HYDROGENATION OF THE β AND γ ISOMERS OF 1,4-BIS(4'-HYDROXY-1',2',5'-TRIMETHYL-4'-PIPERIDYL)-1,3-BUTADIYNE

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The kinetics of the hydrogenation of the β and γ isomers of 1,4-bis(4'-hydroxy-1', 2', 5'-trimethyl-4'-piperidyl)-1,3-butadiyne in methanol and ethanol on the catalysts Raney nickel, platinized carbon, and palladium on supports has been studied. It has been shown that the rates of hydrogenation of the β and γ isomers differ on all the catalysts. In the presence of platinum and nickel, hydrogenation takes place as far as the saturated compound, and in the presence of palladium to the diene.

The difference in the rates of hydrogenation of various isomers was measured long ago. Thus, Paal and Schiedewitz [1,2], hydrogenating the cis and trans isomers of unsaturated acids and their salts, found that the rate of hydrogenation depends not only on their chemical structure but also on the spatial arrangement of the substituents. The cis and trans isomers of phenylbutadiene and vinylacrylic acid [3], allyl esters of oleic and elaidic acids [4], and dimethylstilbene [5] have been subjected to hydrogenation, and the hydrogenation of the individual isomers of acetylenic alcohols has been studied in investigations of Narazov [6] and Sokol'skaya [7].

In the present work, we studied the kinetics of the hydrogenation of the β and γ isomers of 1,4-bis (4'-hydroxy-1',2',5'-trimethyl-4'-piperidyl)-1,3-butadiyne (**Ia** and **Ib**) on the catalysts Raney nickel, platinized carbon, and palladium on various supports in 96% ethanol, methanol, and 0.1 N methanolic solutions of HCl and NaOH at 20 and 30° C with the simultaneous measurement of the potential during the reaction.

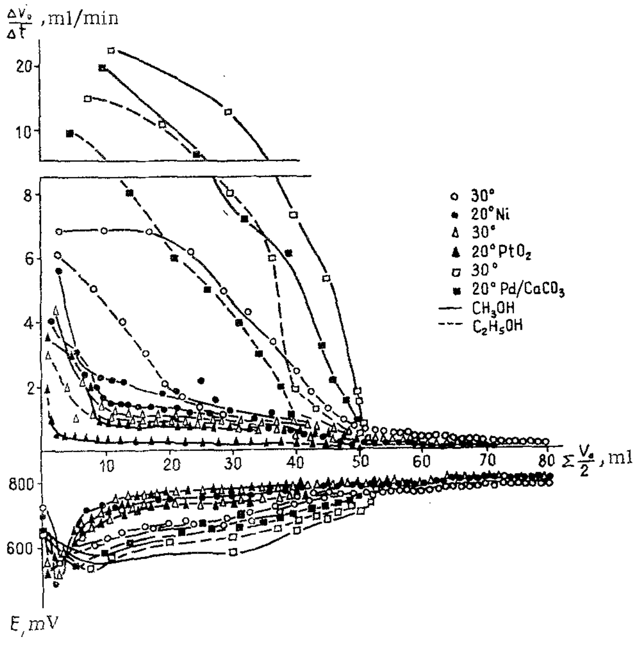


Fig. 1. Kinetic and potentiometric curves of the hydrogenation of the β isomer.

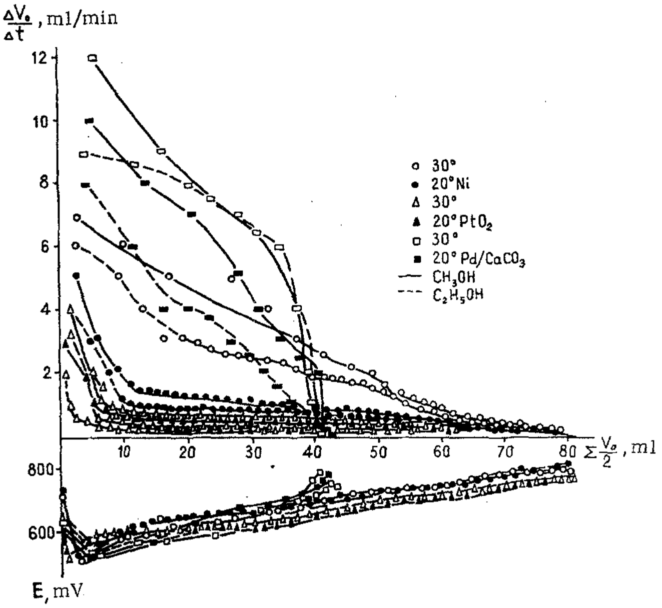
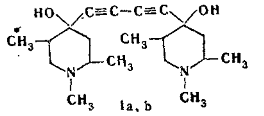


Fig. 2. Kinetic and potentiometric curves of the hydrogenation of the γ isomer.



