

The Homogeneous Hydrogenation of Soybean Oil Methyl Ester

SELECTIVITY OF PLATINUM AND PALLADIUM COMPLEXES

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The soybean, a major crop in the United States as well as in China and Brazil, yields an oil used widely in the manufacture of margarines, salad oils, shortening, and other food products. Before use, however, it must be upgraded by selective hydrogenation of linolenates to linoleates. This paper describes research on platinum complexes that have been found to be highly selective in this reaction. The work was carried out under contract with the U.S. Department of Agriculture and was supervised by the Northern Utilisation Research and Development Division of the Agricultural Research Service.

Although the soybean has been a major agricultural product in the Orient for more than three thousand years, it was virtually unknown in the western world until about forty years ago. Research on the culture, processing and utilisation of soybeans began a few years before that, and was pursued with great vigour, especially in the United States. Through careful plant breeding, the soybean was adapted to American soils and climate, and it soon became a major crop, especially in Illinois, Indiana, Iowa and other mid-western states.

Soybeans contain up to 20 per cent oil, which is pressed or extracted from the beans and is used widely in the manufacture of margarines, shortenings, salad oils and other food products. It also finds wide industrial

use in the manufacture of alkyd and polyamide resins and, in modified form, in drying oils. These uses, however, are much less important than its use in foods. The meal which remains after the oil is extracted from the beans is a valuable by-product, finding extensive use in animal feeds, meat substitutes, and special protein concentrates. World production of soybean oil is much greater than that of any other edible vegetable oil.

Soybean oil is a mixture containing chiefly glycerol esters of long chain organic acids. To simplify the study of this mixture, the glycerol esters are usually converted to methyl esters; thus, each alcohol group is attached to a single acid chain instead of three. Samples of the oil differ somewhat in composition, depending upon the strain of the plant from which the oil came, and the soil and climatic conditions in which the plant grew. A typical oil might contain:

linolenate	7.5	per cent
linoleate	50	„
oleate	27	„
stearate	4	„
palmitate	10	„

All of the double bonds have the *cis* configuration, which is desirable from a practical point of view.

In soybean oil which is to be used in the manufacture of foodstuffs, linolenates are highly objectionable because they have a bitter taste, and palmitates and stearates are somewhat undesirable because, if present in too large amounts, they are difficult to digest. Since it is impractical to separate the desired from the objectional esters in this mixture,



The World's most important edible vegetable oil is extracted from soybeans (or soya beans). Annual production of soybean oil now amounts to over five million metric tonnes. The oil is a mixture of glycerol esters of long-chain organic acids, including undesirable linolenates, palmitates and stearates. These need removal or substantial reduction before consumption.

(Picture courtesy of Unilever Limited)

efforts to upgrade soybean oil have depended largely upon converting linolenates to linoleates by selective hydrogenation. The formation of oleate is less desirable, but even this represents an upgrading of the oil.

Hydrogenation of Linolenic Ester

Unfortunately, the double bonds in linolenic ester are remarkably alike, and one cannot rely on any difference in chemical reactivity which will allow the hydrogenation of one of them to the exclusion of the others, or even a difference in rate of hydrogenation. If there is to be highly selective hydrogenation, it must rest upon some peculiar property of the hydrogenation catalyst, and the mechanism of catalyst operation.

Apparently, the first specific attempts to hydrogenate soybean oil selectively were made by Zajcew (1), who used a palladium catalyst at 114°C and 47 p.s.i. of hydrogen.

There was some selectivity, but his product contained 19.1 per cent of saturates. Allen (2), using a nickel catalyst at 285°F and 30 p.s.i. of hydrogen, was much more successful, for he was able to reduce the content of linolenic ester to 1.0 per cent and to increase the content of oleic ester to 61.5 per cent, leaving the stearate at 5.7 per cent.

Various catalysts have been tested as replacements for nickel in the hydrogenation of vegetable oils on a commercial scale but hitherto nickel, e.g. as formate, has been the most important. Specific attempts to hydrogenate soybean oil have been made using salts of chromium, cobalt, vanadium, etc.

