THE QUESTION OF THE FORMATION OF ISOMERIC FATTY ACIDS IN THE LOW-TEMPERATURE HYDROGENATION OF COTTONSEED OIL IN SOLVENTS

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We hydrogenated cottonseed oil with a palladium catalyst ([1], p. 161) previously saturated with hydrogen and without such saturation, using it either in the completely saturated form (Table 1, expt. 1), or in the completely unsaturated form (expt. 4) or in the form of a mixture of both types. The other experimental conditions were identical.

It can be seen from Table 1 that the preliminary saturation of the catalyst with hydrogen sharply lowers the rate of its absorption as compared with a catalyst not subject to hydrogenation.

The same observation has been made previously by D. V. Sokol'skii [1]. He explained this phenomenon by the assumption that in such cases the activation of the hydrogen and of the unsaturated compound take place on the same active centers of the surface of the catalyst. The hydrogenation of the catalyst leads to the coverage of all the active centers with hydrogen, which excludes the possibility of the activation of the molecules of the unsaturated compounds.

Thus, in the given case it is desirable to add the catalyst to the reaction medium without its preliminary saturation with hydrogen.

By means of further experiments we have investigated the influence of the nature of the solvent on the process of transisomerization (Table 2). The figures given in Table 2 show that in the presence of solvents the process is greatly accelerated as compared with the absence of solvents: almost four times as fast in ethanol and in hexane and almost twice as fast in acetone. This is probably due to a lowering of the viscosity of the medium and the associated weakening of obstacles to diffusion. If the diffusion factor does in fact play a fundamental part in this, with the dilution of the solution after some maximum in the rate of the process has been reached, a decrease should follow because of the lengthening of the path to be followed by the unsaturated molecules from the bulk of the solution to the surface of the catalyst particles, as we observed in the following series of experiments (Table 3). It can be seen from Table 3 that the highest rate of absorption of hydrogen is found at a ratio of oil to solvent of 1 : 2.

TABLE 1. Influence of the Preliminary Saturation of the Catalyst with Hydrogen* on the Rate of Hydrogenation

Expt. No.	Tot. amt. of Pd added, referred to the oil	Amt. of added Pd previously hydrogenated	Iodine No. of the hydrogenizate, I_2
	%		
1	0,05	0,05	66,0
2	0,05	0,02	24,0
3	0,05	0,01	15,8
4	0,05	—	5,1

*Time of hydrogenation in each experiment 20 min; I. No. of the oil 109.2.

In addition, we studied the influence of the amount of palladium catalyst on the rate of the hydrogenation processes and on cis–trans isomerization (Table 4). The results given in Table 4 show that the initial rate of hydrogenation increases in proportion to the amount of catalyst but after some limit has been reached (in our case, 0.06%) there is no further increase in the rate of the process. This phenomenon has been observed several times by other authors.

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TABLE 2. Influence of the Nature of the Solvent on the Hydrogenation Process*

Expt. No.	Solvent	Initial rate of absorp. of hydrogen, ml/min	Tot. duration of the process, min	Amt. of hydrogen absorbed, ml	I. No. of hydrogenizates, % I_2	Proportion of trans acids, %	Mp of hydrogenizates, °C
5	None	10	55	430	57,9	31,45	39,0
6	Acetone	19	26	423	56,4	33,01	39,5
7	Hexane	37	15	420	57,3	31,77	39,0
8	Ethanol	42	13	425	55,1	34,75	40,0

*In each experiment 10 ml of cottonseed oil was hydrogenated in the absence of a solvent or with 25 ml of the given solvent at 50°C using 0.05% of Pd. The initial I. No. was 109.2%.

TABLE 3. Influence of the Degree of Dilution of the Oil with Solvents on the Effect of the Absorption of Hydrogen*

Expt. No.	Amt. of hydrogen absorbed, ml	Initial rate of hydrogenation, ml of H_2/min	Tot. amt. of hydrogen absorbed, ml	Duration of the process, min	Mp of the hydrogenizates, °C
Hydrogenation in hexane at 50°C					
9	10	22	430	25	37
10	20	40	405	20	37
11	40	25	403	30	37
Hydrogenation in acetone at 40°C					
12	10	12	410	65	39
13	20	25	410	30	39
14	40	18	415	30	40
15	50	9	4.0	75	39

*Amount of oil in each experiment 10 ml; catalyst – 0.05% of Pd.

