butanediol on suspended palladium and Raney nickel catalysts under atmospheric pressure at 40°C was studied with the aim to determine the mechanism of 1-butanol formation. The previously unknown pathway of 1-butanol synthesis is realized under these conditions. The content of 1-butanol precursors in hydrogenation catalyzates was estimated by gas–liquid chromatography. The graphic dependence of the content of the intermediates and 1-butanol on time was found. The possibility of increasing the hydrogenation selectivity on Raney Ni catalysts with respect to the target product was revealed.

DOI: 10.1134/S1070427215040059

The selectivity of hydrogenation of 2-butyne-1,4-diol (BYD) to 1,4-butanediol (BAD) is determined by high rage of hydrogenation of the labile intermediate, 2-butene-1,4-diol (BED), on the majority of nickel, copper, platinum, palladium, and other catalysts [1–3]. However, in most cases the reaction selectivity decreased because of the 1-butanol formation.

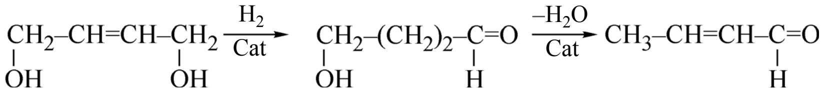
In this study we examined the mechanism of formation of this by-product, decreasing the target product yield.

To this end, we critically analyzed the published and newly obtained experimental data on the transformations of BYD under the conditions of catalytic hydrogenation on palladium (Pd/C-2) and Raney nickel catalysts. According to the published data [4], hydrogenation of acetylenic glycol **1** occurs in steps with the formation of BED (**2**), which either takes up the second mole of hydrogen to form BAD (**3**) or isomerizes into γ-hydroxybutyraldehyde (HBA), which successively



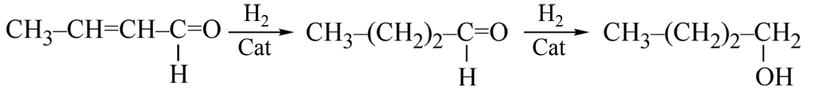
$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{C{\equiv}C}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow[\mathrm{Cat}]{\mathrm{H_2}} \underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH{=}CH}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow[\mathrm{Cat}]{\mathrm{H_2}} \underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \qquad (1)$$

1 **2** **3**



$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH{=}CH}-\underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow[\mathrm{Cat}]{\mathrm{H_2}} \underset{\mathrm{OH}}{\mathrm{CH_2}}-(\mathrm{CH_2})_2-\underset{\mathrm{H}}{\mathrm{C}}{=}\mathrm{O} \xrightarrow[\mathrm{Cat}]{-\mathrm{H_2O}} \mathrm{CH_3}-\mathrm{CH{=}CH}-\underset{\mathrm{H}}{\mathrm{C}}{=}\mathrm{O} \qquad (2)$$

2 **4** **5**



$$\mathrm{CH_3}-\mathrm{CH{=}CH}-\underset{\mathrm{H}}{\mathrm{C}}{=}\mathrm{O} \xrightarrow[\mathrm{Cat}]{\mathrm{H_2}} \mathrm{CH_3}-(\mathrm{CH_2})_2-\underset{\mathrm{H}}{\mathrm{C}}{=}\mathrm{O} \xrightarrow[\mathrm{Cat}]{\mathrm{H_2}} \mathrm{CH_3}-(\mathrm{CH_2})_2-\underset{\mathrm{OH}}{\mathrm{CH_2}} \qquad (3)$$

