Kinetics of Catalytic Transfer Hydrogenation of Some Vegetable Oils

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ABSTRACT: Catalytic transfer hydrogenation of corn, peanut, olive, soybean, and sunflower oils has been studied with aqueous sodium formate solution as hydrogen donor and palladium on carbon as catalyst. Kinetic constants and selectivity have been determined under intensive stirring in the presence of stabilizing agents. Hydrogenation reactions followed first-order kinetics with respect to fatty acids. Besides good selectivity and short reaction time, this method offers safe and easy handling. The presence of linolenic acid retards the migration of double bonds, which explains why soybean oil is the most appropriate for this hydrogenation process.
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KEY WORDS: Catalytic transfer hydrogenation, corn oil, isomerization selectivity, olive oil, peanut oil, saturation selectivity, soybean oil, sunflower oil.

Oils used for edible purposes are produced from natural sources. Sometimes, oils are used without modification, but the requirements for edible oils are often considerably different from those of the natural products, so they have to be modified to reach the appropriate properties. Hydrogenation of vegetable oils is one of the earliest and most common commercial modifying methods. Hydrogenation changes the melting and solidification characteristics of the oils treated and is usually employed to reduce the degree of unsaturation of the naturally occurring triglycerides. Vegetable oils that are hydrogenated contain trienoic and dienoic fatty acids (FA) in a mixture with monoenoic and saturated acids. The main purpose of partial hydrogenation is to obtain monounsaturated from polyunsaturated FA, to obtain new, attractive organoleptic properties and greater chemical stability, especially with regard to oxidation.

The first industrial application of hydrogenation of oils in the liquid phase was Normann's patent (1), in which finely dispersed nickel particles were used for the gas-phase hydrogenation of organic compounds. The use of other metals, such as copper, platinum and palladium, as catalysts is an extension of the possibilities. The industry keeps searching for catalysts that operate under milder conditions and produce lower levels of *trans* isomers. In this respect, palladium catalysts seem to be the most promising (2).

In the search for an optimal hydrogenation procedure, an alternative new method for hydrogenation of edible oils and fats—catalytic transfer hydrogenation (CTH)—is being developed. Differing from the classical techniques with molecular hydrogen, hydrogen donors are used as a source of hydrogen in a catalytic transfer reduction. The generalized Equation 1 represents this process:

$$DH + A \xrightarrow{\text{catalyst}} D + AH \qquad [1]$$

where *A* represents the acceptor and *D* is the hydrogen donor. Hydrogenation is an extremely complex series of saturation and isomerization reactions of the double bonds of unsaturated FA. During the hydrogenation process, not only is hydrogen added to the double bond but also migration and geometrical isomerization of double bonds occur. The complete scheme of the process is complicated; so, many authors have used simplified models. The mechanisms and kinetic models of gas hydrogenation (GH) have been investigated, with the first simple kinetic model for GH of soybean oil proposed by Bailey (3). The simplified set of reactions proposed by Bailey is based on the assumption of a first-order and irreversible reaction and is in satisfactory agreement with experimental data. That model does not account for either positional or geometrical isomers, which are always formed during hydrogenation. The reaction scheme can be written as Equation 2:

$$\mathrm{Le} \xrightarrow{k_{\mathrm{Le}}} \mathrm{L} \xrightarrow{k_{\mathrm{L}}} \mathrm{Ol} \xrightarrow{k_{\mathrm{Ol}}} \mathrm{S} \qquad [2]$$

where Le, L, Ol, and S represent concentrations of linolenic, linoleic, oleic, and stearic FA, respectively, and k_{Le}, k_{L}, and k_{Ol} are the rate constants for hydrogenation of linolenic, linoleic, and oleic FA, respectively. Šmidovnik *et al.* (4,5) also reported a good agreement of model and experimental data when they used this set of reactions to describe CTH of soybean oil.