Ia, b

EXPERIMENTAL

The starting materials Ia and Ib were synthesized in our laboratory and characterized by the following constants: Ia, mp 207°-208° C, R_f 0.94 (Al_2O_3, activity II, acetone-methanol, 1:1), IR spectrum: 2160 cm^{-1} ($-C{\equiv}C-$); Ib, mp 231°-232° C, R_f 0.92 (Al_2O_3, activity II, acetone–methanol, 1:1), IR spectrum: 2170 cm^{-1} ($-C{\equiv}C-$).

A mixture of the β and γ isomers melted at 185°-192° C. Hydrogenation was carried out in a long necked hydrogenation flask with the simultaneous measurement of the potential during the reaction [8]. The Raney nickel was prepared from Ni-Al alloy (33% Ni) by leaching with 20% NaOH. The PtO_2 was prepared by Adams' method [9]. The palladium on various supports was obtained by appropriate methods: Pd/$BaSO_4$ [10, 11], Pd/$CaCO_3$ [12], Pd/SiO_2 [13], and Pd/C [14]. The content of palladium on the supports was 5% (by weight). The following weights of catalyst were taken for the reaction: 1 g for the Ni-Al alloy, which corresponded to 0.33 g of Ni, 0.1 g of PtO_2 (0.071 g of Pt), and 0.3 g of Pd on a support (0.015 g of Pd).

In individual cases, a sample of catalyst was used repeatedly. The weight of substance hydrogenated in each experiment was constant (0.3 g) which corresponded to the addition of 80.9 ml of hydrogen,

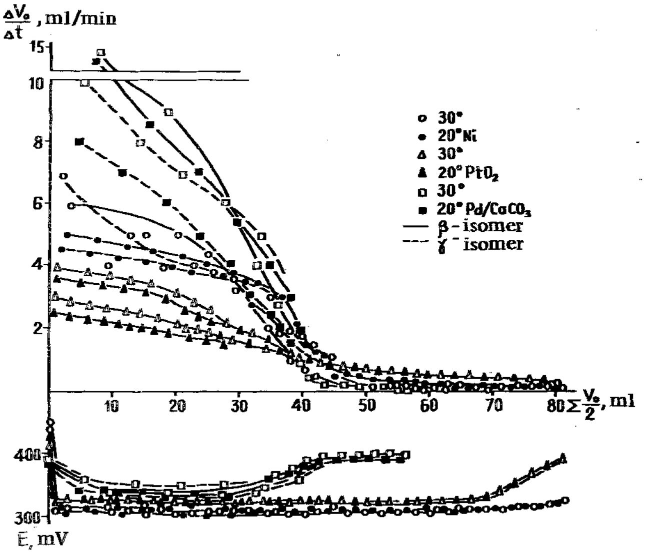


Fig. 3. Comparative kinetic and potentiometric curves of the hydrogenation of the β and γ isomers in a 0.1 N solution of hydrochloric acid in methanol.

under normal conditions calculated for hydrogenation to the saturated compound. The solvents used were 96% ethanol, methanol, and 0.1 N methanolic solutions of HCl and NaOH. The amount of hydrogen absorbed and the potential during the reaction were measured every minute. The results of the investigations were plotted in the form of kinetic and potentiometric curves, the rate of hydrogenation being plotted along the axis of ordinates upwards and the potential downwards, and the amount of hydrogen absorbed along the axis of abscissas.

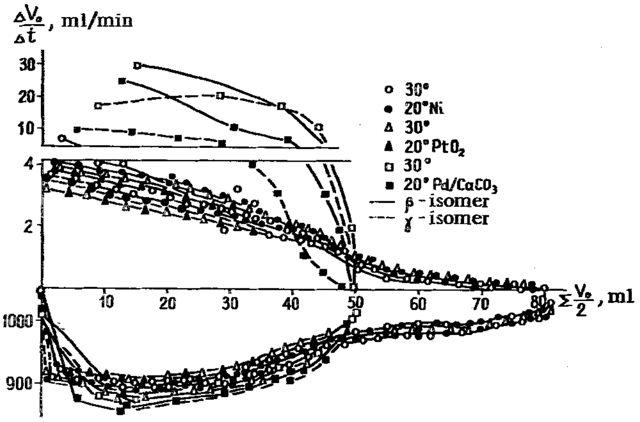


Fig. 4. Comparative kinetic and potentiometric curves of the hydrogenation of the β and γ isomers in a 0.1 N solution of caustic soda in methanol.

Hydrogenation of the β isomer (Ia) on various catalysts. The β isomer (Ia) of the given compound hydrogenated differently according to the nature of the catalyst. Figure 1 shows the kinetic and potentiometric curves of hydrogenation in 96% ethanol and methanol on various catalysts at 20° and 30° C. It can be seen that the rate of hydrogenation depends on the temperature: in 96% ethanol it is lower than in methanol, which is obviously due to the poorer solubility of the substance in ethanol. On a nickel catalyst, hydrogenation takes place at a gradually decreasing rate from the very beginning of the reaction. The theoretically calculated amount of hydrogen is absorbed, which indicates hydrogenation to the saturated compound. An analysis of the reaction products by means of their IR spectra showed the absence of unsaturated bonds. A change in potential of 180 mV in the anode direction takes place in the first minute after the addition of the substance and then gradually returns into the cathode region during the reaction. The rate of hydrogenation depends on the temperature. On PtO$_2$, the shape of the kinetic and potentiometric curves is similar to those on a nickel catalyst.