The catalysts which are the main subject of this paper are platinum complexes. That they are highly selective in the hydrogenation of soybean oil is illustrated by Table I, which gives data from two typical experiments with soybean oil methyl ester (3).

Table I
Hydrogenations of Soybean Oil Methyl Ester with Platinum Complexes

	Composition (%)					
	Palmitate	Stearate	Monoene	Diene	Triene or c-t conjugated diene	t-t conjugated diene
Before hydrogenation	10.9	3.8	28.3	50.5	6.5	—
1 After hydrogenation	11.8	4.4	78.5	5.4	0	—
2 After hydrogenation	11.5	4.4	84.1	—	—	—

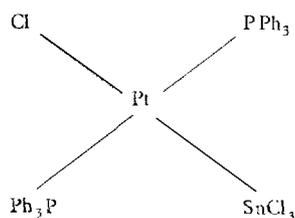
A sample of methyl linolenate, after hydrogenation, showed 26.0 per cent monoene and 74.0 per cent diene, with no stearate and no unreduced triene. Unfortunately the "monoene" in the product is not all methyl oleate, for the unreduced double bond is chiefly of the *trans* configuration and it is not exclusively in the 9-position. While most of the material consists of molecules in which the double bond is near the centre of the chain, there are molecules in which it is as close to the carbonyl group as the fourth carbon atom, and as distant from it as the fifteenth (4).

Catalyst Complexes

Our concept of the catalysts which are described in this article grew out of a note by Cramer, Jenner, Lindsey and Stolberg (5), who reported that, while $H_2PtCl_6 \cdot 6H_2O$ is only a mild catalyst for the homogeneous hydrogenation of ethylene, and tin(II) chloride is not a catalyst at all, a mixture of the two is a remarkably good catalyst. The implication that the two have combined to form a complex has been amply confirmed by later work (6).

Although Cramer et al. (5) had used the Pt-Sn catalyst for the hydrogenation of a compound containing one double bond, we hypothesised that, with a polyolefinic material, it might catalyse the hydrogenation of only a portion of the double bonds in each molecule. Our first experiments were performed with this catalyst, in a solvent con-

sisting of benzene (60 per cent) and methanol (40 per cent) (7). van't Hof and Linsen (8) have also used this catalyst for the hydrogenation of soybean oil. Their results parallel ours. Later, our catalyst was modified by use of bis-triphenyl-phosphine platinum(II) chloride (9) instead of hexachloroplatinic(IV) acid. This, when treated with tin(II) chloride, gives a compound which has the structure



We found this catalyst to be slightly more selective than the original one. The reaction by which tin(II) chloride inserts itself into the Pt-Cl bond is shown to be reversible by the fact that best results are obtained when a tenfold excess of tin(II) chloride is used. A larger excess reduces the efficiency of the catalyst, supposedly by the formation of $Pt(PPh_3)_2(SnCl_3)_2$ (10).

The catalyst can be varied in a large number of ways without loss of its selective hydrogenation ability toward soybean oil methyl ester. Trialkyl phosphines or mixed alkyl-aryl phosphines can be used; in fact, $P(CH_3)_2Ph$ gives a much more active catalyst than does PPh_3 . Methyl-diphenylphosphine, $P(CH_3)Ph_2$, gives a catalyst of intermediate activity. The catalyst made from trimethylphosphine, however, is not very active (11).

In the catalysts which have been mentioned, the phosphine ligands occupy *trans* positions in the complex molecule (12, 13), but this is not an essential feature. Bidentate phosphines, $R_2PCH_2CH_2PR_2$, which must coordinate in *cis* positions, are also effective (12, 13).

Triphenylarsine and triphenylstibine can be used in place of the phosphine. The arsine complex gives a more active catalyst than the phosphine complex, but it is less stable and suffers from the obvious disadvantage of containing a highly toxic material (14). Diphenyl sulphide and selenide can replace the phosphine, also, but do not give highly active catalysts (12). Lead and germanium chlorides can be substituted for tin chloride, but are much inferior (14a).

