

Isomerization During Hydrogenation of Soap: II. Potassium Elaidate and Potassium Linoleate

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Abstract

Potassium elaidate in slightly alkaline solution was hydrogenated for up to 7 hr with 1.5% of Rufert nickel catalyst at 150 C and 20 kg/sq cm pressure. Potassium linoleate was similarly hydrogenated with 1.0% catalyst for 7 hr, and the hydrogenation continued for another 7 hr after addition of 0.5% fresh catalyst. Periodic samples from each were analyzed for component acids. The positional isomers in the *cis* and *trans* monoenes, isolated by preparative argentation thin layer (TLC) or column chromatography, were estimated after oxidation to dicarboxylic acids. Some diene fractions were isolated for further examination. In potassium elaidate hydrogenation, *cis* monoenes were initially produced in considerable amounts, but to a lesser extent thereafter. Positional isomers were similarly distributed in both *cis* and *trans* monoenes after prolonged hydrogenation. In the hydrogenation of potassium linoleate, a drop in iodine value (IV) of 60 units occurred in the first hour, and 38% of *trans* monoenes (in which the 10- and 11-monoenes constitute 32% each) were formed. The IV then fell only slowly, and up to 38% of *cis* monoene (mostly 9- and 12-isomers) was formed. Addition of fresh catalyst caused a major shift of *cis* monoenes to *trans* forms. The diene fraction was mostly nonconjugated material with the first double bond at the 9, 8 and 10-positions. Minor amounts of conjugated dienes were present as well as a dimeric product.

Introduction

Soap hydrogenation data enable the fat hydrogenation reaction to be viewed from a fresh angle. In the earlier paper in the series (1), the hydrogenation pattern of potassium oleate in slightly alkaline solution was studied. Similar studies on potassium elaidate and potassium linoleate are now presented.

Double bond migrations in elaidic acid or esters are stated to resemble those occurring in oleic products either during catalytic hydrogenation (2) or during isomerization over sulphur-poisoned nickel catalyst (3). Allen and Kiess (2) believed that, whether the starting material for hydrogenation was oleic or elaidic ester, an equilibrium ratio of 2:1 is obtained for each isomer. Better analytical procedures indicate that this ratio is probably 4:1 (4).

A Japanese report (5) on the hydrogenation of potassium linoleate at room temperature and pressure states that the reaction was very unselective, saturated acids being formed from the very start. *Trans* isomers constituted half the total monoenes when the IV was between 90 and 70. Hydrogenation of aqueous sodium soap solutions of mainly conjugated diene acids to monoene products has been reported (6). Hydrogenation of methyl linoleate has been widely studied (7-11). High proportions of 10- and 11-*trans* monoenes are produced, perhaps via conjugated intermediates. Isomer distribution in the *cis* and *trans* isomers separately has not been examined.

Materials and Methods

Potassium Soaps

Pure oleic acid was prepared from olive oil mixed acids by two urea adductions (1), isomerized to elaidic acid by oxides of nitrogen (4), and purified by silicic acid chromatography and repeated crystallizations (4). Pure linoleic acid was derived from safflower acids by two urea adductions (12) and vacuum distillation as methyl esters. The elaidic acid and methyl linoleate were saponified with 5% excess of potash in aqueous and ethanolic solution, respectively, and solvent was removed from the latter to give the soaps.

Hydrogenation

The slightly alkaline aqueous soap from 150 g of each fatty material was diluted with an equal volume of water and hydrogenated at 180 C and 20 kg/sq cm pressure for 7 hr with Rufert nickel catalyst (1.5% for elaidate and 1.0% for linoleate) as described earlier (1). In the linoleate hydrogenation, the run was resumed for another 7 hr after addition of 0.5% fresh catalyst. Samples were drawn periodically for analysis.

Analysis

Acids from each soap sample were analyzed for IV and converted into methyl esters. These were examined for IR absorption at 10.36 μ to determine *trans* content, and by polyester and silicone gas liquid chromatography (GLC) for fatty acid components (1). The methyl esters from the elaidate runs were resolved by preparative argentation TLC into saturated, *trans* monoene and *cis* monoene components. For the esters from the linoleate runs, argentation column chromatography yield saturated, *trans* monoene, *cis* monoene and diene components. All the *cis* and *trans* monoene fractions were examined for the proportions of positional isomers (double bond position) by oxidation with von Rudloff reagent (13) and by temperature-programmed silicone GLC (1). All the diene ester fractions after resolution by preparative argentation TLC with 10% ether in light petroleum gave four zones, each of which was collected, examined for UV absorption and then oxidized to determine first double bond positions.