TABLE 4. Influence of the Amount of Catalyst on the Processes of Hydrogenation and cis–trans Isomerization*

Expt. No.	Amt. of Pd, %	Initial rate of hydrogenation, ml of H_2/min	Duration of hydrogenation, min	Tot. amt. of hydrogen absorbed, ml	I. No. of the hydrogenizates, % I_2	Proportion, %		Mp of the hydrogenizates, °C
						trans acids	conjugated dienes	
16	0,01	10	12	205	61,1	37,02	Absent	37
17	0,02	20	12	220	60,6	43,26	0,70	38
18	0,04	35	—	—	—	—	—	—
19	0,06	50	5	200	61,2	45,81	0,68	39
20	0,08	50	5	210	60,6	50,40	Absent	41
21	0,10	50	—	—	—	—	—	—

*In each experiment 5 ml of cottonseed oil was hydrogenated in 25 ml of ethanol at 60°C.

In addition, it can be seen from the same series of experiments that with an increase in the amount of catalyst the proportion of trans acids in the hydrogenates increases and, in parallel with this, the melting point of the fat rises.

On considering the question of the influence of the temperature on the rate of the hydrogenation process, we expected an overall increase in the rate with a rise in the temperature. However, there is information in the literature [2] according to which each solvent has its own temperature optimum at which hydrogenation takes place with the greatest rate. Thus, in acetone the maximum rate of hydrogenation is achieved at 40°C, in hexane at 50°C, and in ethanol at 60°C. Possibily, therefore, at temperatures approaching the boil-

TABLE 5. Dependence of the Rate of the Hydrogenation of Cottonseed Oil on the Temperature of the Process; Composition and Properties of the Hydrogenizates

Expt. No.	Temp. of hydrogenation, °C	Initial rate, ml of H_2/min	Duration of hydrogenation, min	Absorption of hydrogen, ml	Fatty-acid composition						I. No. of the hydrogenizates, % I_2	Proportion, %		mp of the hydrogenizates, %
					$C_{14:0}$	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$		trans acids	conjugated dienes	
					10 ml of oil in 25 ml of hexane; 0.05%									
22	30	20	25	340	1,28	25,20	0,88	8,98	49,72	13,94	66,38	15,32	Absent	34
23	40	34	16	333	0,69	26,26	1,01	7,58	52,84	11,62	65,87	22,21	"	32
24	50	35	14	340	0,98	24,83	0,66	5,79	55,39	12,35	66,21	22,05	"	34
					10 ml of oil in 25 ml of ethanol; 0.05%									
25	30	22	30	410	1,30	24,95	2,75	13,49	48,89	8,62	59,57	18,23	3,5	—
26	40	35	23	410	1,29	27,27	1,39	13,02	53,15	3,88	59,17	20,73	2,2	—
27	60	65	11	410	1,32	23,63	2,58	12,85	52,75	6,37	59,08	32,95	1,96	—

TABLE 6. Influence of the Duration of Hydrogenation on the Composition and Properties of the Hydrogenizates

Expt. No.	Duration of hydrogenation, min	Absorp. of hydrogen, min	Fatt-acid composition, %						I. No. of hydrogenizates, % I_2			mp of the hydrogenizates, °C
			$C_{14:0}$	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$		trans acids	conjugated dienes	
Initial oil			0,67	22,26	1,37	3,09	18,62	53,99	108,41	—	—	—
28	6	105	1,61	23,34	2,54	5,19	31,38	35,94	90,66	3,76	2,56	24
29	11	205	1,45	25,05	1,54	5,49	38,67	27,80	81,39	12,15	Absent	28
30	25	412	1,14	25,16	1,32	8,54	59,85	3,99	58,10	45,24	"	37
31	45	577	1,09	23,62	1,18	20,43	52,24	1,44	47,00	45,80	"	43

TABLE 7. Composition of the Dicarboxylic Acids Produced by the Destructive Oxidation of the Hydrogenizates

