The Effect of Process Conditions On Positional and Geometric Isomerization During Partial Hydrogenation of Trilinolein With Copper Catalyst[1]

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Abstract

The effects of some process conditions on isomer distributions during the partial hydrogenation of trilinolein with a copper type catalyst were studied. Modest effects on diene isomer distributions were noted by changes in temperature. Pressure and catalyst concentration, however, had little or no effect on diene isomer distributions over the range studied. Distribution of monoene isomers appeared to be insensitive to process conditions and extent of the reaction and suggests an equilibrium reaction. Very small amounts of saturates, if any, were formed during the reactions. The data support a conjugation then hydrogenation mechanism for hydrogenation of glyceryl dienoates with copper catalysts.

Introduction

The hydrogenation of linoleic acid to the completely aturated stearic acid form does not usually occur as a stoichemetric reaction whereby two moles of hydrogen are simultaneously reacted with the dienoic acid o form the saturated moiety. Under the conditions usually employed in edible triglyceride hydrogenation, the transformation of glyceryl dienoates, usually proceeds in a series of reactions whereby one of the wo unsaturated bonds is first either saturated by virtue of chemical combination with a mole of hydrogen or the bond may change relationship within he molecule as to position in the carbon chain or geometrical configuration, or both (1,2). Subsequent reaction may or may not saturate the double bond or cause further isomerization.

In recent years, new techniques for analysis of methyl esters of fatty acids have been discovered and older ones improved. A few examples would be IR analysis (3) UV spectrophotometric measurements of onjugation (4,5), counter-current distribution (6), gas chromatography (7), thin layer chromatography TLC) (8) and oxidative cleavage for the determination of the position of the double bonds (9). The development of these techniques led to several studies n the hydrogenation of oleic acid (10–12) including he study of the effect of operating conditions on the migration of double bonds in hydrogenated samples 1).

Some work has been done with higher unsaturated, .g., linoleic, linolenic acids (13–15), but little detailed study of the effects of the operating conditions n the formation of positional and geometrical isomers has been carried out yet because of the staggering amount of analytical effort involved in such a venture.

As a result of recent development in TLC (8) and capillary gas chromatography (7) a simplified procedure has been developed which allows a relatively quick determination of several positional and geometrical isomers of a fatty acid containing up to two double bonds.

In a previous paper (20) we have described the differences in isomer distribution seen between copper and nickel catalyst partial hydrogenation of trilinolein with similar reaction conditions. In this paper, we will describe the effect of varying pressure, temperature and catalyst concentration on the distribution of isomers, both geometric and positional, formed during hydrogenation of trilinolein with a copper catalyst.

Experimental Procedures

A detailed description of the materials, analytical and experimental procedures used was given in the previous paper (20). Briefly, they were as follows.

Materials

Trilinolein was prepared by esterification of glycerol with linoleic acid obtained by solvent fractionation of esters of safflower fatty acids. The triglyceride was further purified by solvent fractionation. Fatty acid composition of the trilinolein used was: 0.3% $C_{16:0}$; 1.3% $C_{18:1}$; 97.8% $C_{18:2}$; and 0.2% $C_{18:3}$. The catalyst used was a copper chromite catalyst promoted with manganese (T970) obtained from the Girdler Catalyst Division of the Chemtron Corp.

Analysis

Methylated samples of the partially hydrogenated trilinolein were fractionated on a preparative scale by TLC into six fractions containing mainly: traces of triene, *cis,cis* diene, *cis,trans* and *trans,cis* diene, *cis* monoene and *trans,trans* diene, *trans* monoene and saturates.

Each of these fractions were quantitatively extracted with chloroform and further fractionated by capillary gas chromatography. The gas chromatographic analyses were performed on 150 ft × 0.01 in. capillary column coated with polyphenyl ether, a method described by Chapman and Kuemmel (16). The composition was determined based on weights of fractions obtained by TLC. Conjugated species as total conjugates were determined independently by UV spectroscopy. Iodine values were calculated based on composition.

Equipment and Operating Procedures

The trilinolein was hydrogenated in a stainless steel batch reactor fitted with baffles and agitator and inlet through which hydrogen could be continuously passed.

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TABLE I
Equilibrium Distribution Values Monoene Isomers Trilinolein Hydrogenation

Isomer	*Cis* as per cent of total *cis,trans* as per cent of total *trans* monoenes: Copper catalyst, %	*Cis* as per cent of total *cis,trans* as per cent of total *trans* monoenes: Nickel catalyst, %
Δ^9 *Cis*	46	54
Δ^{10} *Cis*	18	5.5
$\Delta^{11} + \Delta^{12}$ *Cis*	28	38
Δ^{13} *Cis*	8	2.5
Total	100	100
Δ^9 *Trans*	53	57
Δ^{10} *Trans*	23	24
Δ^{11} *Trans*	12	11
Δ^{12} *Trans*	10	6.5
Δ^{13} *Trans*	2	1.5
Total	100	100

Trilinolein and catalyst were charged to the reactor. Nitrogen was passed through the reactor while heating to reaction temperature.