Saturation selectivities can be calculated from the rate constants as Albright and Wisniak (6) suggested. Saturation selectivities are defined as ratios of the relevant rate constants in Equations 3 and 4:

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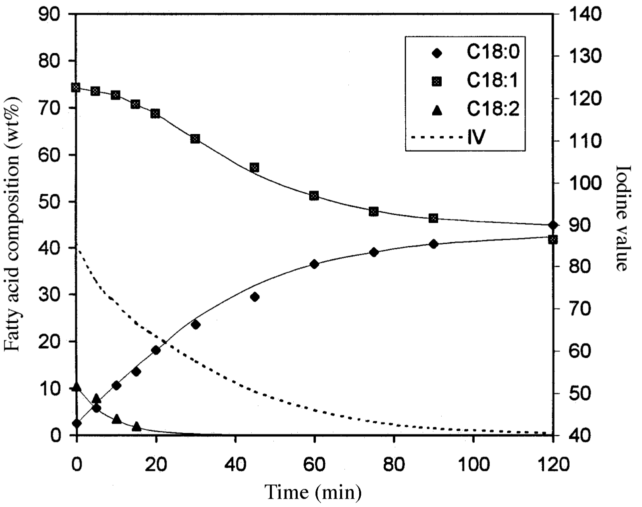

FIG. 1. Catalytic transfer hydrogenation (CTH) of olive oil—experimental data. IV, iodine value.

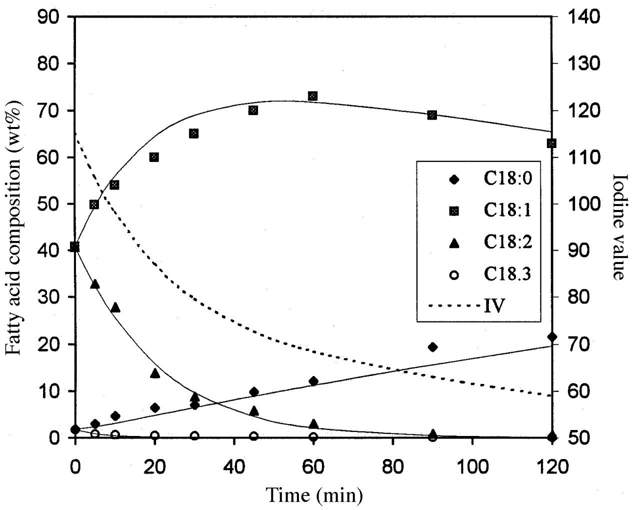

FIG. 2. CTH of peanut oil—experimental data. See Figure 1 for abbreviations.

$$S_{Le} = k_{Le}/k_L \quad [3]$$

$$S_L = k_L/k_{Ol} \quad [4]$$

High-linoleic selectivity (S_L) yields oils with the lowest melting points for a given unsaturation. High-linolenic selectivity (S_{Le}) increases the oxidative stability of oil without changing its liquidity. These ratios should be as high as possible to reach high saturation selectivity. To obtain the products with desired properties, the amount of *trans* isomers formed during the hydrogenation process is also an important factor. Coenen (7) defined the specific isomerization (*cis-trans* isomerization) as the ratio of produced *trans* double bonds and all eliminated double bonds.

As mentioned above, CTH uses some molecules as hydrogen donors. For sodium formate solution, it is believed that sodium formate is not the only hydrogen donor and that water also contributes hydrogen to the reaction. Equation 5 illustrates this process (8):

$$HCOO^- + H_2O + A \rightarrow HCO_3^- + H_2A \quad [5]$$

In this paper, the kinetics of CTH of olive (Fig. 1), peanut (Fig. 2), corn (Fig. 3), soybean (Fig. 4), and sunflower oils (Fig. 5) in a diluted aqueous sodium formate solution in the presence of an emulsifier are presented.

