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Fig. 1. Dependence of the hydrogenation rate of unsaturated compounds and ΔE on pH. Conditions: 0.3 g skeletal Ni; 50 ml buffer solution; 30°; 1 –hexene-1 (0.7 g; alcohol $A_{\mathrm{H}_2} = 150$ ml H_2); 2 –allyl alcohol (0.3 g; $A_{\mathrm{H}_2} = 131.3$ ml H_2); 3 –cinnamyl alcohol (1.0 g; $A_{\mathrm{H}_2} = 167.1$ ml H_2); 4 –DMEC (0.3 g; $A_{2\mathrm{H}_2} = 183.5$ ml H_2); 5 –phenylacetylene (0.3 g; $A_{2\mathrm{H}_2} = 144.9$ ml H_2).

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Abstract

Full Text

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Hydrogenation of Unsaturated Compounds in Buffer Solutions

In hydrogenation in the liquid phase, the medium may influence the rate (1,2,8,10,13,15,17) of the reaction and its direction (14), the amount of hydrogen sorbed (6,7,9,11), the strength of its bond with the catalyst surface (12,18), and its reproducibility (9,19). Foresti showed (3–5) that, in the hydrogenation of certain compounds in buffer solutions (with pH changing during the experiment), as pH increases the catalyst is deactivated (Pt/Pt gauze), but upon acidification its activity is almost completely restored. A systematic study of the effect of solution pH on the rate of hydrogenation of unsaturated compounds on Pt/Pt gauze in buffer solutions, with variation of the catalyst potential, was carried out by Beck and Geriischer (16). Various types of dependence of the hydrogenation rate and of the potential shift on the pH of the medium were obtained.

Fig. 1. Dependence of the hydrogenation rate of unsaturated compounds and ΔE on pH. Conditions: 0.3 g skeletal Ni; 50 ml buffer solution; 30°; 1 –hexene-1 (0.7 g; alcohol $A_{\mathrm{H}_2} = 150$ ml H_2); 2 –allyl alcohol (0.3 g; $A_{\mathrm{H}_2} = 131.3$ ml H_2); 3 –cinnamyl alcohol (1.0 g; $A_{\mathrm{H}_2} = 167.1$ ml H_2); 4 –DMEC (0.3 g; $A_{2\mathrm{H}_2} = 183.5$

Fig. 2

Figure 2: Fig. 2

ml H_2); 5 –phenylacetylene (0.3 g; $A_{2\mathrm{H}_2} = 144.9$ ml H_2).

We studied the hydrogenation of hexene-1, allyl and cinnamyl alcohols, dimethylethynylcarbinol (DMEC), and phenylacetylene on skeletal nickel, platinum black, and palladium on barium sulfate, prepared as usual (20–22), at 5, 30, and 45° in buffer solutions with variation of the catalyst potential (23). The buffer solution consisted of a mixture of 0.04 M H_3BO_3, 0.04 M H_3PO_4, and 0.04 M CH_3COOH in 50% ethanol; by adding 4 N KOH to the solution, the pH was varied in the range 2.4–13.0. None of the anions of this buffer solution was specifically adsorbed on the catalyst surface; the qualitative composition of the mixture remained constant.

Each experiment was carried out to completion at the specified pH value. Electrometric pH control was performed with the aid of a hydrogen electrode, which served as the hydrogenation catalyst, paired with a saturated calomel electrode —by measuring the e.m.f. of this circuit with a high-resistance potentiometer and converting the obtained e.m.f. value (mV) into pH units using Schwabe' s nomogram (25).

The measured pH values differed from the pH of the aqueous buffer solution, with the same amount of alkali added, by no more than 0.1-0.2 pH units. The potentials in solutions with a given pH were almost identical for powdered Pt, Pt, and Ni electrodes.

The hydrogenation procedure and apparatus have been described previously (20,23).

Figure 1 presents curves expressing the dependence of the rate of hydrogenation of unsaturated compounds and the shift of the potential of Raney nickel on pH. As is seen from Fig. 1, the rate of hydrogenation of hexene-1 (curve 1) at 30° decreases continuously as the pH rises from 7.0 to 13.0. The same phenomenon is observed at 5 and 45°. The shift of the potential (ΔE) into the anodic region during the reaction is small (10–20 mV); consequently, the reaction proceeds with the catalyst surface almost completely filled with hydrogen. Calculation of the apparent activation energy from the kinetic and potentiometric data by formula (19) gives well-coinciding results—5-6 kcal/mole—and indicates that the reaction is limited by activation of hexene-1.