Data and Discussion

Reaction Rates

Two levels each of pressure, temperature and catalyst concentration were used. The conditions were: pressure 50 psig, 100 psig; temperature 340 F, 392 F; catalyst 1%, 2% by weight. Increasing pressure, temperature and catalyst concentration produced the expected effect of increasing rate of reaction. Increasing temperature from 340 F to 392 F had a pronounced effect of about a three- to fourfold rate increase whereas increasing pressure and catalyst concentration had more modest effects.

Product Distributions

Dienes. Varying process conditions within the ranges studied had no effect on total diene content at a particular IV during the hydrogenation. Neither pressure nor catalyst concentration had a pronounced effect on the distribution of diene isomers. Temperature does, however, have an effect as shown in Figure 1. Here, we see that a lower temperature results in higher concentration of diene isomers. The slow rate of the hydrogenation reaction at the lower temperature probably allows isomerization reactions to proceed to a greater extent before hydrogenation of one of the bonds occurs.

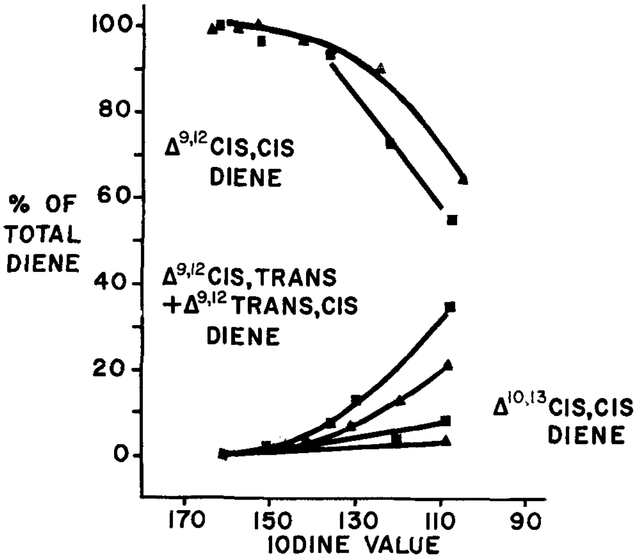

FIG. 1. Diene isomers, as per cent of total diene vs. iodine value—effect of temperature—trilinolein hydrogenation, copper catalyst ■ 340 F, 50 psig, 1% catalyst; ▲ 392 F, 50 psig, 1% catalyst.

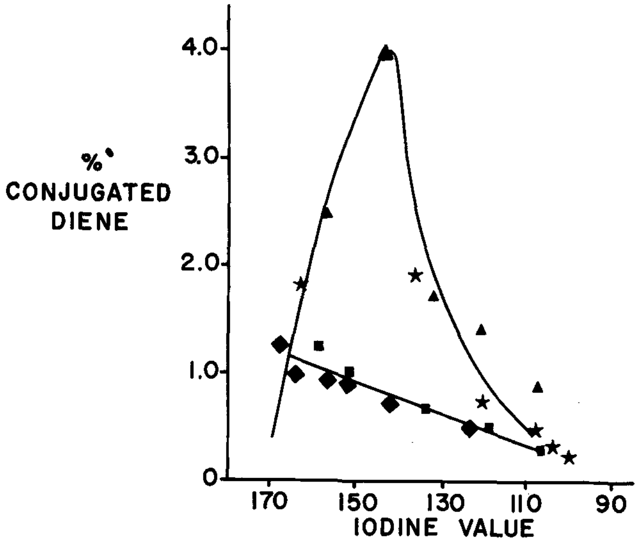

FIG. 2. Conjugated diene as iodine value—trilinolein hydrogenation copper catalyst ▲ 392 F, 50 psig, 1% catalyst; ■ 340 F, 50 psig, 1% catalyst; ◆ 392 F, 100 psig, 1% catalyst; ★ 392 F, 50 psig, 2% catalyst.

Figure 2 shows the effect of process variables on the amount of conjugated diene found. Only small amounts were found; however, we see that increasing temperature and decreasing pressure increases the amount of conjugated diene formed. Catalyst concentration appeared to have little or no effect. It was not possible to determine the species of conjugates in this work. The small amounts of conjugates formed, even though pressure does affect the rate of formation, do not have a pronounced affect on diene isomer distribution and therefore the observation that pressure has little effect on this distribution.

