

# Transfer and Adsorption Steps Affecting Partial Hydrogenation of Triglyceride Oils<sup>1</sup>

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## Abstract

The numerous transfer, adsorption and true hydrogenation steps which occur during the partial hydrogenation of triglyceride oils are reviewed and discussed. Transfer steps involve the transfer or diffusion of the reactants to the catalyst surface and possibly also into the pores of the catalyst. In addition, the reaction products must then also be transferred back to the main body of the triglyceride oil. Such reaction products include not only the saturated groups (formed by the hydrogenation of the unsaturated groups) but also the geometrical and positional isomers of the original unsaturated groups. Once an unsaturated group reaches the catalyst surface, it is generally assumed that it is adsorbed on the catalyst. Polyunsaturated fatty groups are however preferentially adsorbed relative to mono-unsaturated fatty groups. The overall kinetics of hydrogenation affects the relative ratio of the adsorption of the polyunsaturated to the mono-unsaturated groups at the catalyst surface. Transfer and adsorption steps frequently, if not always, are the critical steps in controlling the degree of isomerization and selectivity of reactions in the partial hydrogenation process. Additional information is still needed relative to these steps but the general trends which occur are discussed.

## Introduction

Partial hydrogenations of triglyceride oils involve a large number of steps including transfer (or diffusion, or both), adsorption, hydrogenation, isomerization and desorption steps. The transfer steps can be divided into at least two groups. The first group consists of the transfer of reactants and products to and from the main body (or the bulk) of the liquid oil phase and the outside surface of the catalyst. For catalysts in which considerable number of rather narrow pores are present, diffusion of reactants into and of products out of the pores may be a controlling set of transfer steps. Agitation in the main body of the oil would obviously have little or no effect on diffusional steps in the pores.

Adsorption of the reactants on the catalyst surface has long been recognized as being an important prerequisite, which must occur before the final reactions can occur on the catalyst surface. The various transfer and adsorption steps are known to be very important in affecting (or controlling) the selectivity and the extent of isomerization during hydrogenation. The reason why these steps exert this control is because each of them affects the adsorbed concentrations of reactants at the catalyst surface (1,2,5,8,12,15). Higher ratios of adsorbed unsaturated groups ( $-\text{CH}=\text{CH}-$ ) to adsorbed hydrogen at the catalyst surface result in higher selectivity ratios and in higher amounts of both positional and geometrical isomers of the unsaturated fatty acid groups (1,2). In commercial batch hydrogenations, higher ratios are obtained with decreased agitation, increased temperature, decreased pressure and increased amounts of catalyst.

In many if not all commercial hydrogenations using batch reactors, transfer of the hydrogen gas to the liquid oil is the controlling step of the entire process (1,2,5,12). Transfer and adsorption steps for the unsaturated groups of the fatty chain also have a large effect on selectivity and isomerization, but the importance of such steps appears to have been presented only in part in the past. The purpose of the present paper is to clarify the number and character of the transfer and adsorption steps and to indicate more fully their importance in controlling the overall hydrogenation sequence.

## Summary of Steps Involved

Allen and Kiess (6,7) and recently Dutton (11) have discussed the chemical steps between an unsaturated fatty group and atomic hydrogen which occur on the catalyst surface. When transfer, adsorption and desorption steps are also considered in the reaction model, it is obvious that a highly complicated series of steps are occurring. Steps which occur during the partial hydrogenation of a *cis*-monounsaturated fatty group (C) are summarized in Figure 1. As indicated, part of C is hydrogenated to form a saturated fatty group (S) and part is isomerized. Only two isomers designated as I<sub>1</sub> and I<sub>2</sub> are shown on Figure 1. Many more isomers are actually produced however (6,10). When methyl oleate or methyl elaidate are partially hydrogenated as many as 31 isomers have been detected in the main body of the oil phase; obviously many more steps occur than shown in Figure 1.

Each unsaturated group ( $-\text{CH}=\text{CH}-$ ) of the fatty acid chain can transfer back and forth between the main body of the oil (designated with a subscript "oil") and the bulk surface of the catalyst (designated with a subscript "surface"). These unsaturated groups can be adsorbed on the catalyst surface (designated with a subscript "ads"). Some of the adsorbed groups are later desorbed.

Each adsorbed unsaturated group can react with a hydrogen atom to form an unstable complex which is a partially hydrogenated double bond ( $-\text{CH}_2-\text{CH}-$ ). Some of the complexes react with another hydrogen atom to complete the saturation of the double bond.