EXPERIMENTAL PROCEDURES

Materials. Hydrogenation was carried out with different commercial vegetable oils: soybean and olive oils were supplied by GEA-Slovenska Bistrica (Slovenka Bistrica, Slovenia), and sunflower, peanut, and corn oils were supplied by Oljarica Kranj (Kranj, Slovenia). Aqueous sodium formate (Fluka, Steinheim, Germany) solution was used as hydrogen donor, and palladium on activated carbon (E 101 NN/D 10% Degussa, Hanau, Germany) as catalyst. The stabilizer used was Mayodan M-612, supplied by Grindsted Companies (Aarhus, Denmark).

Methods of analysis. FA contents were determined as fatty acid methyl esters as prepared by IUPAC method II.D.19 (9). For analysis, an SP-2560 fused-silica capillary column (100 m × 0.25 mm inside diameter, 0.20 μm film thickness; Supelco, Bellefonte, PA) was used in a Varian 3400 (Walnut Creek, CA) gas chromatograph, equipped with an all-glass splitter system and flame-ionization detector. The gas chromatograph was operated at 150–200°C, with a heating rate of 3°C/min and a helium carrier gas flow rate of 1.2 mL/min.

Hydrogenation procedures. Oil with emulsifier, donor solution, and catalyst were agitated in a 250-mL round-bottomed flask. A mechanical stirrer with a 3-cm round-shaped Teflon blade was used. The thermostated water bath was used for the flask. Progress of the hydrogenation reaction was monitored by determining the FA composition of the samples that

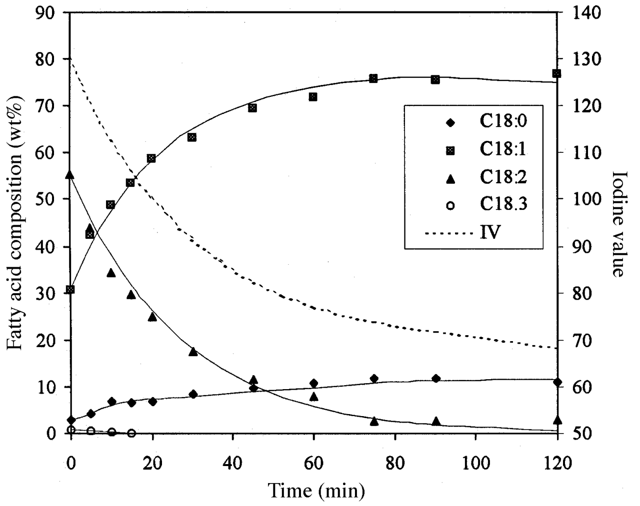

FIG. 3. CTH of corn oil—experimental data. See Figure 1 for abbreviations.

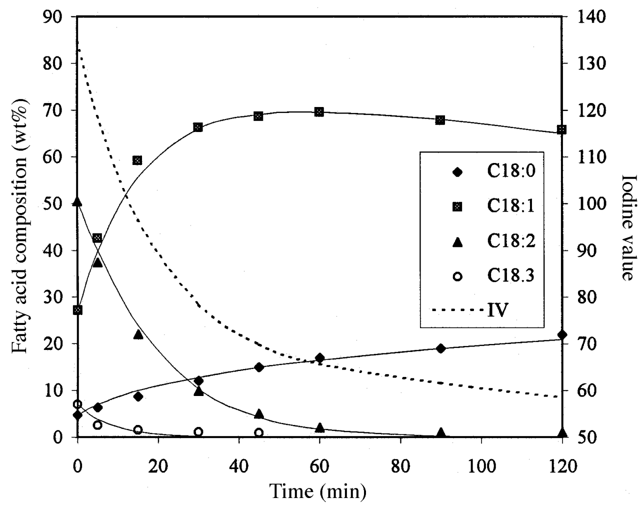

FIG. 4. CTH of soybean oil—experimental data. See Figure 1 for abbreviations.

were periodically removed during the process. Analysis was carried out by gas chromatography.