The characteristic shape of the conjugated dienes versus iodine value curves lends credence to a hydrogenation mechanism of conjugation followed by hydrogenation of one of the conjugated double bonds with copper catalysts. Such curves are frequently found in an intermediate type of reaction such as

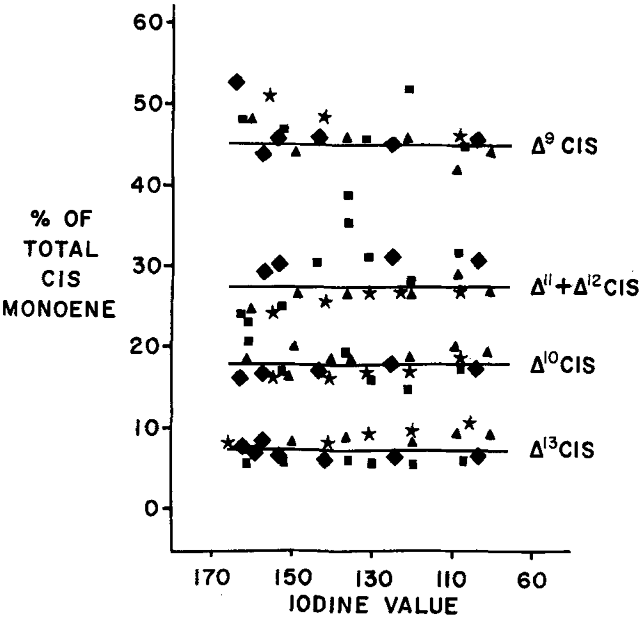

FIG. 3. *Cis* monoene isomers as per cent of total *cis* monoene vs. iodine value—trilinolein hydrogenation copper catalyst ■ 340 F, 50 psig, 1% catalyst; ▲ 392 F, 50 psig, 1% catalyst; ◆ 392 F, 100 psig, 1% catalyst; ★ 392 F, 50 psig, 2% catalyst.

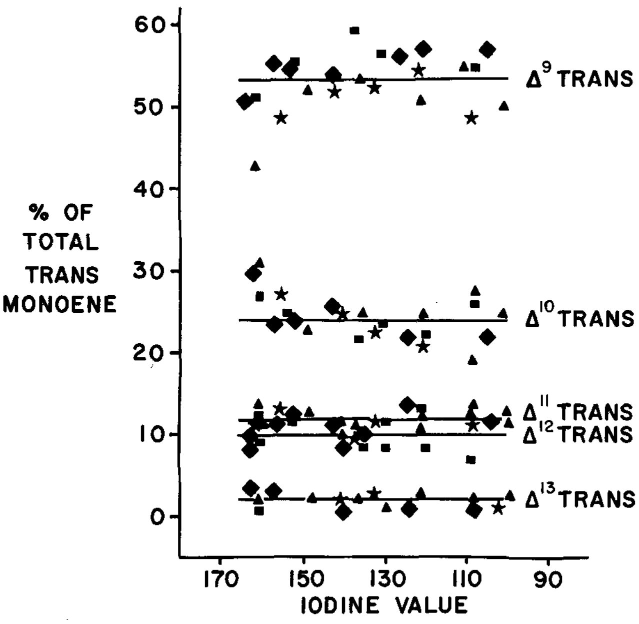

FIG. 4. *Trans* monoene isomers as per cent of total *trans* monoene vs. iodine value, trilinolein hydrogenation copper catalyst ■ 340 F, 50 psig, 1% catalyst; ▲ 392 F, 50 psig, 1% catalyst; ◆ 392 F, 100 psig, 1% catalyst; ★ 392 F, 50 psig, 2% catalyst.

A → B → C when the concentration of B is plotted against time or extent of the reaction. This mechanism, of course, has previously been proposed by many others (2,11,18,19) and has been recently further proposed by the studies of Koritala (21) at Northern Regional Laboratories. Only traces of *trans, trans* dienes were found. This somewhat unexpected small amount was found in a similar study using nickel as catalyst.

Monoenes. The percentage of monoenes as *trans* monoene isomers rapidly approached an equilibrium value of about 70% as hydrogenation proceeded attaining this value at an iodine value of about 160. This apparent equilibrium has been previously pointed out to be about the theoretical distribution for *trans, cis* isomers at temperatures encountered in this work.

Figures 3 and 4 show distribution of several *cis* isomers and several *trans* isomers expressed as fractions of total *cis* monoenes and *trans* monoenes respectively. Two things are readily apparent from these figures. First, the distribution does not appear to vary during the hydrogenation and, secondly, variations of reaction conditions appear to have little effect on the distributions within the range of variables studied. The so-called equilibrium values for the various monoene isomer distributions are summarized in Table I together with the distribution seen in a similar study with nickel catalyst. As was shown in our previous paper, this Table shows that the distribution for monoene isomers is different for the copper catalyst than it was with the nickel catalyst. The *trans* isomer distributions were similar for both catalysts.

Saturates. Saturate level shows little change with iodine value. The data are fairly scattered most likely because the values were determined by difference on a total composition basis. No apparent correlation with process variables is indicated and total saturates increase only slightly over the iodine value range 100–160. This result is similar to that found by other investigators of copper catalysts. They are very selective for diene to monoene formation with little saturates formed under normal vegetable oil hydrogenation conditions. A mechanism for hydrogenation with copper catalysts of first conjugation followed by hydrogenation of one of the conjugated bonds best explains this result.

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