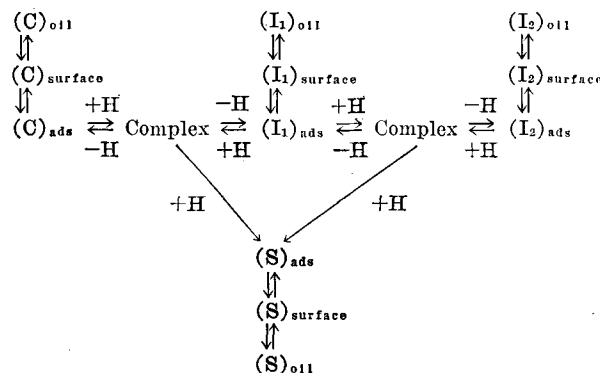


FIG. 1. Simplified summary of transfer, adsorption, desorption, hydrogenation and isomerization steps for partial hydrogenation of *cis*-monounsaturated group (C). Only two isomers (I<sub>1</sub> and I<sub>2</sub>) of C are shown, although many more are detected in the main body of the oil.

<sup>1</sup> One of 10 papers to be published from the Symposium "Hydrogenation," presented at the AOCs Meeting, New Orleans, April 1970.

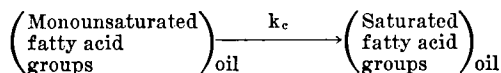
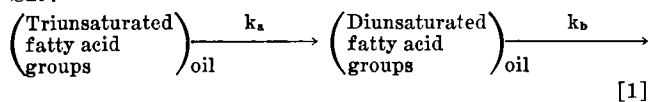
These saturated groups (-CH<sub>2</sub>-CH<sub>2</sub>-), designated as S, may or may not be initially adsorbed on the catalyst surface. If they are adsorbed, the bonding energy of adsorption is probably very low. The remainder of the unstable complexes decompose to reform unsaturated groups and hydrogen atoms. The unsaturated groups formed by this decomposition may be at a new position on the fatty chain and/or may have a different geometrical configuration as compared to the initial unsaturated group in C.

Similar complicated series of steps also occur when one of the double bonds of a polyunsaturated fatty chain is hydrogenated. Isomerization reactions also occur in these cases, and at least part of the two or more double bonds on the chain are conjugated before the hydrogenation of the first double bond. As has been indicated earlier (1,2,5), two or more double bonds on a given chain may be hydrogenated while the fatty acid chain remains at the catalyst surface and before the chain is transferred back to the main body of the oil. For example, linoleate groups appear to be hydrogenated directly to stearate groups.

### Adsorption of Unsaturated Groups on Catalyst Surface

The type of adsorption that occurs on the catalyst surface during hydrogenation is not definitely known as yet. Chemisorption is thought by many investigators to be the main type but others believe physical adsorption may be the prevalent type (12,15). Regardless of the actual type(s) of adsorption occurring, the selectivity ratio (SR) defined as the ratio of the rate of hydrogenation of polyunsaturates to the rate of the monounsaturates can be explained by the preferred adsorption of polyunsaturated as compared to monounsaturated groups (1,2,5,12,15). The adsorption of saturated groups would be even less preferred than that for the monounsaturated groups. These adsorption steps are of course reversible, and desorption of saturated groups is more pronounced than the desorption of monounsaturated and of especially polyunsaturated groups.

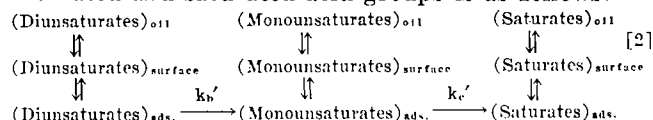
Mathematical modeling of the main reaction steps which occur during hydrogenation has been found to be most useful for characterizing the reaction, but all models proposed to date leave much to be desired from a strict theoretical basis. For example, the following model is commonly used (3,8,14) for measuring the SR:



These three types of hydrogenation steps are considered to be irreversible and first order. The concentration of each fatty acid group has been assumed to be that in the oil phase. In this model, SR is generally defined as the ratio of  $k_b/k_c$ . Constant  $k_a$  is often assumed to be about 1.5 to 2.0 times greater than  $k_b$  (3,14). Modeling such as above has become very popular since it was first demonstrated that either analog computers (15) or digital computers (3) can be used to solve the equations.