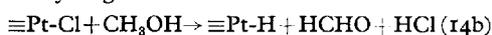
The palladium complex, $Pd(PPh_3)_2Cl_2 + SnCl_2 \cdot 2H_2O$ is more active than the corresponding platinum complex and shows good selectivity. It has to be used at a lower temperature, however, for it is considerably less stable (14b).

Bis-triphenylphosphine-dicyano-palladate (II), $Pd(PPh_3)_2(CN)_2$, (14b) and bis-triphenylphosphine nickel iodide, $Ni(PPh_3)_2I_2$, (15) are selective catalysts, even without the addition of tin chloride, but in the presence of either of these catalysts, the hydrogenation is slow. The ligands CN^- and I^- , like $SnCl_3^-$, are weak σ donors and strong π acceptors (6, 10, 16) and are thus able to adjust the electron density around the Group VIII metal so that it can hold both the hydrogen and the olefin in the coordination sphere, but can release them to combine with each other.

For hydrogenation with the platinum catalyst, a temperature of 90° to 110°C is maintained, and a hydrogen pressure of about 500 p.s.i. At lower temperatures and pressures, isomerisation takes place, but not hydrogenation. In certain applications, this may be a useful property. Bond and Hellier (17) have made detailed studies of the isomerisation of 1-pentene using a mixture of H_2PtCl_6 and $SnCl_2 \cdot 2H_2O$. They report that, initially, *trans*-2-pentene is formed in greater

than the equilibrium amount, but within an hour and a half, equilibrium is reached (81 per cent *trans*-2-, 17.5 per cent *cis*-2-, 1.5 per cent 1-pentene).

The solvent which was used in our first experiments (a mixture of benzene and methanol) was chosen because it readily dissolves both the soybean oil and the catalyst. It soon became evident, however, that in the absence of hydrogen (and probably, to some extent, in its presence) this solvent serves as a hydrogenating agent by converting the chloroplatinum complex to the hydrido complex, which, in turn, transfers its hydrogen atom to the substrate:



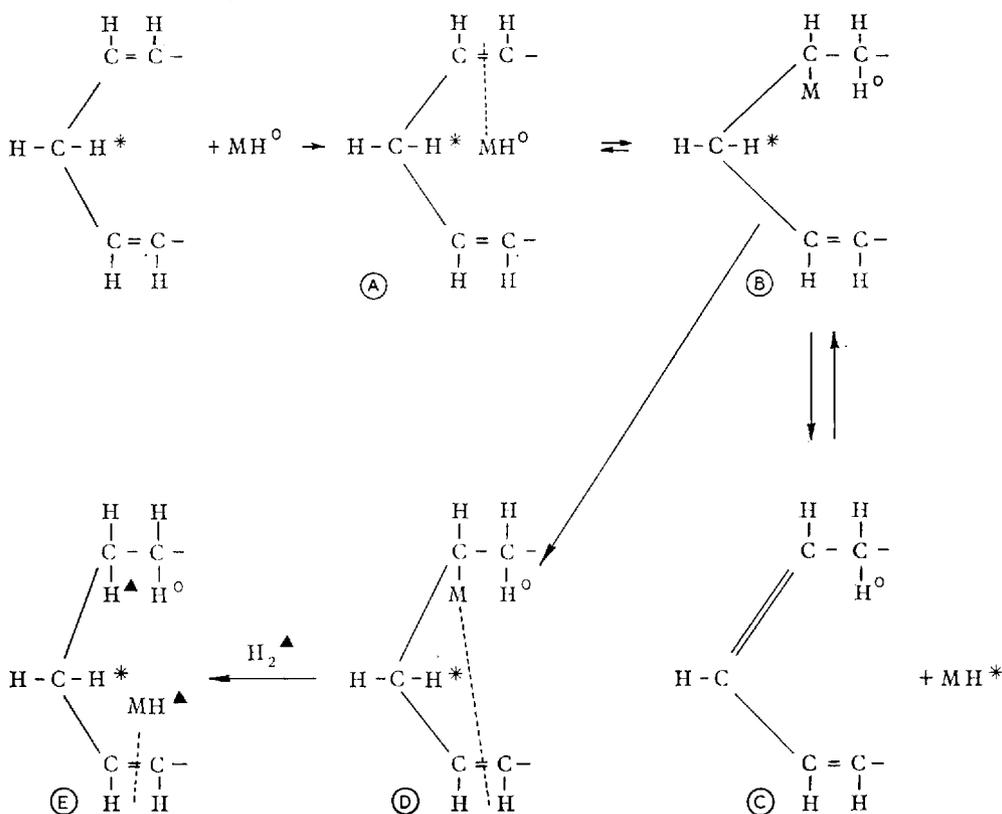
Platinum(II) contains ten electrons less than the next rare gas, so it can coordinate with five donor atoms. Normally, it shows a coordination number of only four, but the presence of the fifth coordination position is essential to its catalytic activity, for it is through this that the olefin group is attached.