Operating conditions. The following composition and conditions were used for the process: oil, 50.00 g; donor—HCOONa, 9.44 g; water, 50.00 g; catalyst—10% Pd/C, 1.00 g; stabilizer—Mayodan M-612, 0.20 g; temperature, 80°C; agitation, 600 min^{-1}; pressure, atmospheric.

RESULTS AND DISCUSSION

CTH of oils with sodium formate solution as hydrogen donor and palladium on activated carbon as catalyst proceeds in a complex three-phase system (oil–water–solid catalyst); so, the appropriate amounts of each component should be present for a successful hydrogenation. Based on previous studies and the reports of other authors (4,5,8), the concentration of sodium formate was chosen to be 9.4 g HCOONa/50 g water (or 2.8 M HCOONa) as an optimum for all experiments. Higher concentrations slow down the reaction. This happens probably because the reaction proceeds through competitive adsorption of water and formate to identical active sites on the catalytic surface (8–10).

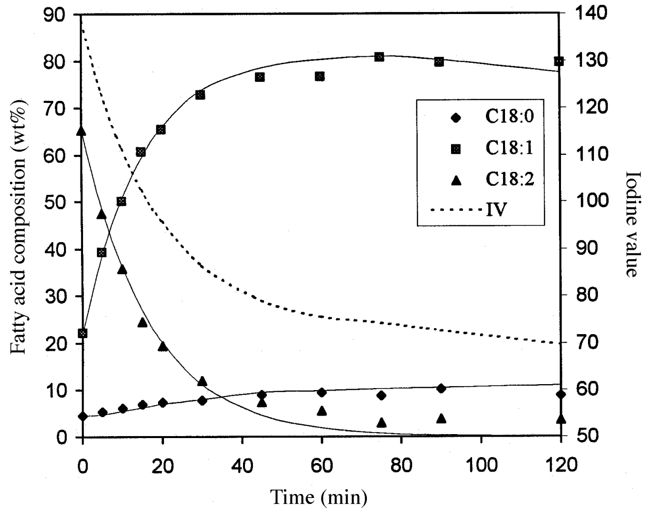

FIG. 5. CTH of sunflower oil—experimental data. See Figure 1 for abbreviations.

In the three-phase system, reaction can only proceed in the oil–water interface where catalyst must also be present. Because of this, the liquid-liquid interface is one of the most important factors to influence the reaction rate and has to be large enough. The use of a stabilizer reduces the surface tension, thus enlarging the interface (11). With simultaneous solving of differential equations, which are derived from the simplified Bailey's reaction equation (Eq. 2), the rate constants are calculated in Equations 6–8 from the experimental data (Tables 1–3):

$$\frac{dC_{\text{Le}}}{dt} = -k_{\text{Le}}C_{\text{Le}} \tag{6}$$

$$\frac{dC_{\text{L}}}{dt} = -k_{\text{L}}C_{\text{L}} + k_{\text{Le}}C_{\text{Le}} \tag{7}$$

$$\frac{dC_{\text{Ol}}}{dt} = -k_{\text{Ol}}C_{\text{Ol}} + k_{\text{L}}C_{\text{L}} \tag{8}$$

where *dC/dt* represents a rate of formation.

Based on the calculated saturation selectivities, some conclusions could be made; k_{Le} and k_{L} are quite similar in comparison with k_{Ol}. This behavior may indicate that conjugated double bonds are formed by migration of double bonds (12) in polyunsaturated compounds (triunsaturated and diunsaturated) during hydrogenation. This results in a higher reactivity of dienes and especially trienes in comparison with monounsaturated compounds. The hydrogenation of monoenoic compounds is much slower.

