Catalytic Transfer Hydrogenation of Soybean Oil Methyl Ester Using Inorganic Formic Acid Salts as Donors

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The hydrogenation of soybean oil methyl esters using aqueous formic acid salts solutions and heterogeneous palladium-on-carbon catalyst was investigated. Complete hydrogenation of the methyl ester was achieved by mixing a concentrated aqueous alkali formate solution with the methyl ester at 80 C in the presence of the catalyst (0.2-0.4% Pd). At the initial stages of the reaction, the selectivity was significantly higher than conventional hydrogenation (hydrogenation under pressure) performed with the same catalyste. *Cis-trans* isomerization was similar to the behavior of conventional techniques.

Since the first review (1) dealing with the subject, catalytic transfer hydrogenation has become a widely used tool. The reaction may be represented by the general equation [1], where D and A are the hydrogen donor and acceptor, respectively:

$$DH_2 + A \xrightarrow{cat} D + AH_2 \qquad [1]$$

The transfer hydrogenation of fats by various donors has been studied by several workers. Basu et al. 2,3) have shown that alcohols (particularly 2-propanol) can be used as hydrogen donors, but only under relatively extreme conditions, resulting in reduced selectivity. Later, Tagawa et al. (4-6) improved the selectivity by using high amounts (up to 20% w/w) of homogeneous catalysts [e.g. $RhH_2(PPh_3)_4$]. Applying various donors (including formic acid), they found homogeneous catalysts to be more selective than the corresponding heterogeneous catalysts (7).

The importance of selectivity and *trans* double bond formation in different oil hydrogenation processes has been emphasized and discussed exhaustively (8). Various concepts of selectivity have been suggested in the past (9). We adopted the following definitions (10):

$$C_{18:3} \xrightarrow{kLe} C_{18:2} \xrightarrow{kL} C_{18:1} \xrightarrow{kO} C_{18:0}$$

$$S_L = k_{Le}/k_L \quad S_O = k_L/k_O$$

High values of S_L and S_O are advantageous in most products, while the optimal amount of *trans* double bonds depends on the type of product (8). For hydrogenation in presence of Pd-on-carbon catalysts, the reported values for S_L and S_O vary between 1.3-2.9 (11-13) and 25-40 (13), respectively. The degree of *trans* double bond content (expressed as percent of total double bond) of the product depends mainly on the degree of hydrogenation of the fat (final iodine value) and varies between 20% (IV = 115) to 50% (IV = 65) (11-13), but reports are very contradictory (14).

Alkali metal formates react with hydrogen acceptors in the presence of Pd-on-carbon catalyst according to equation [2] (15,16).

$$HCOO^- + H_2O + A \xrightarrow{Pd/C} HCO_3^- + H_2A \qquad [2]$$

Recently, it has been shown that formates are superior to other hydrogen donors (15,17). They are very reactive donors, and the side reaction, liberation of gaseous hydrogen according to Equation 3, is relatively slow (15,16). For comparison, formic acid rapidly decomposes into CO_2 and H_2 when brought into contact with transition metals (15).

$$HCOO^- + H_2O \xrightarrow{Pd/C} HCO_3^- + H_2 \qquad [3]$$

The utilization of formic acid salts to obtain either selective or complete (IV <3) hydrogenation of soybean oil methyl ester, depending on the duration of the reaction, is presented in this paper. The latter has not been achieved to date under hydrogen transfer conditions (2-7).

EXPERIMENTAL

Materials. Soybean oil methyl ester was prepared from commercial soybean oil, which was purified and transesterified by the method of Glass (18). The methyl ester obtained had an iodine value of 133. The formic acid salts (Fluka) and the formic acid (Merck) were of the highest purity available. The catalysts used for hydrogenations were:

	Water content wt/wt catalyst
Pd-on carbon (Engelhard)	47%
Raney nickel (Harshaw)	50%
Nysel DM.3 (Harshaw)	dry

Methods of analysis. The iodine values were determined by the Hanus method (19). A 10% DEGS-PS on 80/100 mesh Supelcoport column at 200 C was used for GC determination of the fatty acid composition. *Trans* unsaturation was measured by IR absorption according to the method recommended by the A.O.C.S. (20). The residual formate at the end of the reactions was determined by potentiometric titrations using 2N HCl-solutions and an arbitrarily set endpoint (pH 2.4). Titrations of standard solutions showed that the accuracy of the procedure was better than ±20%. This was found to be enough for our purposes. Alternative procedures are much more labourious (21-24).