Acid	Experiment						
	16	17	19	20	25	26	27
Succinic, C_4	—	—	—	—	0,78	1,39	1,70
Suberic, C_8	11,68	7,93	4,10	11,01	17,90	18,37	13,20
Azelaic, C_9	32,14	25,75	24,32	30,85	38,15	26,22	19,53
Sebacic, C_{10}	13,47	21,25	17,71	14,00	12,62	15,21	16,30
Nonanedicarboxylic, C_{11}	13,39	20,27	20,27	17,65	10,12	13,71	16,10
Decanedicarboxylic, C_{12}	29,32	24,30	29,70	23,71	19,13	23,91	29,81
Brassylic, C_{13}	—	—	3,90	2,78	1,30	1,19	3,27

TABLE 8. Fragments from the Destructive Oxidation of the Hydrogenizates

Percentage of bonds	Experiment						
	16	17	19	20	25	26	27
Moving closer	26,86	41,52	37,98	31,65	22,74	28,92	32,40
Moving apart	11,68	7,93	8,00	13,79	19,20	19,56	16,47
Undergoing no migration	61,46	50,65	54,02	54,56	57,28	50,13	49,34

ing point of the solvent, its rheological properties change significantly or such peculiar hydrodynamic conditions are created in the reaction medium that they are reflected in the kinetics of the process. Nevertheless, experimentally (Table 5) no such breaks on the curves of T° versus $\Delta v/\Delta t$ were found.

While in the preceding experiments (see Table 4) an increase in the amount of trans acids was found with an increase in the amount of catalyst, here we find the same increase in the amount of trans acids with a rise in the temperature of hydrogenation.

Apparently, the factors accelerating the hydrogenation process promote the process of geometrical (cis—trans) isomerization simultaneously, to some extent.

Finally, the last series of experiments (Table 6) was performed with the aim of investigating the influence of the duration of hydrogenation and of the contact of the oil with the catalyst on the fatty-acid composition and properties of the hydrogenizates. In each experiment of this series 10 ml of oil was hydrogenated in 25 ml of hexane at 50°C with 0.05% of Pd.

It can be seen from Table 6 that saturation with hydrogen in the presence of palladium takes place with a high degree of selectivity, which is especially important, in particular, in the preparation of hydrogenated fats for food purposes. The index of selectivity determined by the graphic-analytical method proved to be 0.886 in this case [3].

In the initial stages of the hydrogenation process an accumulation of the trans acids takes place, but after a definite limit their amount begins to fall because of their saturation.

In some samples of hydrogenizates,dienes with conjugated double bonds were detected. This shows that in addition to geometrical isomerization,position isomerization (migration of double bonds) takes place. In order to follow this phenomenon, we subjected some samples to destructive oxidation by Hilditch's method [4]. The composition of the dicarboxylic acids included in the fragments obtained as the result of oxidation is given in Table 7.

Native oleic acid, and also Δ^{12}-isooleic acid, formed from linoleic acid by the saturation of the Δ^9 double bond, give the C_9 and C_{11} dicarboxylic acids on oxidative degradation; however, when the two double bonds of linoleic acid approach one another the C_{10} and C_{11} acids are formed, and when they move apart, the C_8 and C_{13} acids. Table 8 was constructed taking this into account.

The figures of this table show that 50-60% of the unsaturated acids retain their double bonds in the native positions, while in the remainder the double bonds migrate mainly towards one another. Most frequently, the migration of the bonds towards one another takes place to a 3-5-times greater extent than their movement apart which, of course, is explained by the thermodynamic factor: the transition of a system of two separated double bonds into a conjugated system is accompanied by the evolution of 1.8-3.5 kcal/mole.

We detected the presence of conjugated dienes in a number of experiments, but in extremely small amounts, since they are hydrogenated almost immediately [5] with conversion into monoenic acid.

EXPERIMENTAL

The fatty-acid compositions of the hydrogenizates were determined on a UKh-2 gas-liquid chromatograph at 200°C with a column 2.5 m long. Poly(ethylene succinate) was used as the mobile phase [6].

The methyl esters of the fatty acids were oxidized by the method described previously [7]. The proportion of trans acids was found from the IR spectra obtained on a UR-10 instrument.

SUMMARY

The hydrogenation of cottonseed oil in hexane and ethanol is accompanied by geometrical and positional isomerizations in the fatty-acid radicals.

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