During the hydrogenation process, both geometrical and positional isomerizations take place. As a result of these processes, the number of chromatographic peaks (Fig. 6) strongly increases. Qualitative determination of all peaks formed as a consequence of isomerization is difficult. To determine the isomerization level, we use a modified Coenen (7) definition and present isomerization selectivity (*Si*) in Equation 9 as:

$$Si = \frac{\text{“iso”-forms}}{\text{all hydrogenated double bonds}} \tag{9}$$

TABLE 1
Saturation and Isomerization Selectivities for Olive, Peanut, Corn, Soybean, and Sunflower Oils[a]

	Olive	Peanut	Corn	Soybean	Sunflower
k_{Le} (min^{-1})	—	0.145	0.139	0.170	—
k_{L} (min^{-1})	0.11	0.047	0.038	0.062	0.059
k_{Ol} (min^{-1})	0.001	0.002	0.002	0.002	0.002
S_{Le}	—	3.1	3.7	2.7	—
S_{L}	11	18.8	22.4	38.8	32.8
Si	0.74	0.87	0.84	0.47	0.80

[a] Saturation and isomerization selectivities are calculated from Equations 3 for S_{Le}, 4 for S_{L}, and 9 for *Si*, where S_{Le} is high-linolenic selectivity, S_{L} is high-linoleic selectivity, and *Si* is isomerization selectivity.

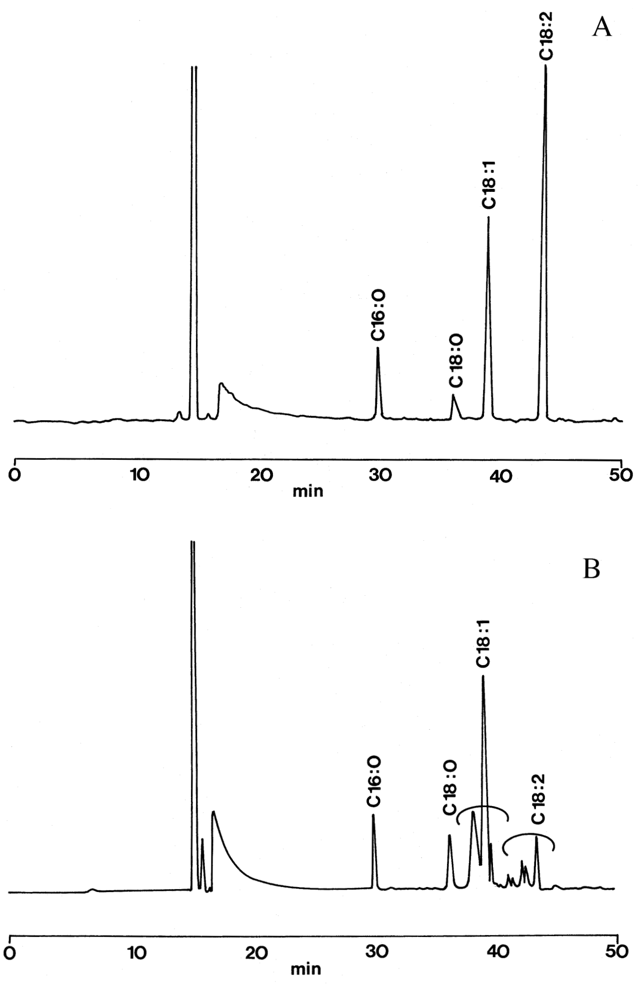

FIG. 6. Chromatograms of untreated (A) and partially hydrogenated (B) corn oil as analyzed on an SP 2650 capillary column (Supelco, Bellefonte, PA).

"Iso"-forms of fatty acids are all positional and geometrical (*trans*) isomers except for naturally occurring FA.

The behavior of olive, corn, and sunflower oils seems to be strange (Fig. 7) because the isomerization degree is the highest at the beginning and then decreases. It is reasonable to suppose that double-bond migration begins before hydrogenation occurs. As a result of double-bond migration, more reactive conjugated dienes are formed. These dienes are quickly hydrogenated, and therefore the degree of isomerization decreases.