Hydrogenation procedures. The influences of variables on the reactivity of the transfer hydrogenation were determined using a standard procedure. Weighed amounts of methyl ester (5 g), catalyst and donor solutions were agitated mechanically at 900 rpm in a stoppered 25 × 150 mm test tube, which was immersed in

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a water bath at 80 ± 0.1 C. After 16 hr the oil phase (which included the catalyst) was diluted with chloroform and separated from the aqueous phase. After filtering of the catalyst, the chloroform was evaporated and the iodine value determined. (The chloroform was needed to facilitate filtration because of lack of a filter press.)

In some experiments hydrogen evolution was measured volumetrically. For this purpose the reaction test tube was equipped with an outlet which was connected to a gas trap, after passing through a carbon dioxide scrubber (aq. sodium hydroxide). Selectivity was investigated by hydrogenation of larger batches (20 g) of methyl ester. The selectivity coefficients have been calculated according to the equations used by Okkerse et al. (10). Reaction conditions were unchanged (aqueous potassium formate, 10% Pd-on-carbon, mechanical agitation, 80 C). Aliquots for GC analysis were withdrawn at different time intervals and diluted with chloroform before injection. The iodine values were calculated from the GC data obtained.

RESULTS AND DISCUSSION

Potassium formate was chosen as reagent because of its high solubility in water (330 g/100 g H_2O at 20 C(25)) compared to other formic acid salts. This enables application of very concentrated solutions. The iodine value (IV) obtained after hydrogenating the soybean oil methyl ester (initial IV = 133) in reactions run overnight (16 hr) was chosen as standard criterion in order to determine the effect of various parameters on the reactivity of the transfer hydrogenation reaction.

Effect of temperature. All reactions were run at 80 C. At this temperature no loss of water occurred during the course of the reaction. Below this temperature (20 C and 50 C) hydrogenation was minor even after 16 hr. Heating to higher temperatures (up to 110 C) did not result in further acceleration of the reaction, probably because increased water evaporation caused drying of the solution. At higher temperatures it is thus recommended that pressure vessels be used.

Effect of agitation. Agitation had a marked influence on the reaction rates. We found mechanical agitation to be necessary, because the results were not reproducible when magnetic stirring was applied. Up to a rate of 450 rpm the reaction rate increased with the stirring rate. Above this value, the reaction rate was constant and independent of the stirring rate.

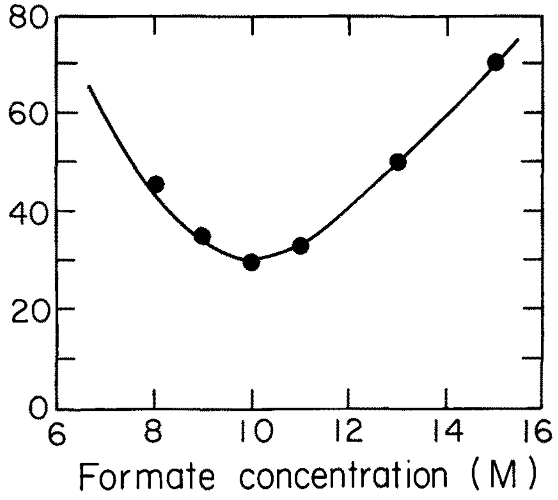

FIG. 1. Effect of initial KOOCH concentration on the hydrogenation of the oil. Reaction conditions: 5 g oil, 10% Pd/C (0.2% Pd), 2 mol KOOCH/mol of double bond (DB), mechanical stirrer at 900 rpm, 80 C, 16 hr.

Effect of potassium formate concentration. The potassium formate concentration determines the activities of both the formate and the water. It must be kept in mind that the latter participates stoichiometrically in the reaction Equation 2 (15,16).