Fig. 2. Dependence of the rate of hydrogenation of unsaturated compounds and ΔE on pH. Conditions: 0.1 g Pd/BaSO$_4$; 50 ml of buffer solution; 30°; 1—hexene-1; 2—allyl alcohol; 3—cinnamyl alcohol; 4—DMEK; 5—phenylacetylene.

The rate of hydrogenation of allyl alcohol, on the contrary, increases somewhat with increasing pH (Fig. 1, 2); the very same occurs at 5 and 45°, and at 5° the reaction rate is almost 4 times lower than at 30°. With increasing pH, ΔE

rises from 60 to 80 mV. The rate of hydrogenation of cinnamyl alcohol (Fig. 1, 3) increases with increasing pH at an ever-increasing ΔE (from 80 to 110 mV). The shift of the potential and the value of the apparent activation energy (7-8 kcal/min) indicate an equal degree of adsorption and activation both of hydrogen and of the unsaturated compound.

The rate of hydrogenation of DMEK with increasing pH (Fig. 1, 4) increases considerably: from 13.0 to 28.0 ml H_2 per min. when ΔE changes from 80 to 100 mV in the case of hydrogenation of the triple bond, and from 12.0 to 25.0 ml H_2 per min. and ΔE from 70 to 90 mV in hydrogenation of the double bond formed (dimethylvinylcarbinol). An increase in the hydrogenation rate with increasing pH also occurs at 5 and 45°.

The influence of alkali is probably associated with improvement of the conditions for hydrogenation of DMEK owing to a shift of the equilibrium on the nickel surface (24):

$$H_{2\mathrm{gas}} \rightleftarrows H_{2\mathrm{ads}} \rightleftarrows 2H_{\mathrm{ads}}$$

toward the formation of H_{ads}, which effects the hydrogenation. The rate of hydrogenation of phenylacetylene (both of the triple bond and of the double bond formed) in the pH range 6.5-10.5 increases, and with further increase in pH changes little; in this case the triple bond is hydrogenated at a lower rate than the double bond (styrene).

Thus, in hydrogenation on Raney nickel there are different types of dependence of the reaction rate on pH: with increasing pH the rate of hydrogenation decreases (hexene-1), or increases (allyl and cinnamyl alcohols, DMEK), or passes through a maximum at pH 9.5-10.5 (phenylacetylene).

In hydrogenation on $Pd/BaSO_4$ and on platinum black, the pH range was extended from 2.5 to 13.0.

The rate of hydrogenation of hexene-1 at 5° on $Pd/BaSO_4$ in the pH interval 2.4-7.5 remains almost constant; with further increase in pH it falls (from 8.0 to 0.8 ml/min) as ΔE decreases (from 70 to 0). An analogous phenomenon is observed at 30° (Fig. 2, 1); in this case ΔE in magnitude is almost

are half as small, while the reaction rates are higher. Consequently, at 30° a smaller fraction of the surface can provide better activation of the reacting substances. In acidic solutions (pH 2.4-6.5), a good hydrogenation rate is ensured by hydrogen ions ([26]); in an alkaline medium the reaction proceeds at the expense of atomically adsorbed hydrogen ([19]).

Allyl alcohol at 30° in the pH range 2.4-8.0 is hydrogenated at an almost constant rate, which decreases only slightly with increasing pH (Fig. 2, 2); ΔE decreases with increasing pH (from 100 to 30 mV). In an alkaline medium the hydrogenation rate decreases owing to a slowing of the sorption and atomization of hydrogen on Pd from the gas phase ([27]).

Fig. 3. Dependence of the hydrogenation rate of unsaturated compounds and ΔE on pH. Conditions: 0.1 g PtO_2; 50 ml buffer solution; 5°. The designations are the same as in Fig. 2

Figure 3: Fig. 3. Dependence of the hydrogenation rate of unsaturated compounds and ΔE on pH. Conditions: 0.1 g PtO_2; 50 ml buffer solution; 5°. The designations are the same as in Fig. 2

The hydrogenation rate of cinnamyl alcohol at 5° in the pH range 2.4–12.5 passes through a small maximum (at pH 7.5–10.5; at 30°, pH 8.1); above pH 10.0–11.0 the rate falls (Fig. 2, 3); ΔE decreases with increasing pH.