In analysis of the samples from the linoleate run, the *trans* monoene percentage determined by actual isolation tallied closely with that from IR absorption. Any contribution from *trans*-containing diene was negligible.

Results and Discussion

Analytical Accuracy

Five mixtures of pure methyl stearate, elaidate and oleate were made up in proportions roughly corresponding to those later found in the elaidate hydrogenation. Analyses by GLC and IR absorption shown in Table I validated the analytical procedure.

Reproducibility

Two different lots of potassium linoleate (IV of acids 176.5 and 173.2) were hydrogenated in two

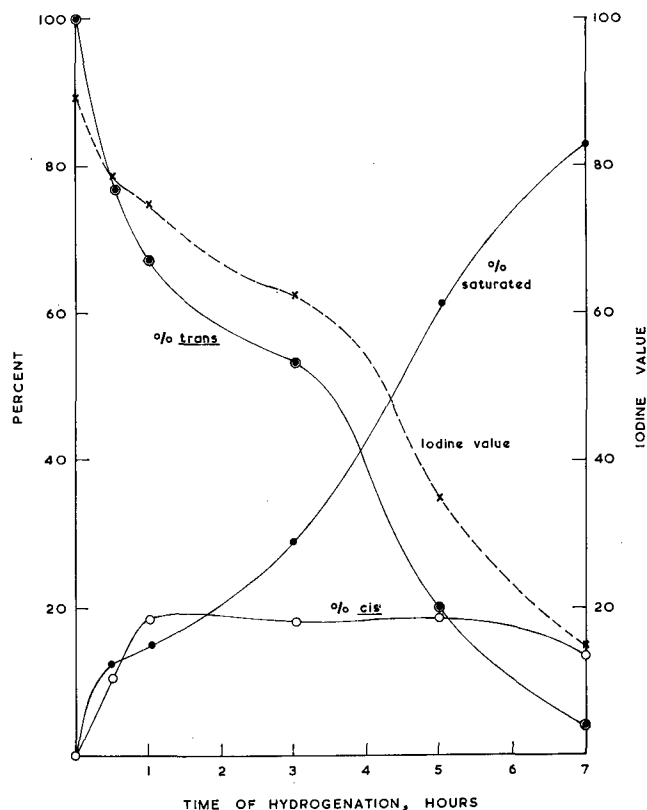


FIG. 1. Iodine values and percentage composition during progressive hydrogenation of potassium elaidate. X, iodine value; ·, saturated; ⊙, *trans* monoene; ○, *cis* monoene.

stages as described with 1% catalyst for 7 hr, and after addition of 0.5% fresh catalyst, for a further 7 hr. The correspondence in IV of the fatty acids between the two runs indicates good reproducibility of the hydrogenation: Run 1—First stage, 0 hr (176.5); ½ hr (142.5); 1 hr (125.8); 3 hr (113.7); 5 hr (108.1); 7 hr (94.2); Second stage, ½ hr (92.4); 1 hr (87.3); 3 hr (85.0); 7 hr (83.3). Run 2—First stage, 0 hr (173.2); ½ hr (139.7); 1 hr (125.3); 3 hr (111.7); 5 hr (106.1); 7 hr (95.6); Second stage, ½ hr (93.0); 1 hr (87.2); 3 hr (84.4); 7 hr (81.2).

Analytical Data

Changes that occurred in IV and in the proportions of each constituent during progressive hydrogenation of potassium elaidate are shown in Figure 1. The absolute molar percentages of the isomers constituting each *cis* and *trans* monoene are shown in Table II.

Figure 2 illustrates the changes in IV when potassium linoleate was hydrogenated in two stages. Table III shows the corresponding analytical data for the products drawn at intervals, and the *cis* and *trans* monoene isomers are expressed as absolute molar percentages.

Hydrogenation of Potassium Elaidate

Saturation occurred steadily throughout hydrogenation (Fig. 1). The IV curve shows the flattening in its middle portion which was found in the hydrogenations of potassium oleate (1) and of linoleate (Fig. 2).