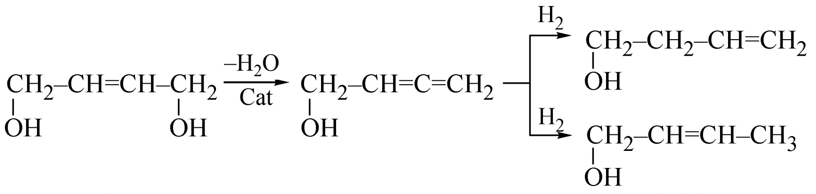
5 **6** **7**

Table 1. Physicochemical characteristics of compounds **2** and **8**–**10**

Compound	Parameter
2-Butene-1,4-diol (**2**) [5, 6]	Liquid with characteristic odor. Exists as *trans* and *cis* isomers. Boiling point, °C/mmHg (MPa): mixture of isomers: from 232 to 235/760 (0.1) from 105 to 107/2 (0.0003) *cis isomer*: 235/760 (0.1); 132/16 (0.002) *trans* isomer: 131/13 (0.002); from 125 to 127/10 (0.001) Refractive index: mixture of isomers: from 1.476 to 1.478 *cis isomer*: 1.4782 *trans isomer*: 1.4755 Density at 20°C, g cm^{-3}: mixture of isomers: from 1.067 to 1.074 *cis isomer*: 1.0698 *trans* isomer: 1.0800 Crystallization point, °C: *cis isomer*: 4 *trans* isomer: 25
2,3-Butadien-1-ol (**8**) [7]	Transparent lacrimatory liquid with sharp odor. Boiling point, °C/mmHg (MPa): from 140 to 140.5/780 (0.1) from 126 to 127/756 (0.1) from 68 to 70/57 (0.008) from 68 to 69/45 (0.006) Refractive index: 1.4759 Density at 20°C, g cm^{-3}: 0.9164
2-Buten-1-ol (**9**) [8, 9]	Transparent lacrimatory liquid with sharp odor. Boiling point, °C/mmHg (MPa): *cis isomer*: from 122 to 123/760 (0.1) *trans* isomer: 121.2/760 (0.1) Refractive index: *cis isomer*: 1.4342 *trans* isomer: 1.4285 Density at 20°C, g cm^{-3}: *cis isomer*: 0.8662 *trans* isomer: 0.8532
3-Buten-1-ol (**10**) [10]	Transparent colorless liquid with specific odor. Boiling point, °C/mmHg (MPa): from 112.5 to 113.5/755 (0.1) Refractive index: 1.4227 Density at 20°C, g cm^{-3}: 0.8454

transforms into 2-butenal (**5**), 1-butanal (**6**), and, finally, 1-butanol (**7**) (BTN).

As we found, 1-butanol (**7**) is also formed via one more, previously unknown, pathway. It involves hydrogenolysis and dehydration of 2-butene-1,4-diol (**2**) via C–OH bond into allenic alcohol, 2,3-butadien-1-ol (**8**), followed by its hydrogenation into 3-buten-1-ol (**9**) or 2-buten-1-ol (crotyl alcohol) (**10**) and then into 1-butanol (**7**):



$$\underset{\displaystyle OH}{CH_2}-CH=CH-\underset{\displaystyle OH}{CH_2} \xrightarrow[\text{Cat}]{-H_2O} \underset{\displaystyle OH}{CH_2}-CH=C=CH_2 - \left\{ \begin{array}{l} \xrightarrow{H_2} \underset{\displaystyle OH}{CH_2}-CH_2-CH=CH_2 \\ \xrightarrow{H_2} \underset{\displaystyle OH}{CH_2}-CH=CH-CH_3 \end{array} \right. \qquad (4)$$

2 **8** **9, 10**

These intermediates were identified using reference samples. The physicochemical characteristics of compounds **2** and **8**–**10** are given in Table 1. Their content in hydrogenation catalyzates was estimated by gas–liquid chromatography.

EXPERIMENTAL

The hydrogenation catalyzates were analyzed on a Tsvet-100M-152 chromatograph equipped with a flame ionization detector. A metal column 2 m long and 3 mm in diameter was packed with Chromaton N-Super or N-AW-DMCS, fraction 0.16–0.20 mm, impregnated with 15% polyethylene glycol (PEG) of molecular mass 15 000–20 000.