The above SR model is oversimplified since it does not indicate the actual adsorbed concentrations on the catalyst surface. It can be assumed that the resistances to transfer (or diffusion) for each fatty acid group to and from the oil are essentially identical since each acid group has a similar molecular weight. Adsorption phenomena however tend to increase the relative

ratio of polyunsaturated to monounsaturated groups which are adsorbed on the catalyst surface as compared to the ratio in the main body of the oil. A more realistic model for a triglyceride oil, such as cottonseed oil, which contains diunsaturated, monounsaturated and saturated acid groups is as follows:



The hydrogenation steps on the surface approximate first order kinetics based on the adsorbed concentrations of diunsaturated and monounsaturated fatty acid groups (12,15). If the actual concentrations at the catalyst surface were known, then the average values of the rate constants,  $k_b'$  and  $k_c'$ , could be determined. The actual ratio of  $k_b'/k_c'$  probably is the range from about 1.0 to 2.0. Such a conclusion was made using the following reasoning. At high degrees of unsaturation, diunsaturated fatty acid groups are hydrogenated preferentially especially at high SR values. At lower iodine values, monounsaturated groups are primarily the only ones left to be hydrogenated. Yet the value of  $k'$  in the following overall rate equation decreases to only a relatively small extent (5,12,15) during the course of a given batch run conducted over a wide range of iodine values (IV); hence the values of  $k_b'$  and  $k_c'$  must be reasonably similar:

$$\text{Overall rate of hydrogenation} = - \frac{d(\text{I.V.})}{d(\text{time})} = k'(\text{IV}) \quad [3]$$

The ratio of the rates of hydrogenation of diunsaturates to those of monounsaturates can be expressed as follows using first the simple model (equation 1) and then the more complicated model (equation 2):

$$\frac{\frac{d(\text{diunsaturates})}{dt}}{\frac{d(\text{monounsaturates})}{dt}} = \frac{k_b(\text{diunsaturates})_{o11}}{k_c(\text{monounsaturates})_{o11}} = \frac{k_b'(\text{diunsaturates})_{\text{ads.}}}{k_c'(\text{monounsaturates})_{\text{ads.}}} \quad [4]$$

Rearranging and remembering that  $k_b/k_c = \text{SR}$ :

$$\text{SR} = R(k_b'/k_c') \quad [5]$$

where

$$R = \frac{\left( \frac{\text{diunsaturates}}{\text{monounsaturates}} \right)_{\text{ads.}}}{\left( \frac{\text{diunsaturates}}{\text{monounsaturates}} \right)_{o11}} \quad [6]$$

R is a quantitative measure of the accumulation of diunsaturates at the catalyst surface because of their preferential adsorption. Since  $k_b'/k_c'$  likely varies from about 1 to 2, R can be approximated for any given SR.

The maximum SR that can be obtained for a given catalyst must depend primarily on the equilibrium composition of the adsorbed groups at the catalyst surface. Such equilibrium compositions will be functions of temperature and the composition of the triglyceride oils. The maximum SR values possible using commercial nickel catalysts are perhaps 100 or maybe slightly greater. The lowest SR values possible are however thought to be about 1 to 2. In the latter case, the ratio of adsorbed diunsaturates to adsorbed monounsaturates at the catalyst surface would be one. SR values of less than 2 were obtained by Wisniak and Albright (4,15) at high pressures and at high rates of agitation. R values then likely vary from about 1 to 50-100 for commercial nickel catalysts.

A complicated series of transfer, adsorption and desorption steps are involved as R values increase. Desorption and adsorption steps occur for monounsaturates and diunsaturates (and higher polyunsaturates in some cases) as the adsorbed concentrations of the monounsaturated and diunsaturated groups on the catalyst surface approach the theoretical equilibrium concentrations which would be obtained if no hydrogenations occurred. As these adsorption and desorption steps occur on the catalyst surface, transfer steps of the diunsaturates and of the monounsaturates certainly also occur. The diunsaturates transfer mainly from the main body of the oil phase to the catalyst surface whereas the monounsaturates move primarily in the other direction. These transfer steps are relatively slow in relation to other steps of the hydrogenation process especially for nonselective hydrogenations, and hence resistances to these transfer steps affect the actual concentrations of diunsaturates (and triunsaturates) and of monounsaturates at the catalyst surface. Measuring SR as the ratio of  $k_b/k_c$  by the model shown in Equation 1 then incorporates the resistances to mass transfer, the approach toward equilibrium of adsorbed species on the catalyst surface, and also the resistances to the hydrogenation reactions as measured by  $1/k_p'$  and  $1/k_c'$ . Constants  $k_b$  and  $k_c$  are hence not true reaction rate constants, and they instead must be considered as only pseudo rate constants. The model shown in Equation 1 can at best be only considered semi-theoretical and should be used with caution in making any theoretical conclusions.