Cis and Trans Monoenes. Initially, the *trans* 9-monoene was practically the only component. The new *cis* monoene produced in the first hour showed considerable double bond scattering, as does the *trans* monoene although to a lesser degree. After 7 hr of hy-

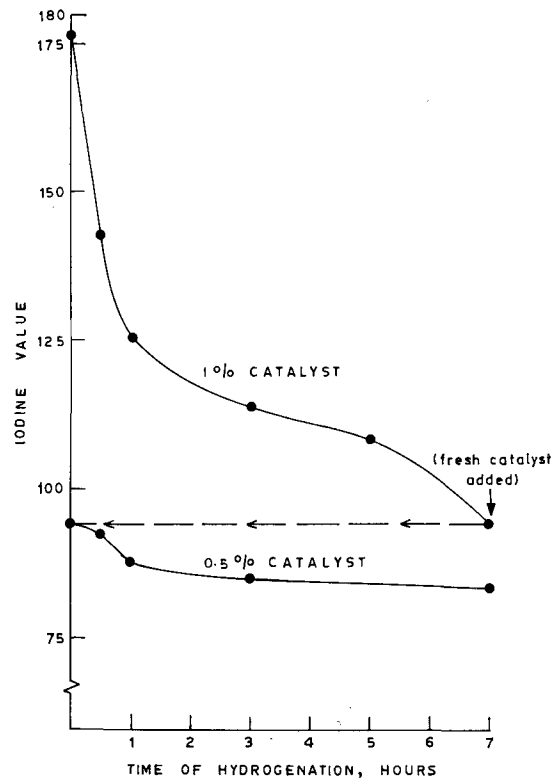


FIG. 2. Reduction in iodine value with progressive hydrogenation of potassium linoleate (1% catalyst for 7 hr, and 0.5% fresh catalyst for another 7 hr).

drogenation the 8-, 9-, 10-, 11- and 12-isomers were the main constituents both of the *trans* and of the *cis* monoenes. The proportions of these isomers in each of these monoenes were remarkably similar, being 10, 35, 30, 15 and 5% (total 95%), respectively. Yet the weights or incremental proportions in which these isomers are actually present were quite different. To illustrate, after 7 hr of hydrogenation, 100 moles of the total *cis* monoene (constitutes 13.1% of the total) contained 10.9 moles of the *cis* 8-isomer, and 100 moles of the total *trans* monoene (constitutes 3.8% of the total) contained 10.0 moles of the *trans* 8-isomer. There is thus an apparent molar correspondence. Yet the actual weights of the *cis* 8-monoene and *trans* 8-monoene present in 100 g of the hydrogenated product were 1.4 g ($13.1 \times 10.9/100$) and 0.38 g ($3.8 \times 10.0/100$). There was therefore no weight correspondence. The drive towards a balance in the isomer proportions appeared to set in from the very start of the reaction. It was also apparent in the earlier work on potassium oleate (1).

In the first hour of hydrogenation of potassium elaidate about 18% of total *cis* monoenes were developed. Thereafter this level was maintained for the

TABLE I
Analyses of Synthetic Mixtures

Mixture		Stearate, %	Elaidate, %	Oleate, %
A	Given	13.0	76.1	10.9
	Found	13.6	78.6	7.8
B	Given	32.7	36.2	31.1
	Found	33.1	37.3	29.6
C	Given	37.0	11.0	52.0
	Found	36.4	11.6	52.0
D	Given	63.5	11.3	25.2
	Found	63.9	11.7	24.4
E	Given	68.3	18.2	13.5
	Found	69.8	18.4	11.8

TABLE II
Product Analysis in the Progressive Hydrogenation of Potassium Elaidate: Analysis of Dicarboxylic Acid Products of Oxidation of *cis* and *trans* Monoenes

Product	I.V.	Satd. acids % mole	Monoene isomers, position of double bond											
			Mole per cent of fraction, absolute											
			6	7	8	9	10	11	12	13	14			
Starting material														
Elaidate	89.2	1.5	98.5
½ hr Hydrogenated product														
Total	78.5	12.6	6.5	86.5	6.0	1.0
<i>cis</i> fraction (10.5%)	0.9	11.6	63.9	20.8	2.8
<i>trans</i> fraction (76.9%)	6.1	89.4	3.8	0.7
1 hr Hydrogenated product														
Total	74.8	14.3	9.2	79.5	9.9	1.4
<i>cis</i> fraction (18.4%)	0.7	23.4	52.4	21.9	1.6
<i>trans</i> fraction (67.3%)	6.0	86.5	6.3	1.2
3 hr Hydrogenated product														
Total	62.4	28.6	0.3	0.5	9.5	71.6	15.0	2.4	0.4	0.3
<i>cis</i> fraction (18.1%)	0.8	0.9	14.1	48.4	29.1	4.3	0.7	1.1	0.6
<i>trans</i> fraction (53.3%)	0.3	0.4	7.4	78.5	11.1	1.8	0.5
5 hr Hydrogenated product														
Total	35.7	61.3	0.5	1.8	12.9	40.6	27.4	10.8	3.9	1.6	0.5
<i>cis</i> fraction (19.3%)	1.3	1.5	14.9	34.1	32.9	10.9	3.2	1.2
<i>trans</i> fraction (19.4%)	0.5	1.6	12.7	47.5	25.3	8.4	2.7	1.0	0.3
7 hr Hydrogenated product														
Total	14.6	83.1	1.8	11.2	32.5	27.8	16.0	6.5	3.0	1.2
<i>cis</i> fraction (13.1%)	0.4	1.1	10.9	34.1	29.7	15.1	6.1	2.1	0.5
<i>trans</i> fraction (3.8%)	0.7	1.5	10.0	37.2	26.0	16.1	5.4	2.4	0.7