In the presence of hydrogen and the olefin, the platinum compound is converted to the five coordinate complex $[Pt(PPh_3)_2(SnCl_3)H(ol)]$ (12). Several compounds of this general formula have been isolated, including those in which "ol" represents 4-octene and 1,4-cyclohexadiene. 1,5-Cyclooctadiene forms a compound in which each double bond is attached to a molecule of the catalyst. The presence of any strongly coordinating substance blocks the fifth coordination position and destroys the catalytic activity of the platinum. Even the solvent may play this role. It has been found that hydrogenations with the platinum-tin catalyst proceed about five times as fast in methylene chloride as in the benzene-methanol mixture, and that they do not go at all in pyridine (12). Methylene chloride and other chlorinated hydrocarbons are poor solvents for the catalyst, but, even so, they offer a great advantage.

Catalyst Selectivity

The selectivity of the platinum-tin catalysts toward large polyenes apparently rests upon

the fact that only conjugated systems are attacked. If the double bonds are not conjugated, the molecule must isomerise to conjugation before hydrogenation can take place. In a polyolefinic molecule, isomerisation and hydrogenation take place alternately until only one double bond remains, but the process must then stop. The following mechanism is suggested (12): (M represents the $\text{Pt}(\text{PPh}_3)_2\text{SnCl}_3$ fragment of the catalyst. Some of the hydrogen atoms are marked, but only so the reader may more easily follow the discussion. No experiments with labelled materials have been performed in our work.)



Compound A contains a π bond, which readily converts reversibly to the σ bonded compound B. Instead of reverting to A, B may equally well go to the conjugated C, this step also being reversible. The platinum atom in B may, however, attach itself to the adjacent double bond through a π -linkage, forming D. The metal-carbon σ bond in D is broken upon hydrogenation to give E. The double bond

in E may migrate along the chain until it approaches another double bond, whereupon the hydrogenation step is repeated, until only one double bond remains. The presence of D or a similar molecule is thought to be necessary for the hydrogenation of the metal-carbon σ bond.

It is not necessary that the double bonds be close together in the original molecule. The dienoic ester $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$, in which the double bonds are separated by six carbon atoms, is readily reduced to the monoene stage (18).

Although soybean oil methyl ester, cyclooctadiene, and other fairly large polyene molecules undergo hydrogenation to the monoene stage, short chain olefins behave quite differently.