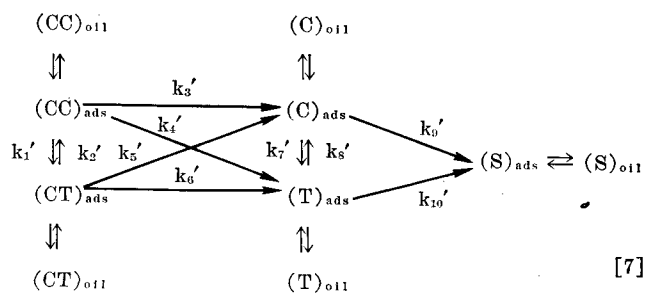
Models such as Equation 1 have proved most useful in quantizing SR values accurately and quickly, but it should be recognized that grouping all diunsaturates or all monounsaturates is implicitly assuming that the transfer and adsorption characteristics of each member of the group are at least similar. Although this assumption is not completely valid, as will be discussed, relative to the isomerization model to be discussed next, the assumption is sufficiently good for the selectivity model.

### Isomerization Models

Albright et al. (4) presented earlier an isomerization model for triglycerides that contain diunsaturated, monounsaturated and saturated fatty acid groups in order to quantize geometrical isomerization. The fatty acid groups were divided into five families: (a) *cis,cis*-diunsaturates (CC); (b) *cis,trans*-diunsaturates (CT); (c) *cis*-monounsaturates (C); (d) *trans*-monounsaturates (T); and (e) saturates (S).

Some *trans,trans*-diunsaturated groups (TT) also occur, but the amounts are probably very small. Dividing the diunsaturates into two (or possibly three) groups and the monounsaturates into groups is necessary for the development of a geometrical isomerization model.

Assuming transfer, adsorption and desorption steps for the overall process, the model would include terms for the concentrations of CC, CT, C, T and S in both the oil phase (main body of oil) and as adsorbed on the catalyst surface. The  $k'$  terms as shown in the model below are average values of the true rate constants for the hydrogenation and isomerization reactions on the catalyst surface. Such  $k'$  values could be used to determine an isomerization index (II) which would be a quantitative measure of the ratio of the rate of isomerization of a particular unsaturated group to the rate of hydrogenation of that group.



The above model is in many respects merely an expansion of Equation 2 used to measure SR. The model is however simplified in that each combination of transfer and adsorption steps and of desorption and transfer steps is depicted as it were a single step. The approach of the adsorbed concentration of each of the five families of fatty acid groups toward the equilibrium concentration of that family depends on the operating conditions (including especially agitation) and the IV of the oil. Unfortunately sufficient data are not available at present to more than qualitatively discuss the approach toward equilibrium. The type of data required would include reliable equilibrium and kinetic data for both adsorption and desorption. It seems probable however that each isomer in each of the above five groups has relatively similar adsorption and desorption characteristics so that the above groupings are reasonable.

If it is further assumed that all diunsaturated groups (CC, CT and also TT) are much more strongly adsorbed (and hence less likely to be desorbed) than monounsaturated groups (C and T), some interesting conclusions can be made if one considers the general chronological series of events occurring during hydrogenation.

1. The net transfer of CC during hydrogenation is always from the main body of the oil phase toward the catalyst surface where either it is hydrogenated or it is first isomerized and perhaps later hydrogenated.

2. During the initial stages of hydrogenation, a small amount of CT (and perhaps TT) is transferred from the catalyst surface to the main body of oil. Only a small amount is transferred since all diunsaturated fatty acid groups are strongly adsorbed on the surface. So although only a small amount of these *trans*-containing diunsaturated fatty acid groups are detected in the main body of the oil, a relatively high concentration of them remains adsorbed on the surface, and they are readily available there for hydrogenation to a monounsaturated group. In later stages of the hydrogenation, when most of the diunsaturated groups have been hydrogenated, the net transfer of these groups is from the oil phase to the catalyst surface.

3. Both C and T are produced by the partial hydrogenation of diunsaturated fatty acid groups. Although Equation 7 indicates that both C and T can be produced from either CC or CT, it is probable that C is produced primarily from CC and T from mainly CT or possibly TT (4). At higher degrees of unsaturations, there is a net production of C and especially of T so that the net transfers of both C and T are from the catalyst surface to the main body of the oil. Once most of the diunsaturated groups have been hydrogenated, there is a net decrease in the quantities of monounsaturated groups produced. At this stage of hydrogenation, the net transfers of C and T are from the oil to the catalyst surface.

4. There is always an increase in the amount of saturated fatty acid groups as hydrogenation pro-

gresses. As a consequence, the net transfer of S is always from the catalyst surface to the oil phase.

