THE CHEMICAL PROCESS ACCOMPANYING THE HYDROGENATION OF FATS

I. GEOMETRICAL ISOMERIZATION

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The industry of the heterogeneous catalytic hydrogenation of liquid fats (vegetable oils and whale oils) in order to convert them into solid fats arose shortly before the First World War. Laboratory investigations in this direction the results of which are reflected in the papers of Sabatier and Senderens, Paal, Skita, V. N. Ipat'ev (Ipatieff), S. A. Fokin, and others [1] date from an even earlier period.

Over the course of several decades, the hydrogenation process has been treated as a process of the addition of hydrogen to the radicals of unsaturated fatty acids (oleic, linoleic, etc.) at the positions of the multiple bonds. However, in the last two or three decades a number of papers have appeared by S. Yu. Elovich, B. N. Tyutyunnikov, A. A. Zinov'ev, D. V. Sokol'skii, and others showing that, in addition to the main process (hydrogenation proper), other processes also take place [geometrical (cis-trans) isomerization and the migration of double bonds].

In the present paper we shall dwell on the question of geometrical isomerization. This process of the conversion of cis isomers into trans isomers is accompanied by a marked change in the physical properties of the fatty acids and, it stands to reason, of their glycerides. Thus, for example, cis-octadecenoic (oleic) acid with mp 16.3-18.4°C is converted into the trans acid (elaidic) with mp 46.5°C. To the numerous observations of other authors we shall add some of our own characterizing the influence of the hydrogenation conditions on the accumulation of trans isomers in the oil.

The results of some of our experiments are given in Tables 1-3. These tables show that copper–nickel catalysts with different ratios of the metals affect the accumulation of trans isomers in different ways. Particular interest is presented by the circumstance that the isomerizing activity of the catalysts changes with their composition, just like their hydrogenating capacity, which is characterized by a fall in the iodine number of the fat (Δ I No.) (see Table 3). Catalysts with a ratio of the metals of 1:1 are the most active both in the hydrogenation processes proper and in cis-trans isomerization.

TABLE 1. Accumulation of trans Acids in Hydrogenizates as a Function of the Amount of Disperse Copper–Nickel Catalyst

Time of hydrogenation, min	Amt. of catalyst (% of total metals on oil)		
	0,05	0,10	0,20
30	0,16	0,12	1,79
60	0,14	0,36	4,61
90	0,50	1,61	6,90
120	0,96	2,76	11,15
150	1,22	3,45	10,85
180	1,98	5,22	10,09
270	2,09	7,80	7,86
330	4,06	7,61	—
390	4,26	4,49	—

With a rise in the temperature of the process the rates of hydrogenation and of isomerization rise (see Table 2). The trans acids accumulate gradually, but beyond a certain limit their amount begins to decrease because of their conversion into the saturated acids. With an increase in the amount of catalyst, the rate of isomerization rises, like the rate of hydrogenation (see Table 1). All these facts show that the mechanisms of the two reactions must be similar.

The mechanism of the hydrogenation of ethylenic compounds has been explained by A. A. Balandin from the point of view of his multiplet theory. We shall adhere to this theory in treating isomerization phenomena.

Let us dwell on the question of the mechanism of the hydrogenation of ethylenes, since we assert that the mechanism of geometrical isomerization

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TABLE 2. Influence of the Temperature on the Accumulation of trans Acids

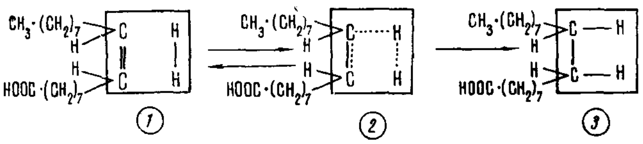
Temperature of process, °C	Maximum amt. of trans acids, %	Time of accumulation of amt., min
80	Traces	300
100	3,46	120
120	11,15	120
180	19,46	30
200	29,63	30

TABLE 3. Influence of the Composition of Disperse Copper–Nickel Catalysts on the Accumulation of trans Acids

Ni : Cu ratio	10:0	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8	1:9
Content of trans acids, %	Traces	3,78	13,64	11,59	12,27	19,73	13,34	14,57	11,05	0
Δ I. No., %	7,22	38,45	58,33	58,46	52,32	59,25	55,05	52,61	53,31	1,39

Note. Amount of catalyst 0.2% of total metals on the weight of the oil; amount of oil 250 g; rate of feed of hydrogen 5 liters/min; temperature 200°C.

is similar to that of hydrogenation. The hydrogenation of oleic acid, for example, takes place in accordance with scheme 1.