Figure 1 shows the iodine value obtained with different initial donor concentrations. Hydrogenation is most efficient at a concentration of 10M potassium formate. (At this concentration the solution contains 3 mol H_2O/mol KOOCH). Accordingly, all further reactions were carried out at this concentration.

Effect of excess potassium formate. Excess of potassium formate is needed, since some of the formate decomposes, yielding molecular hydrogen which is lost, and because the concentration of the formate decreases, as the reaction proceeds, resulting in reduced hydrogenation rates. Some experiments are summarized in Table 1.

Comparison of the amount of molecular hydrogen formed by decomposition of potassium formate and of

TABLE 1

Effect of Excess KOOCH on IV of Hydrogenated Fat[a]

Run	Initial KOOCH (mmol)	Molar ratio KOOCH/DB	final IV	KOOCH consumed for hydrogenation calc (mmol)	H_2 liberated (mmol)	KOOCH residue determ by titration (mmol) (±20%)
1	30	1.2	45	17	5	9
2	40	1.6	18	22	8	7
3	50	2.0	10	23	7	15
4	60	2.4	11	23	10	24
5	50[b]	2.0	98	7	41	–

[a] Reaction conditions: 5 g fat, 0.3% Pd, KOOCH-10M, mechanical stirring at 900 rpm, 80 C, 16 hr.

[b] Formic acid.

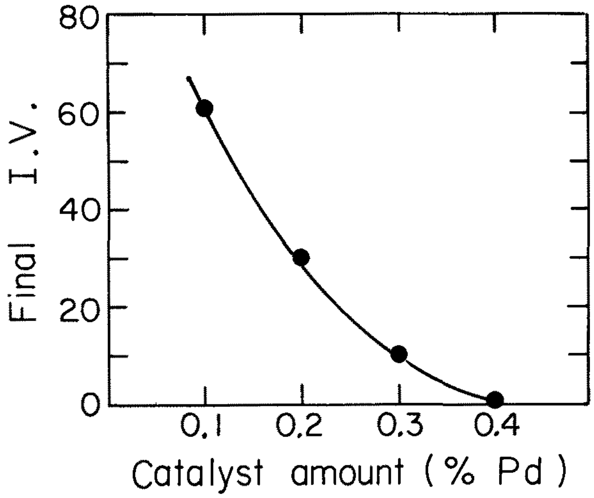

FIG. 2. Effect of the amount of catalyst. Reaction conditions: 5 g methyl ester, 50 mmol KOOCH (10M), 10% Pd/C-catalyst, 80 C, 16 hr.

formic acid (Equation 3), and the yield of saturated oil obtained with these two donors, emphasizes their different efficiencies. It can be seen that most of the excess donor does not decompose, but remains as residue, which may be recovered. At a molar ratio of 2 (donor to double bond) the reduction in the iodine value reaches its maximum, and a further increase in the amount of donor does not enhance the hydrogenation of the methyl ester.

In all the succeeding experiments a molar ratio of 2 (donor to double bond) was used to avoid control of the hydrogenation rate by the donor. Although it might be an interestig approach, no attempt was made to improve the selectivity of the reaction by using less than stoichiometric amounts of the donor. Further, the relation between formate concentration and the selectivity was not tested, although it might be expected to increase at lower concentrations.

Effect of type and amount of catalyst. The only effective catalyst, among those tried, was Pd-on-carbon. Hardly any hydrogenation occurred ($\Delta IV < 10$) even after 24 hr when such well established hydrogenation catalysts as Raney nickel or Nysel's DM3 were used. (Ninety to ninety-five per cent of the initial amount of potassium formate was detected in the residue, proving that the donor had not decomposed.) Reactions carried out using different Pd-on-carbon catalysts (2, 5 α 10% Pd-on-carbon) but with equal total amounts of Pd gave similar results.