The kinetic curves of BYD consumption and accumulation of the major hydrogenation products (BTN, HBA, BED, BAD) on the above-indicated catalysts were presented previously [11]. This study was focused exclusively on intermediates of the 1-butanol synthesis. To this end, we performed exhaustive hydrogenation of BYD at 40°C in a 100 cm^3 long-necked reactor fixed in a shaking machine. The required temperature in the reactor and buret was maintained by feeding temperature-controlled water into their jackets. The reactor was charged with 1.32 g of crystalline BYD, 20 cm^3 of water, and calculated amount of finely dispersed catalyst (10 wt % relative to BYD). The reaction completion was judged from the hydrogen uptake, measured with a 300 cm^3 gas buret. The Pd/C-2 catalyst (2.0 wt % Pd on OUB coal) was prepared by application of palladium(II) chloride from its hydrochloric acid solution onto the support, followed by the palladium reduction to metal with formaldehyde [12]. Selective nickel catalyst W-6 was prepared by leaching of Raney nickel–aluminum alloy with a 20 wt % NaOH solution [13].

The graphic dependences of the relative amounts of the intermediates and 1-butanol on time were constructed (Table 2; Figs. 1a, 1b). The composition of the intermediates shows that 4-hydroxy-1-butanal (**4**)

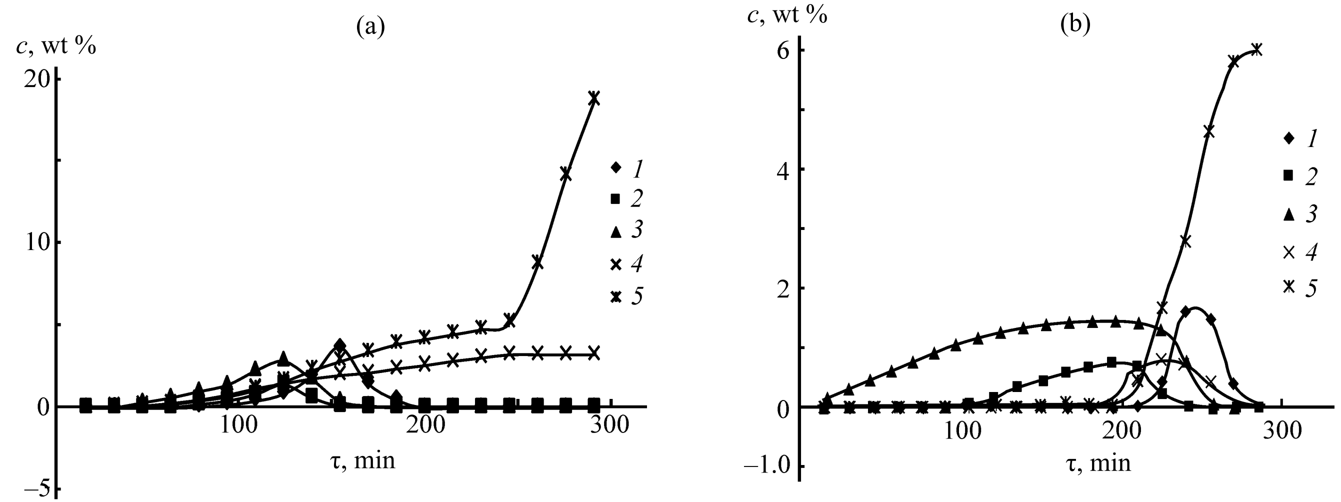


Fig. 1. Kinetic curves of accumulation of intermediates preceding 1-butanol formation. (*c*) Concentration and (τ) time. Catalyst: (a) Pd/C-2 and (b) Raney nickel. (a) (*1*) 2-buten-1-ol, (*2*) 3-buten-1-ol, (*3*) 2,3-butadien-1-ol, (*4*) 4-hydroxybutanal, and (*5*) 1-butanol; (b) (*1*) 2-buten-1-ol, (*2*) 3-buten-1-ol, (*3*) 2,3-butadien-1-ol, (*4*) 2-butenal, and (*5*) 1-butanol.