Scheme 1

The distances between the centers of the atoms of nickel in its face-centered crystal lattice are 2.49 and 3.52 Å. The investigations of Sherman et al. [2] have shown that the optimum distance for the activated sorption of hydrogen on nickel is 3.5 Å. Thus a structural correspondence is observed here.

As can be seen from scheme 1, the first half of the process is composed of the operations of the cleavage of the π bond between the carbon atoms and the σ bond between the hydrogen atoms with the simultaneous formation of sorption bonds between the atoms of the index group and the catalyst. The heat effect [3] of this part of the process is

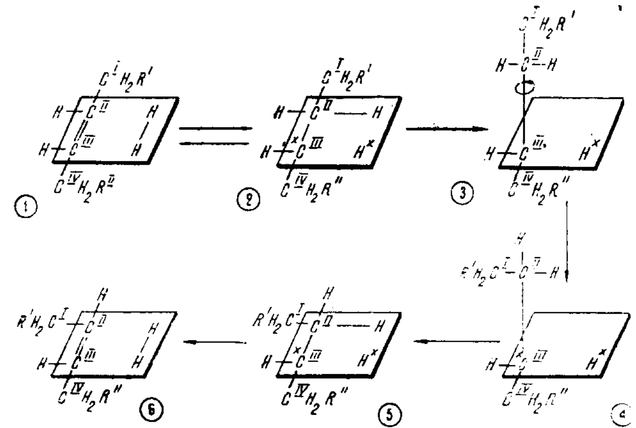
$$\varepsilon' = -(Q_{C=C}+Q_{H-H}) + (2Q_{C-K}+2Q_{H-K})$$
$$= -(63.2+104.2)+(2\cdot 29.0+2\cdot 56.6) = 7.8 \text{ kcal}$$

In the second half of the process, new bonds are established between the carbon and the hydrogen and the sorption bonds are broken, as a result of which the molecule of the saturated acid is desorbed. The heat effect is expressed by the formula $\varepsilon'' = 2Q_{C-H} - (2Q_{C-K} + 2Q_{H-K}) = 2\cdot 98.7 - (2\cdot 99.0 + 2\cdot 58.6) = 22.2$ kcal.

Further, Balandin proposes to calculate the following parameters: the heat effect of the reaction $u = -(Q_{C=C}+Q_{H-H}) - 2Q_{C-H} = -(63.2+104.2)+2\cdot 98.7 = 30.0$ kcal; the sum of the energies of the reacting bonds: $S = Q_{C=C}+Q_{H-H}+2Q_{C-H} = 63.2+104.2+2\cdot 98.7 = 364.8$ kcal; and the adsorption potential of the catalyst: $q = 2Q_{C-K}+2Q_{H-K} = 2\cdot 29.0+2\cdot 58.6 = 175.2$ kcal.

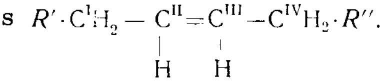
On the basis of these indices, Balandin formulates the principle of energy correspondence in the following way: "The principle of energy correspondence is that in the selection of an active catalyst for an endothermic reaction it is necessary that the adsorption potential of the catalyst q should approximate as closely as possible to half the sum of the energies of the reacting bonds, s/2 – the mean of the energies of the bonds undergoing cleavage and those being newly formed. For the most active catalyst, the energy barrier is equal to half the heat effect of the reaction catalyzed ... in the case of an exothermic reaction, for the most active catalyst the adsorption potential differs from half the energies of the reacting bonds by not more than half the heat of the reaction: $|q - S/2| \leq u/2$ ([4], pp. 113-114).