next 4 hr. If *cis* monoenes were being saturated, this quantity was replenished by formation from *trans* monoenes. The rate of such formation of *cis* monoenes can be calculated if the relative rates of saturation of *cis* and *trans* forms are known. If the latter are equal, the rate of production of *cis* monoene at the five time points at which samples were drawn (½, 1, 3, 5 and 7 hr) is found to be 33.6, 17.4, 3.4, 8.8 and 2.4% per hour. In the last 2 hr of hydrogenation, the *trans* monoenes appeared to be lost by saturation about 2.5 times faster than the *cis* monoenes. If this relative saturation rate is assumed, the rate of formation of *cis* monoenes from *trans* at the same five time-points comes to 28.2, 16.8, 4.0, 5.3 and nil % per hour. Thus whatever the actual figures, the initially high rate of formation of *cis* monoenes from *trans* was seen to drop sharply about 2 hr after the hydrogenation commenced. Yet the double bond scattering in each species continued to occur to the end.

Nature of Monoene Hydrogenation

In the later stages of prolonged hydrogenation of the soap of monoene acids, both oleate and elaidate, the ability to create the opposite geometric forms seemed to drop. The equilibrium between the isomeric forms continued to be established independently for the *cis* species and for the *trans* species, and led to the same end-pattern balance in each. Towards the end of a hydrogenation, *trans* species appeared to hydrogenate faster than *cis* species.

Hydrogenation of Potassium Linoleate

Rate of Saturation. The saturation curve with time (Fig. 2) shows the flattening in its middle portion which appears to characterize soap hydrogenations. When fresh catalyst was added, rapid saturation was resumed.

Nature of Dienes. The amounts of dienes, as determined by silver ion TLC separation and weighing, showed the following progressive proportions: With 1.0% catalyst—0 hr, 98% diene; ½ hr, 57% diene; 1 hr, 45% diene; 7 hr, 18% diene. With further 0.5% catalyst—7 + ½ hr, 15% diene; 7 + 1 hr, 14% diene; 7 + 7 hr, 11% diene. Each diene

thus isolated yielded, by further argentation TLC, four zones, termed A, B, C and D in order of migration. Zone C was the only major constituent. The zones from the diene, constituting 15%, present in the 7 + ½ hr hydrogenation product were studied further. Zone C showed no UV maximum. The product was oxidized with permanganate-periodate, and the chloroform extracts, which normally constitute the dibasic acids, were esterified and subjected to GLC. Most of the peaks were recognizable as those of homologous dibasic acid esters, and C₈, C₉ and C₁₀ were major and C₇, C₁₁ and C₁₂ minor peaks. Thus Zone C, constituting the major part of the diene may consist mainly of non-conjugated diene whose first double bond is mainly at the 9, 8 and 10 positions.

Zones A and B, the fast-moving minor components, showed strong conjugated diene absorption at 232 m μ . GLC of the von Rudloff oxidation products by temperature-programming from 120 C to 230 C gave, in addition to identifiable dibasic ester peaks, a number of unidentifiable peaks well beyond the C₁₂ dibasic ester range.

Zone D is a minor component which in silver ion TLC remains at the starting point. It showed no UV absorption maxima. Temperature-programmed GLC of the permanganate-periodate oxidation products gave peaks of considerable size well beyond azelate. One, emerging at 184 C, was the major component of the oxidation product of Zone D.

