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Abstract

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SELECTIVE HYDROGENATION OF MONOSACCHARIDES AND POLYHYDRIC ALCOHOLS

I. As shown in the scientific and patent literature (for a review, see ([1])), and also by our experiments (([1]), cf. ([2])), over Ni catalysts in aqueous solution at 150–300 atm of hydrogen the following reactions take place.

1. Monosaccharides at 120–130° are hydrogenated practically completely into the corresponding polyhydric alcohols: xylose into xylitol, glucose into sorbitol, etc.
2. With an increase in temperature, hydroxyl groups are split off from the alcohols, primarily terminal ones; thus, from glycerol 1,2-propylene glycol is formed, and from the latter isopropyl alcohol. Higher alcohols lose hydroxyls with more difficulty than lower ones.
3. Still more difficultly, when hydrogen is deficient (for example, with insufficient stirring), from monoses, in amounts up to several percent, uronic acids are formed, producing an acid reaction of the medium.
4. These reactions are partly competed with, but in general occur at an even higher temperature (220–230°), by reactions involving cleavage of the C —C bond, most often in the middle of the molecule. Thus, from sorbitol under certain conditions propylene glycol and glycerol are formed.

Depending on the structure of the molecules, the indicated sequence is sometimes somewhat disturbed, but the general regularity emerges quite clearly from the experimental material.

II. Among the works concerning the mechanism of these reactions, two are of interest: those of Schmidt ([3]) and, especially, of Natta, Rigamonti, and Beati ([4]). Both deal with Ni catalysts. Schmidt ([3]), on the basis of extensive material, concludes that in the hydrogenolysis of carbohydrates rupture of the C—C bond occurs in position 3,4. He explains this by the fact that the pentitols and hexitols formed at 200° are partially dehydrogenated back to pentoses and hexoses, the aldehyde group of which enolizes; as a result, the adjacent C—C bond is strengthened and weakened, and then the next C—C bond following it is ruptured. Schmidt' s explanation, however, is refuted by the fact that at a hydrogen pressure of 150–300 atm at 220° any appreciable dehydrogenation is unlikely.

Natta, Rigamonti, and Beati ([4]) believe that the reaction which first occurs is the one with the lower free energy ΔF (at 298° K). However, first, this is not theoretically substantiated, and second, it is justified experimentally only for individual series of compounds, and not in the general case. If the rule of the Italian authors were always valid, then, for example, in the hydrogenation of hexitol the hydroxyl groups would first be split off (since the splitting off of a primary hydroxyl corresponds to $\Delta F = -22\,000$ cal/mol, and of a secondary one to $\Delta F = -18\,000$ cal/mol), while glycerol could not be formed at all (since here $\Delta F = -4600$ cal/mol). This completely contradicts experience.

III. Below, the multiplet theory of catalysis ([5]) is applied to the reactions under consideration; it gives the correct sequence in hydro-

ration and hydrogenolysis of various compounds ([5]), including derivatives of furan ([6]), triptycene ([7]), and organic peroxides ([8]).

The multiplet theory singles out in the molecule the reacting atoms into the so-called index, doublet group:

$$\boxed{\begin{matrix} A & D \\ B & C \end{matrix}} \longrightarrow \boxed{\begin{matrix} A \cdots D \\ B \cdots C \end{matrix}} (M) \longrightarrow \boxed{\begin{matrix} A - D \\ B - C \end{matrix}} \tag{1}$$

These atoms come into contact (although not necessarily simultaneously) with the catalyst K. In this case the reaction rate is the greater, the better the structural and energetic correspondence is satisfied. In the case under consideration, structural correspondence does indeed take place, as was shown earlier for the same atoms ([5]). Energetic correspondence is satisfied the more fully, the lower the energy barrier $(-E)$, or, in other words, the greater the value

$$E = -Q_{AB} - Q_{CD} + (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}), \tag{2}$$

where Q denotes bond energies, and A, B, C, D, K are the same atoms as in formula (1).

Thus, the larger E, the greater the reaction rate. It should be emphasized that E is a kinetic quantity—this is the energy of formation of the multiplet active complex (equal to 4/3 of the activation energy, with the opposite sign), and not the heat of reaction, considered in principle by Berto, or ΔF by the Italian authors.