For the exothermic hydrogenation of oleic acid we obtain $|175.2 - 364.8/2| = 7.2 < 30/2$. Thus, here energy correspondence is observed. The phenomenon of geometrical isomerization is closely connected with the very process of hydrogenation. However, while hydrogenation is fairly clearly explained by scheme 1 above, in order to explain the mechanism of isomerization we must have recourse to the idea of an intermediate stage of semihydrogenation. On this approach, Balandin states: "In the ideal case, all the atoms of the index group must come into contact with the catalyst although not necessarily simultaneously ... different atoms of hydrogen and of the olefin are adsorbed in a definite sequence, giving rise to a so-called semihydrogenated form and hydrogen atoms adsorbed on the surface" ([4], p. 18).



Scheme 2

Scheme 2 shows the process of the cis-trans isomerization of some olefin – for example, the oleic acid that we mentioned above. For greater clarity the scheme is given in stereoscopic form. Four carbon atoms have been isolated from the hydrocarbon chain of the olefin and have been numbered with Roman numerals. On both sides of these four carbon atoms further methylene and functional groups (methyl, carboxyl, or ester groupings) are assumed to be present. These "tails" on the left and right are denoted by the symbols R' and R". Thus, the general form of the initial compounds is

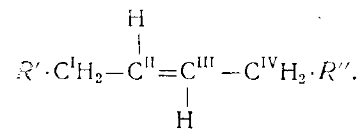


$$R'\cdot C^{I}H_2-\underset{\displaystyle H}{\underset{|}{C^{II}}}=\underset{\displaystyle H}{\underset{|}{C^{III}}}-C^{IV}H_2\cdot R''.$$

The initial cis-olefinic compound is shown in plane 1 (scheme 2), and here in the region of location of the index grouping there are two carbon atoms (C^{II} and C^{III}) connected by a double bond and a molecule of hydrogen, i.e., in this case the index grouping is the same as in hydrogenation. Through a stage of the formation of a multiplet complex, a compound is formed by semihydrogenation, which is illustrated in plane 2. As a result of the cleavage of the π bond between carbon atoms C^{II} and C^{III} and the bond between the hydrogen atoms of the molecule, and also because of the appearance of the $C^{II}-H$ bond, a hydrogen radical H^{x} and a complex radical containing a tervalent carbon atom ${}^{x}C^{III}$ are formed. These radicals remain sorbed on the surface of the catalyst, which does not exclude the possibility of their lateral diffusion ([4], p. 19). At this stage of the process, the reaction is reversible, as is indicated by the two arrows between planes 1 and 2.

Atom C^{II}, fully saturated, is less firmly bound to the active centers of the catalyst than the atom ${}^{x}C^{III}$. It is desorbed from the surface of the catalyst, but the molecule as a whole continues to be bound to the catalyst through C^{III} (plane 3). The possibility is opened up for the free rotation of all the groupings of atoms attached to C^{II} (passage from plane 3 to plane 4). A new approach of the C^{II} atom to the surface of the catalyst (passage from plane 4 to plane 5) is not excluded, but in this case the position of the index groups will be different from that in plane 2. And, finally, because of the reversibility of hydrogenation-dehydrogenation both the hydrogen molecule and the π bond between C^{II} and C^{III} are regenerated.

If we compare the compounds shown in plane 1 and plane 6, we shall see extremely similar olefins differing only by the mutual arrangement of the nonindex groups: the cis modification of the compound undergoing hydrogenation is converted by a series of transitions into the trans modification:



$$R'\cdot C^{I}H_2-\overset{\displaystyle H}{\overset{|}{C^{II}}}=\underset{\displaystyle H}{\underset{|}{C^{III}}}-C^{IV}H_2\cdot R''.$$

The reversible transformation of the trans compound into the cis isomer is less likely for thermodynamic reasons.

It is quite obvious that in the process considered there are both structural and energy correspondences, since the same index group takes part in them as in the hydrogenation process and the change in conformations leading to the appearance of the trans configuration is accompanied by the evolution of heat.

EXPERIMENTAL

Cottonseed oil was hydrogenated with a disperse copper–nickel catalyst in a reaction flask of the Favorskii type with means of stirring and a device for taking samples during the process.

The amount of trans acids was determined by IR spectroscopy on a UR-10 double-beam spectrophotometer.

SUMMARY

1. It has been shown for numerous examples that the catalytic hydrogenation of fats is accompanied by the cis-trans isomerization of the radicals of the unsaturated acids.

2. A scheme is proposed which explains the mechanism of the isomerization through a process of the hydrogenation-dehydrogenation of the olefinic compounds.

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