It was surmised that fatty polymers could yield these oxidation peaks. Linoleate is known to pass through conjugated forms during hydrogenation (8). Combination of conjugated dienes with monoenes or other dienes to give both linear and cyclic dimers is well known to occur in the drying or bodying of oils. The reaction is now even used to prepare dimer acids (14). Coenen et al. (15) have shown that up to 1% of aromatic fatty acids were formed in hydrogenation of unsaturated oils at 200 C using 300 liters of hydrogen/kg/hr.

A sample of molecularly-distilled dimer acids (composition: 90.2% dimer, 5.2% monomer and 4.6% polymer) was oxidized and the chloroform extracts esterified and subjected to GLC. The normal aliphatic dibasic esters from C₇ to C₁₁ were clearly identifiable

TABLE III
Product Analysis in the Progressive Hydrogenation of Potassium Linoleate: Analysis of Dicarboxylic Acid Products of Oxidation of *cis* and *trans* Monoenes

Product	I.V.	Monoene isomers, position of double bond																		
		% mole		Mole per cent of fraction, absolute																
		Satd.	Diene	7	8	9	10	11	12	13	14	15								
Starting material																				
Linoleate	176.5	Nil	98.1			0.5	99.5													
<i>cis</i> monoene (1.9%)						(total product)														
½ hr Hydrogenated product																				
Total	142.9	57.5			4.3	60.9	13.7	12.8	5.8	1.7	0.8								
<i>cis</i> monoene (4.9%)							28.8	3.3	7.2	50.1	7.2	3.4								
<i>trans</i> monoene (37.6%)						5.9	12.1	36.1	33.5	6.6	3.9	1.5	0.4							
1 hr Hydrogenated product																				
Total	125.8	45.3	0.7		6.1	49.1	17.3	15.8	9.3	1.7									
<i>cis</i> monoene (13.2%)						2.4	38.5	9.7	7.9	38.2	2.6	0.7								
<i>trans</i> monoene (41.5%)						4.5	9.2	35.7	37.0	8.7	4.4	0.5								
3 hr Hydrogenated product																				
Total	113.7	1.9	35.2	0.6		6.4	40.7	18.2	17.9	11.2	4.4	0.6								
<i>cis</i> monoene (21.0%)				0.3		3.0	40.4	6.7	10.1	33.2	5.4	0.9								
<i>trans</i> monoene (41.9%)						3.9	7.5	34.2	37.0	9.9	6.1	0.8	0.6							
5 hr Hydrogenated product																				
Total	108.1	3.6	24.7	0.7		6.3	38.2	18.6	17.8	14.8	2.9	0.7								
<i>cis</i> monoene (30.7%)				0.5		3.1	43.6	7.1	9.3	32.8	2.1	0.8	0.7							
<i>trans</i> monoene (41.0%)						6.1	11.6	32.2	33.2	10.4	5.1	1.0	0.4							
7 hr Hydrogenated product																				
Total	94.2	4.0	17.1	1.1		5.3	33.3	19.5	18.0	18.2	3.6	1.0								
<i>cis</i> monoene (38.7%)						3.0	41.4	8.5	10.0	32.9	3.4	0.8								
<i>trans</i> monoene (40.2%)				0.7		5.7	10.5	32.6	31.6	10.9	6.6	1.1	0.3							
0.5% Fresh catalyst added and hydrogenation resumed																				
½ hr Hydrogenated product																				
Total	88.5	10.2	14.7	0.3 + 1.9		6.8	30.2	18.7	17.3	19.0	4.5	1.3								
<i>cis</i> monoene (33.6%)				0.4		3.6	39.8	8.5	10.2	34.4	2.0	0.6	0.5							
<i>trans</i> monoene (41.5%)				0.8		6.1	11.5	30.2	29.5	13.3	6.3	1.4	0.9							
1 hr Hydrogenated product																				
Total	87.8	10.9	13.9	2.0		8.2	22.8	23.5	23.0	14.0	5.2	1.3								
<i>cis</i> monoene (13.7%)						3.5	40.9	9.1	9.8	33.7	2.1	0.9								
<i>trans</i> monoene (61.5%)				1.3		6.0	10.2	30.0	31.0	11.6	7.6	1.2	1.1							
3 hr Hydrogenated product																				
Total	85.0	11.1	13.1	2.4		8.7	23.8	24.7	21.6	13.2	4.6	1.0								
<i>cis</i> monoene (13.1%)				1.3		5.7	37.8	8.1	9.3	33.7	2.6	1.5								
<i>trans</i> monoene (62.7%)				1.2		6.9	14.7	29.8	28.9	11.5	6.1	0.9								
7 hr Hydrogenated product																				
Total	83.3	12.4	11.3	0.2 + 2.0		7.0	22.0	23.6	23.9	15.1	4.1	1.6	0.5							
<i>cis</i> monoene (11.1%)				1.0		3.5	39.4	8.4	8.0	36.2	2.1	0.8	0.6							
<i>trans</i> monoene (65.2%)				1.2		6.3	12.4	28.6	30.1	13.1	5.8	1.3	1.2							