Taking the indices of the reactions of interest to us and substituting into equation (2) the values of Q (a summary of which is given in ([9])), for the Ni catalyst we obtain the results presented in Table 1. Upon rupture of C–C bonds, $E > -48000$ kcal/mole, since here these bonds experience a well-known considerable weakening owing to the presence of hydroxyls near them. This weakening will be amenable to exact quantitative accounting when the individual bond energies have been measured. However, even now the sequence of reactions in Table 1

corresponds to experiment (see point I), in contrast to the theoretical results of previous authors (see point II).

Table 1

Calculated comparative ease E of reactions over Ni (effect of the nature of the atoms in the index)

No.	Type of reaction	Reaction index	E_{calc}, cal/mole
1	Hydrogenation of the carbonyl bond of monosaccharides	$>C \quad H$ $\parallel \quad \mid$ $O \quad H$	-10000
2	Reduction of an alcohol group, hydrogenolysis of the C–O bond	$\geq C \quad H$ $\mid \quad \mid$ $O \quad H$	-17000
3	Cannizzaro reaction, formation of uronic acids	$>C \quad H$ $\parallel \quad \mid$ $O \quad C\leq$	-32000
4	Rupture of the carbon chain of an alcohol, hydrogenolysis of the C–C bond	$\geq C \quad H$ $\mid \quad \mid$ $\geq C \quad H$	>-48000

Incidentally, the data of Table 1 clearly show that in the case of monosaccharides the open, oxo form must be hydrogenated, for which $E = -10000$ cal/mole, and not the cyclic forms predominating in aqueous solution, for which E is smaller ($E = -17000$ cal/mole). At the same time, as the hydrogenation of acetals over Ni shows ([10]), the second oxygen atom in the α-position does not weaken the C–O bond too strongly.

IV. The influence of structure on the rate of a reaction of one type occurs as a result of the influence of framework substituents. Thus, the introduction of a substituent, for example at atom A in formula (1), affects Q_{AB} and

Q_{AK} in formula (2). Because of this E changes ([11]), and consequently so does the reaction rate. The calculation gives the following.

Varying the quantities containing A in equation (2), in the equation for the heat of reaction $u = Q_{\mathrm{AD}} + Q_{\mathrm{BC}} - Q_{\mathrm{AB}} - Q_{\mathrm{CD}}$ (cf. formula (1)), and in the known thermodynamic equation $\Delta F = -u - T\Delta S$, where S is entropy, we obtain

$$\begin{aligned} \delta E &= \delta Q_{\mathrm{AK}} - \delta Q_{\mathrm{AB}}, \\ \delta u &= \delta Q_{\mathrm{AD}} - \delta Q_{\mathrm{AB}}, \\ \delta\Delta F &= -\delta u - T\delta\Delta S. \end{aligned} \tag{3}$$

It follows from equations (3) that, if a substituent is introduced at A, then

$$\delta E = -\delta\Delta F - (T\delta\Delta S - \delta Q_{\mathrm{AD}} + \delta Q_{\mathrm{AK}}). \tag{4}$$

For condensed (i.e., solid and liquid) systems, $\delta\Delta S$ should be small; the quantities δQ_{AD} and δQ_{AK} are also small in comparison with $\delta\Delta F$ and, moreover, enter equation (4) with different signs. Therefore, if no gases are evolved during the reaction, then in equation (4) the quantity in parentheses should be small. Hydrogen is present in the system in all cases. On the basis of everything stated above,

$$\Delta E \simeq -\delta\Delta F. \tag{5}$$

Thus, the reaction should proceed the more readily, the greater the decrease in the free energy of the reaction $\delta\Delta F$ caused by substitution. Equations (4) and (5) differ from the regularity of Natta, Rigamonti, and Beati above all in that they concern variations of $\delta\Delta F$, and not the ΔF themselves. In addition, equations (4) and (5) are theoretically substantiated.