The effect of the catalyst amount on the hydrogenation of the methyl ester is shown in Figure 2. Use of 0.4% Pd resulted in complete saturation. At lower levels of catalyst, prolonging the reaction (from 16 to 72 hr) resulted in a minor reduction of the iodine value only. (With 0.1% Pd the IV was reduced from 60 to 48). This might be due to deactivation of the catalyst caused by the precipitation of potassium bicarbonate [solubility at 60 C, 60 g/100 g H_2O only (25) formed during the reaction Equation 2]. Poisoning of the catalyst by impurities from the methyl ester can be excluded because of the relatively high amounts of catalyst used in com-

TABLE 2

Change in Methyl Ester Composition During Hydrogenation With Potassium Formate

	Composition determined by GC[a]							
IV (calc)	C_{18} triene	C_{18} diene	C_{18} monoene	C_{18} sat	C_{16} sat	% *trans*[b]	S_L[c] = k_1/k_2	S_O[c] = k_2/k_3
133[d]	8.0	54.0	22.6	3.4	12.0			
124	4.3	51.2	29.0	3.5	11.9	8	5.2	
121	3.6	49.1	31.9	3.4	12.0	15	4.4	
117	2.4	46.8	35.3	3.5	12.0	19	4.7	
105	0.3	36.7	47.4	3.6	11.9	25	6.0	95
102	—	34.0	50.4	3.6	11.8	26		115
94		25.0	59.2	3.8	12.0	35		100
79		9.0	74.5	4.5	11.9	37		100
74		3.4	79.6	5.0	12.0	39		120
70			82.0	6.0	11.9	38		
61			71.3	16.7	11.9	66		
51			59.2	28.8	11.9	72		
33			38.1	49.9	12.0	86		
9[e]			10.6	77.4	11.9	76		

Reaction conditions: 20 g oil, 20 ml KOOCH 10M, (0.3% Pd), mechanical stirrer, 80 C. Samples were withdrawn at different time intervals, and, after dilution with chloroform and filtration of the catalyst, they were analyzed by G.C.

[a] For accuracy, each sample was injected at least 3 times.

[b] Expressed as percent of total unsaturation.

[c] Selectivities were calculated based on the compositions of the starting methyl ester and of the sample to which they were related.

[d] Composition of original methyl ester.

[e] Maximum conversion obtained.

TABLE 3

Reactivity of Different Formic Acid Salts[a]

Cation	Final IV
Na^+	< 2
NH_4^+	3
K^+	30

[a]Reaction conditions: 5 g methyl ester, 50 mmol formate (10M), 10% Pd/C (0.2% Pd), 80 C, 16 hr.

parison to conventional hydrogenation (13). We did not attempt to reuse the catalyst. It has been shown recently that Pd-on-carbon catalyst can be recycled after use in formate transfer hydrogenation (Wiener, H., S.Vandel and Y. Sasson, unpublished data).

Comparison of different formic acid salts. When comparing different formic acid salts as donors, it was found that sodium formate and ammonium formate were somewhat more reactive that potassium formate. (In order to obtain a 10M solution of sodium formate the salt and the water were added separately to the reaction mixture, which was then heated to 80 C, resulting in complete dissolution of the salt.) The results are shown in Table 3. Although the differences are not very pronounced, these results are surprising. Preliminary experiments performed in our laboratory with different organic substrates had shown potassium formate to be superior to sodium and ammonium formate (Wiener, H., S. Vandel and Y. Sasson, unpublished data).

Selectivities in formate transfer hydrogenation of soybean oil. A typical hydrogenation of soybean oil methyl ester run with 0.3% Pd (10% Pd/C-catalyst) and 10M potassium formate solution is summarized in Table 2. The average S_L and S_O selectivities are approximately 5 and 100, respectively. The selectivities found are unexpectedly high compared to conventional hydrogenations using Pd/C-catalyst (Introduction and 11-13). Thus, a relatively small loss of linoleic acid occurs, during the elimination of linolenic acid from the oil. Although less pronounced, this effect is similar to that observed with copper catalysts (10). On the other hand, *trans* double bond formation was rather typical for such reactions. UV inspection did not detect any conjugated bonds in the samples investigated. The improved selectivities obtained can be explained in terms of a strongly hydrogen-deficient catalyst surface (8). Because the catalyst is dispersed in the oil phase and not in the aqueous phase (this was proved in preliminary experiments in our laboratory), the hydrogenation rate apparently is controlled by the slow mass transfer of formate and water to the catalyst's surface. This also explains the relatively long reaction time required and the need for strong agitation.

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