TABLE 2
Fatty Acids Composition (wt%) and Iodine Values (IV) of Untreated Oils

	Olive	Peanut	Corn	Soybean	Sunflower
16:0	12.7	14.7	10.4	10.8	7.9
18:0	2.6	1.9	2.8	4.7	4.5
18:1	74.3	40.9	30.6	27.1	22.2
18:2	10.4	40.7	55.4	50.4	65.2
18:3	—	1.8	0.8	7.0	0.2
IV	86	115	130	137	139

TABLE 3
Fatty Acids Composition (wt%) and Iodine Values (IV) of Partially Hydrogenated Oils

	Olive	Peanut	Corn	Soybean	Sunflower
16:0	12.8	14.9	10.4	10.8	7.8
18:0	45.4	21.6	11.0	23.7	9.0
18:1	41.8	62.9	76.2	65.5	79.6
18:2	—	0.6	2.8	—	3.6
18:3	—	—	—	—	—
IV	37	57	73	59	78

Double-bond migration in the first stage of the hydrogenation process occurs with olive and sunflower oils, which contain no linolenic FA, and with corn oil, which contains only traces of the latter (Tables 1–3).

For soybean and peanut oils, the situation is reversed (Fig. 7). It seems that double-bond migration is retarded at the beginning. The peanut and soybean oils contain linolenic FA. The lowest level of double-bond migration is achieved by soybean oil, which contains the highest amount of linolenic FA (Tables 1–3). Also, the hydrogenation rate is the highest for soybean oil.

We conclude that the presence of linolenic FA retards the migration of double bonds and, at the same time, accelerates hydrogenation. The reason for this behavior lies in the fact that linoleic FA contains two double bonds which may promote the formation of highly reactive conjugated dienes. These conjugated dienes could be easily hydrogenated, even under conditions where the amount of hydrogen on the catalyst surface is the limiting factor of the whole hydrogenation process. Under such conditions, all other FA are heavily hydrogenated; that is why only migration of double bond takes place.

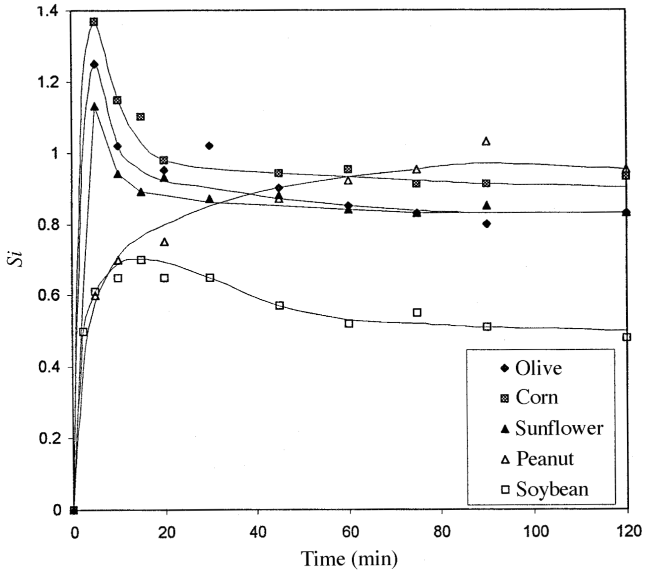

FIG. 7. The isomerization process occurring during CTH—experimental data. See Figure 1 for abbreviation. *Si,* isomerization selectivity.

CTH of examined vegetable oils in a solution of sodium formate follows the simplified Bailey's model of the first-order kinetic reaction with respect to the oil compound, when the kinetic regime is achieved by intensive stirring and by adding an emulsifier.

CTH with a solution of sodium formate as hydrogen donor is a simple and useful alternative to hydrogenate vegetable oils. Besides good selectivity and short reaction time, this method offers safe and easy handling.

We conclude that the presence of linolenic acid retards the migration of double bonds, which explains why soybean oil is the most appropriate oil for this hydrogenation process.

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