The relative concentrations of CC, CT, C and T adsorbed at the catalyst surface are obviously much different than the concentrations in the oil phase mainly because of the variations in adsorptivity of the various families. In addition however, the actual adsorbed concentrations of each family are often quite different than the equilibrium concentrations which would be realized if no hydrogenations occurred. These latter differences are caused by the relatively slow approach to equilibrium caused by the rather slow transfer steps involved. As a general rule, the actual adsorbed concentrations are greater than the equilibrium concentrations when the net transfer of a family is from the catalyst surface to the main body of the oil. The reverse is true when the net transfer of a family is from the oil to the catalyst surface.

For CC, the actual adsorbed concentration on the catalyst surface can always be assumed to be less than the equilibrium concentration. As the SR values for the hydrogenation increase, the actual concentration approaches the equilibrium concentration.

In the case of CT, C or T, the actual adsorbed concentrations are greater than the equilibrium concentrations during those phases of hydrogenation when there is a net production of that group. The adsorbed concentrations are less however during later stages of hydrogenation when there is a net decrease in the amount of that group in the system.

The actual adsorbed concentrations of unsaturated fatty groups and of hydrogen on the catalyst surface are most critical relative to all aspects of hydrogenation—rate of hydrogenation, selectivity and isomerization. These actual concentrations are complex functions of many variables, some of which are listed below:

1. Agitation which is a key factor in controlling the resistances to transfer of reactants to the catalyst surface and of products away from the surface.

2. For catalysts containing considerable pore area, the transfer in the pores is controlled only by diffusional processes. Adsorbed concentrations in the bottom of a narrow pore are certainly different than those at or near the lip of the pore.

3. Temperature has a relatively small effect on diffusion values but probably a greater effect on the viscosity of the oils. The latter is important in affecting the thickness of a laminar boundary layer around catalyst particles. Both diffusion values and viscosity then affect the overall transfer resistances. In addition, temperature has a major effect on the kinetics of the overall reaction as well as that at each catalyst site. Temperature affects the time between reactions on a given catalyst site and also the time available for R to approach toward the equilibrium value which would result in a high SR. It probably also affects the value of equilibrium R to a relatively small extent.

Indirectly pressure and the amount of granular catalyst used during hydrogenation also affect the actual adsorbed concentrations of reactants at the catalyst surface. Each variable affects the overall rate of reaction and hence the amounts of various unsaturated groups which are transferred to the catalyst surface.

Ignoring the transfer-adsorption and the desorption-transfer steps of Equation 7, results in an isomerization model (4) which is really quite empirical in

nature. Such a simplified model is however of utility for quantizing the II which should prove most helpful in characterizing geometrical isomerization. When a better understanding and reliable data are available for the transfer, adsorption and desorption steps, Equation 7 will be a preferred model for determining II.

### Modeling of Reaction Sequences

As has been indicated earlier, any modeling of the reaction sequences which occur during hydrogenation should ideally always include transfer, adsorption and reaction steps. Since however adequate data are not yet available, all models to date have grouped the transfer, adsorption and reaction steps as a single one. Such models can provide valuable information relative to the mechanism, but it should be emphasized that the rate constants determined are only pseudo reaction rate constants which are affected by the transfer, adsorption and true chemical steps of the overall reaction sequence.

Recently the rates of disappearance (or hydrogenation) of several isomeric monoenes were investigated in a vapor-phase process (13). Differences in the rates as determined from a mathematical model were noted for a large number of these isomers. Based on the data presented, it is impossible to determine if these differences were caused by differences in the rates of transfer, in the rates or degrees of adsorption on the catalyst surface, or in the rates of actual hydrogenation steps on the surface. One would expect that the general conclusions for the vapor-phase hydrogenation process might be quite different than those for a liquid-phase process. In particular, the resistances to transfer of the reactants to the catalyst surface would be very different in the two processes. Transfer of hydrogen is often the controlling step in liquid-phase processes, but in a vapor-phase process the resistances to hydrogen transfer would certainly be much less.

In a vapor-phase process, the shapes and sizes of the isomeric monoenes would likely be quite different; perhaps a greater difference would exist than in a liquid-phase process. Such differences in shape and size would certainly cause differences in the rates of transfer of the various monoenes to the catalyst surface.

The reaction model proposed recently (11) for the reduction of linolenate esters using a copper-chromite catalyst does an excellent job of predicting the reaction scheme in the main body of the liquid. The model does not necessarily give any indications however of the concentrations at the catalyst surface. Hence it is possible that the actual reaction sequence is different or more complicated than the one proposed. The adsorption and reaction rate characteristics on copper-chromite surfaces are undoubtedly much different than those on nickel surfaces.

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[Received May 12, 1970]