Table 2

Calculated comparative ease δE of the course of hydrogenolysis reactions of C–O bonds in polyhydric alcohols over Ni (effect of substituents on reaction 2 of Table 1)

No.	Reaction	$\delta E = -\delta\Delta F_{\mathrm{calc.}}$, cal/mol
1	Hexitol → methylpentitol + H_2O	2600
2	Pentitol → methylerythritol + H_2O	2600

No.	Reaction	$\delta E = -\delta\Delta F_{\text{calc.}}$, cal/mol
3	Erythritol → methylglycerol + H_2O	2700
4	Erythritol → butene-triol-(1,2,4) + H_2O	−300
5	Glycerol → propylene glycol-(1,2) + H_2O	2100
6	Glycerol → propylene glycol-(1,3) + H_2O	−1300
7	Propylene glycol → *n*-propyl alcohol + H_2O	−1600
8	Propylene glycol → isopropyl alcohol + H_2O	2500
9	Ethylene glycol → ethyl alcohol + H_2O	−2700

For the hydrolysis of the compounds under consideration, Tables 2 and 3 give the values of $\delta\Delta F$, since the ΔF values of the Italian authors[4] were calculated from the free energies of formation according to the data of Parks and Huffman[12]. As the origin for $\delta\Delta F$, the mean between the limiting values of this quantity in the given table was adopted. Reactions giving gaseous methane are not included in Tables 2 and 3 for the reasons indicated above.

It can be seen that the sequence of reactions calculated from $\delta\Delta F$ is in agreement with experiment. Preferential rupture of the carbon chain indeed occurs in the middle (see Nos. 1, 4, 12 of Table 3) and is explained by the fact that here the value of $Q_{\text{C–C}}$ is the smallest, increasing toward the ends of the chain. Primary hydroxyls are split off more easily than secondary ones (see Nos. 3 and 5 in Table 2). In Table 1, in reaction 4, the influence of hydroxyl groups is taken into account summarily by indicating that $E > -48{,}000$ cal/mol. However, it is clear that the more hydroxyl groups accumulate, the more the C–C bond should be weakened. This consideration, unlike that of the Italian authors, is able to explain why in higher alcohols–hexitols and pentitols–rupture of the C –C bond precedes cleavage of hydroxyls,

whereas for the lower ones–glycerol and ethylene glycol–the opposite is true. Therefore, the formation of 1,2-propylene glycol from glycerol (see no. 5, Table 3) proves to be regular; moreover, the fact that precisely the 1,2- and not the 1,3-

isomer is formed (see nos. 5 and 6, Table 2) is in agreement with experiment. This explains why, in the hydrogenolysis of sorbitol, a mixture of propylene glycol and glycerol of varying composition is obtained.

Table 3

Calculated relative ease δE of the occurrence of hydrogenolysis reactions of C–C bonds in polyhydric alcohols over Ni (effect of substituents on reaction 4 of Table 1)

No.	Reaction	$\delta E = -\delta\Delta E_{\text{calc}}$, cal/mol
1	Hexitol → 2 moles of glycerol	1200
2	Hexitol → erythritol + ethylene glycol	400
3	Hexitol → methanol + pentitol	160
4	Methylpentitol → glycerol + propylene glycol	700
5	Methylpentitol → methylglycerol + ethylene glycol	500
6	Methylpentitol → methylerythritol + methanol	−1060
7	Pentitol → ethylene glycol + glycerol	1100
8	Pentitol → erythritol + methanol	−40
9	Methylerythritol → ethylene glycol + propylene glycol	600
10	Methylerythritol → ethanol + glycerol	−600
11	Methylerythritol → methanol + methylglycerol	−40
12	Erythritol → 2 molecules of ethylene glycol	1200

No.	Reaction	$\delta E = -\delta\Delta E_{\text{calc}}$, cal/mol
13	Erythritol → glycerol + methanol	200
14	Methylglycerol → ethanol + ethylene glycol	−1200
15	Methylglycerol → methanol + propylene glycol	200
16	Glycerol → ethylene glycol + methanol	−40

In essence, the values of δE from Tables 2 and 3 should be added to E from Table 1. This is the main difference from the calculation methods of previous authors, making it possible to avoid the contradictions with experiment indicated in section II. The influence of the nature of the catalyst is taken into account by terms with the signs K in equations (2) and (4).

Thus, the application of the multiplet theory appears highly promising in the field of hydrogenation of monosaccharides and polyhydric alcohols, as is evident from Tables 1, 2, and 3; we intend to continue developing these questions.

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Note: Figure translations are in progress. See original paper for figures.