Table 2. Variation with time of the composition of intermediates preceding 1-butanol formation in the course of BYD hydrogenation at 40°C

τ, min	Weight fraction of reaction products in hydrogenation catalyzates, %									
	Pd/C catalyst (POUB-2)					Raney Ni catalyst				
	2-buten-1-ol	3- buten-1-ol	2,3-butadien-1-ol	4-hydroxybutanal	1-butanol	2-buten-1-ol	3- buten-1-ol	2,3-butadien-1-ol	2-butenal	1-butanol
15	0	0	0	0.01	0.01	0	0	0.16	0.01	0
30	0	0	0	0.04	0.04	0	0	0.30	0.02	0
45	0	0	0.3	0.14	0.14	0	0	0.46	0.04	0
60	0	0	0.6	0.3	0.24	0	0	0.64	0.04	0
75	0.06	0.2	1.0	0.5	0.46	0	0	0.80	0.04	0
90	0.2	0.4	1.4	0.8	0.7	0	0	0.98	0.04	0
105	0.42	0.8	2.3	1.2	1.1	0	0.06	1.12	0.04	0
120	0.86	1.4	2.9	1.5	1.6	0	0.16	1.24	0.04	0
135	1.94	0.6	1.8	1.8	2.3	0	0.32	1.32	0.04	0
150	3.7	0.1	0.4	2.0	2.86	0	0.46	1.38	0.04	0
165	1.5	0.04	0.1	2.14	3.4	0	0.60	1.44	0.06	0
180	0.5	0	0	2.4	3.9	0	0.66	1.46	0.06	0
195	0	0	0	2.6	4.2	0	0.72	1.44	0.1	0
210	0	0	0	2.86	4.5	0	0.70	1.40	0.68	0.4
225	0	0	0	3.06	4.8	0.4	0.20	1.30	0.80	1.7
240	0	0	0	3.26	5.2	1.6	0	0.80	0.70	2.8
255	0	0	0	3.26	8.8	1.5	0	0	0.40	4.6
270	0	0	0	3.26	14.2	0.4	0	0	0.10	5.8
285	0	0	0	3.26	18.8	0	0	0	0	6.0

on palladium catalysts does not undergo dehydration to 2-butenal [scheme (2)] and therefore cannot transform into 1-butanol (**7**), whereas on Raney Ni catalysts this process is possible. However, 1-butanol (**7**) is formed more probably via pathway (4). This assumption is confirmed by the experimental data obtained in this study.

CONCLUSIONS

(1) Experiments on exhaustive hydrogenation of 2-butyne-1,4-diol on suspended palladium and Raney Ni catalysts at atmospheric pressure revealed the previously unknown mechanism of 1-butanol formation.

(2) When the hydrogenation is performed on Raney nickel catalysts, the 1-butanol yield is 3 times smaller. This fact can be used in the modern technology for 1,4-butanediol synthesis on suspended catalysts for enhancing the process selectivity.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Science Foundation (project no. 14-23-00078).

REFERENCES

1. Reppe, W., *Ann.*, 1955, vol. 39, pp. 596–601.
2. GDR Patent 248113, 1987.
3. Polish Patent 138901, 1988.
4. Jonson, A.W., *J. Chem. Soc.*, 1946, vol. 96, pp. 1009–1012.
5. *Khimickeskii entsiklopedicheskii slovar'* (Chemical

Encyclopedic Dictionary), Knunyants, I.L., Ed., Moscow: Sov. Entsiklopediya, 1983.

6. *Beilsteins Handbuch der organischen Chemie*, 1918, 3th ed., vol. 1, pp. 2255–2256.
7. Carothers, W.H., *J. Am. Chem. Soc.*, 1933, vol. 55, pp. 2807–2812.
8. Yonng, W.G., *J. Am. Chem. Soc.*, 1936, vol. 58, pp. 100–107.
9. Hatch, L.F., *J. Am. Chem. Soc.*, 1950, vol. 72, pp. 727–733.
10. *Beilsteins Handbuch der organischen Chemie*, 1918, 3rd ed., vol. 1, p. 1896.
11. Pyatnitsyna, E.V. and El'chaninov, M.M., *Russ. J. Appl. Chem.*, 2013, vol. 86, no. 3, pp. 394–397.
12. Mandel'shtam, T.V., Ioffe, B.V., Artsibasheva, Yu.P., and Bolotov, B.A., *Sovremennye metody organicheskogo sinteza* (Modern Methods of Organic Synthesis), Leningrad: Leningr. Gos. Univ., 1974.
13. Adkins, H. and Billica, H.R., *J. Am. Chem. Soc.*, 1955, vol. 70, pp. 695–701.