Hydrogenation in the presence of palladium on a support takes place quite differently. The amount of hydrogen theoretically calculated for hydrogenation is not absorbed, which indicates incomplete hydrogenation. Analysis of the reaction products showed that hydrogenation takes place as far as the formation of a double bond. It can be seen from the potentiometric curves (Fig. 1) that the potential changes by 50-60 mV in the anode direction in the first minute and returns into the cathode direction during the reaction. The rate of hydrogenation increases with a rise in the temperature.

Hydrogenation of the γ isomer (Ic) on various catalysts. The kinetic and potentiometric curves of the hydrogenation of the γ isomer (Fig. 2) are similar to the corresponding curves for the β isomer, but the rates of their hydrogenation differ greatly. The difference in the rates of hydrogenation of the β and γ isomers, which is greatest for the palladium catalyst, is obviously connected with the different spatial arrangement of the diacetylene group. In the presence of palladium and nickel catalysts, the γ isomer hydrogenates exhaustively in the presence of palladium to the diene derivative. It is characteristic that in Pt catalysis the rate of hydrogenation scarcely depends on the temperature. In ethanol, the process takes place more slowly than in methanol with all catalysts.

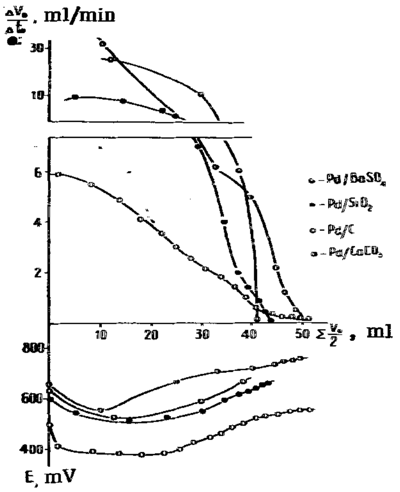


Fig. 5. Comparative kinetic and potentiometric curves of the hydrogenation of the β and γ isomers in the presence of palladium deposited on various supports.

Hydrogenation of Ia and Ib in various media. The rate of hydrogenation of the two isomers depends on the medium. Thus, in a 0.1 N methanolic solution of hydrochloric acid the hydrogenation of both isomers takes place somewhat more slowly than in pure methanol. Figure 3 shows the kinetic and potentiometric hydrogenation curves for the two isomers in acidified methanol. It can be seen that with the use of nickel and platinum catalysts the rate of hydrogenation scarcely depends on the temperature while when palladium on a support is used the influence of the temperature is more considerable. In the presence of platinum and nickel, hydrogenation takes place with a fall in the rate from the very beginning of the reaction while in Pd catalysis retardation is observed only in the addition of the second mole of hydrogen. In the given solvent, the γ isomer hydrogenates more slowly with all the catalysts than the β isomer. The lower rate of the reaction in the acidified solution as compared with the rate of hydrogenation in pure methanol is possibly connected with the formation of hydrochlorides which are less soluble in methanol. In the hydrogenation of the isomers in a 0.1 N methanolic solution of NaOH (catalysts — Ni and Pt), the second mole of hydrogen adds very slowly and with palladium catalysis the hydrogenation ceases at the formation of the diene derivatives. Figure 4 shows the kinetic and potentiometric curves of the hydrogenation of the two isomers in alkaline methanol solution.

Hydrogenation of Ia and Ib on supported palladium catalysts. The hydrogenation of the individual isomers in the presence of palladium (5% of Pd) deposited on various supports ($BaSO_4$, $CaCO_3$, SiO_2, C) was checked. The rate of hydrogenation of the isomers mentioned depends on the nature of the support (Fig. 5). The rate of hydrogenation with palladium catalysts on supports can be arranged in the following sequence with respect to the nature of the support:

$$Pd/(BaSO_4 > CaCO_3 > SiO_2 > C)$$

In all cases, practically only the diacetylene bond is hydrogenated and the diene bond formed in the hydrogenation process is either not hydrogenated at all or is hydrogenated at a very low rate.

It must be mentioned that the isomers hydrogenate at different rates: the β isomer faster than the γ isomer. Calculation of the specific activity of the catalysts (the rate calculated to 1 g of active metal) permits them to be arranged in the following sequence:

$$Pd > Ni > Pt$$

The hydrogenation products do not poison the surface of the catalysts appreciably. On hydrogenation of two successive samples of substance under the same conditions, the rate does not fall.

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