The apparent activation energy, calculated from potentiometric data ($\Delta E = 120$ mV), is 9 kcal/mole, which indicates that the reaction is limited by hydrogen activation.

Hydrogenation of DMEK on $Pd/BaSO_4$ in the pH range 2.4–13.0 proceeds with an ever-increasing rate: at 30° from 50.0 to 64.0 ml H_2 per min (Fig. 2, 4), and at 5° from 22.0 to 34.0 ml H_2 per min. The shift of the potential into the anodic region increases from 130 to 200 mV. The relatively high rate of the reaction occurring on a surface almost devoid of hydrogen indicates the participation in the reaction of hydrogen from the inner layers of palladium.

Fig. 3. Dependence of the hydrogenation rate of unsaturated compounds and ΔE on pH. Conditions: 0.1 g PtO_2; 50 ml buffer solution; 5°. The designations are the same as in Fig. 2.

The hydrogenation rate of the triple bond of phenylacetylene on $Pd/BaSO_4$ passes through a small maximum: at pH 7.0 (5°) and pH 8.1 (30°) (Fig. 2, 5); the hydrogenation rate of the double bond (styrene) increases with increasing pH. The shift of the potential into the anodic region is large: from 360 to 700 mV at 5° and from 240 to 400 mV at 30°.

Hydrogenation of 1-hexene at 5° on platinum black in the pH range 2.4–13.0 proceeds with a gradually decreasing rate, while ΔE changes from 3.5 to 5 mV (Fig. 3, 1).

Allyl alcohol is hydrogenated on platinum black at a considerably lower rate; in the pH range 8.2–10.5 a maximum is observed, to which the maximum value of ΔE corresponds (Fig. 3, 2).

Hydrogenation of cinnamyl alcohol on platinum black proceeds at a rate that changes little in the pH range 2.4–10.5; with further increase in pH the reaction rate falls (Fig. 3, 3); ΔE is small (8–10 mV); consequently, the reaction proceeds with considerable filling of the catalyst surface by hydrogen.

During hydrogenation of DMEK on platinum black (Fig. 3, 4) at 5° there is a gradual increase in the hydrogenation rate both of the triple bond and of the double bond formed in the pH range 2.4–10.5; with further increase in pH the rate falls; hydrogenation of the $> C = C <$ bond proceeds at a higher rate at a constant value of ΔE, equal to 25 mV.

The rate of hydrogenation of phenylacetylene (of the triple bond and the double bond formed) in the pH interval 2.4-12.5 increases, while the rate of hydrogenation of the benzene ring decreases from 0.8 to 0.0 ml H_2/min; ΔE is small: 30-55 mV ($-C \equiv C-$); 25-40 mV ($-C = C-$) and 3.0-1.0 mV (ring).

Thus, the most general regularity is that, as the shift in the catalyst potential decreases with increasing pH, the rate of hydrogenation of the unsaturated compound also decreases. The following types of dependence of the hydrogenation rate on pH were found: (a) systematic decrease in the reaction rate with increasing pH (hexene-1; Ni; Pt); in this case direct participation of hydrogen ions in the reaction should be assumed. (b) The reaction rate does not depend on pH up to a value of 7 (hexene-1; allyl alcohol; Pd); in this case, the reaction is probably inhibited by adsorption of cations or hydroxyls, leading to recharging of the surface ([28]). (c) The reaction rate does not depend on increasing pH in the interval 2.4-13.0 (DMEC, phenylacetylene; Pt). In this case the unsaturated compound displaces all adsorbed cations and anions from the catalyst surface. (d) The reaction rate increases with increasing pH (cinnamyl alcohol, DMES on Ni; allyl alcohol on Pt), which is due to the strength of the bond between hydrogen and the catalyst surface.

In view of the increase in the energy of the bond between hydrogen and the catalyst surface in the sequence Pt > Ni > Pd, these cases are realized on different catalysts at different pH values.

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