by inspection and co-chromatography. Beyond these appeared a series of peaks with a particularly large one emerging at 184 C, which qualitatively resembled those obtained from the oxidized Zones A, B and D. These runs were made at different times under non-identical conditions. Another diene was isolated from a hydrogenated peanut soapstock sample. The oxidation product was run at the same time as that from the commercial dimer acid, and gave peaks which were readily superimposable (16). Hence Zones A, B and D would appear to carry polymeric products derived from linoleate. All three are minor zones. The bulk of the diene that passed into Zone C is nonconjugated material in which some double bond migration of the original linoleate has occurred.

Proportions of Saturates and Monoenes. In the first 7 hr of hydrogenation, only 4% stearate was formed (Table II) even when the IV had dropped by 82 units. Linoleate was transformed mainly to monoenes. In the first half hour, 38% of *trans* monoene was formed but no new *cis* monoene. In the next half hour 8% new *cis* monoene was formed but only 4% of new *trans* monoene. The present study of potassium elaidate hydrogenation showed that this *cis* monoene could also arise from *trans* monoene with a fresh catalyst. After 7 hr, *trans* monoene still remained at 40% and *cis* monoene constituted 39%. Addition of fresh catalyst caused a loss of 7 units of IV in the first hour, but the main effect was the conversion of 21% of *cis* to *trans* monoenes. This monoene shift occurred even though

18% of dienes were still present, only 4% of which was reduced. After 7 + 7 hr hydrogenation over 1 + 0.5% of catalyst, the product of hydrogenation of potassium linoleate consisted of 12% saturates, 11% *cis* monoene, 65% *trans* monoene and 11% diene.

Nature of Monoenes. The *cis* monoene isomer, except for the first half hour of hydrogenation (when some linoleate contamination could occur during TLC isolation) consisted mostly of the 9- and 12-isomers. Proportions of other isomers were small and constant. The *trans* monoene consisted of about 35% each of the 10- and 11-isomers. High proportions of total *trans* monoene were found in hydrogenation of methyl linoleate (8). Considerable percentages of 10- and 11-isomers in the total monoene (9) have been shown. This is however the first demonstration of the actual proportions of the isomers in isolated *trans* and *cis* monoenes. Conjugation of linoleate can give two conjugated dienes; hydrogenation of these by 1,2 or 3,4 or 1,4 mechanisms will yield the following monoenes:

Conjugated diene from linoleate		Addition of hydrogen	
10 <i>t</i> ,	12 <i>c</i>	1,2	3,4
9 <i>c</i> ,	11 <i>t</i>	12 <i>c</i>	10 <i>t</i>
		11 <i>t</i>	9 <i>c</i>
			1,4
			11 <i>t</i>
			10 <i>t</i>

Thus the products actually found, namely 10 *t* and 11 *t*, 9 *c* and 12 *c*, are accounted for on a conjugated diene basis. On a fresh catalyst, the 1,4 addition mechanism appears to be preferred since 10 *t* and 11 *t* are the main products produced.

Cis monoenes increase as the hydrogenation proceeds. If these were to arise from *trans* monoenes, they should consist of 9-, 10-, 11- and 12-isomers, whereas mostly 9- and 12-isomers were present. *Cis* monoenes could arise either by simple molecular hydrogenation of linoleate on a used catalyst, or by hydrogenation of conjugated dienes such that the new *trans* bonds (10 *t* or 11 *t*) are preferentially hydrogenated leaving the *cis* bonds (12 *c* or 9 *c*).

With the addition of 0.5% of fresh catalyst after 7 hr, a large shift of 21% from *cis* to *trans* monoene occurred. Yet the molar proportions of isomers remained unaltered both in the *cis* monoenes which were thus altered, or more remarkably, in the *trans* monoenes which were produced. Normally when a monoene gives rise to the opposite geometric forms during hydrogenation, considerable double bond scattering occurs. It is suggested that the present finding may be connected with the unusual nature of the diene, whose adsorption on the catalyst surface alters the hydrogenation characteristics of the latter.

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