In such cases, even monoenes may be hydrogenated easily (19). Those with terminal double bonds are readily hydrogenated

Table II					
Catalytic Hydrogenation of Some Monoenes with $(PPh_3)_2PtCl(SnCl_3)$ in Benzene-Methanol 34 atm. H_2 , 90°C, 3 hours					
	1-isomer %	2-isomer %		3-isomer %	Saturated hydrocarbon %
		<i>cis</i>	<i>trans</i>		
ethylene					100 *
propylene	66				34
1-butene	12.0	30.3	46.4		11.3
<i>cis</i> -2-butene	0	71.1	27.3		1.6
<i>trans</i> -2-butene	0	9.8	89.6		0.6
1-pentene	11.6	30.2	47.2		11.6
2-pentene**	3.0	27.7	67.5		1.8
1-hexene	12.5	28.5	41.6	5.4	12.0
2-hexene	no observable hydrogenation				
3-hexene	no observable hydrogenation				

* 97% after 1 hour
** This material was 47.9% *cis* and 52.1% *trans*

to saturation, but show an even greater tendency to isomerise to those with internal double bonds. Both processes probably proceed through the formation of σ bonded complexes. When the double bond is internal, hydrogenation takes place very slowly; perhaps there is no hydrogenation except as terminal olefins are formed by isomerisation.

As the chain is lengthened, the hydrogenation becomes progressively slower. Apparently, the light molecules form relatively stable complexes with the catalyst. These are susceptible to hydrogenation, but, because of entropy effects, the heavier molecules and those with internal double bonds form complexes of such low stability

Table III									
Hydrogenation of the Isomeric Hexadienes with $(PPh_3)_2PtCl(SnCl_3)$ in Benzene-Methanol 3 hours, 500 psi									
Diene used	1-hexene	2-hexene		3-hexene	<i>n</i> -hexane	hexadiene			
		<i>cis</i>	<i>trans</i>			1,5	1,4	1,3	2,4
1,5	0.8	5.8	12.2	1.0	2.5	0	17.0	2.0	58.7
1,4	0	5.0	12.5	0	0	0	5.7	3.6	73.2
1,3	0	0		7.5	0	0	0	73.1	19.4
2,4	0		0.9	0	0	0	1.3	1.8	96.0

that the σ bonded complex does not form. The hydrogenation of some short chain monoenes is illustrated in Table II (19b).

With short chain dienes, rearrangement to the conjugated isomer accompanies hydrogenation and in some cases is much more rapid. Once the conjugated hydrocarbon is formed, it does not hydrogenate to any marked extent (19b). This is seemingly because it forms such a stable complex with the platinum that no further reaction can take place. Evidence for this is found in the fact that the addition of a little butadiene to soybean oil methyl ester completely inhibits the hydrogenation of the latter. Table III illustrates the behaviour of the hexadienes (19b). It reveals a great tendency to form conjugated systems, and that migration of terminal double bonds to interior positions takes place easily. Even when double bonds are terminal, the formation of hexane is overshadowed by the formation of a molecule with internal double bonds (preferably conjugated).

Studies on this system are continuing in attempts to develop more active catalysts as well as heterogeneous catalysts which will show a high degree of specificity.

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Further Advances in Catalytic Hydrogenation

NEW REACTIONS WITH PALLADIUM AND RHODIUM CATALYSTS

Workers from Hoffman-La Roche reported to a recent symposium held by the New York Academy of Sciences that acid chlorides can be converted to aldehydes by a modified Rosenmund reaction using palladium on charcoal catalyst poisoned with quinoline-sulphur inhibitor. The development of this reaction at 50 lb/in² has reduced catalyst requirements and it opens the way to manufacture of pharmaceutical chemicals from cheaper aldehyde intermediates by using cheap hydrogen instead of expensive hydrides for hydrogenation of pure acid chlorides. The end point of the reaction was determined by seeing how much hydrogen had been used. The conventional Rosenmund reaction

barium sulphate moderator was not needed.

A group from Monsanto showed that optically active phosphine complexes of rhodium(III) can catalyse hydrogenation of olefins to optically active products. For example, 28 per cent optical purity, i.e., 64 per cent of one optical isomer and 36 per cent of the other, was obtained during hydrogenation of α -phenylacrylic acid to α -phenylpropionic acid at 300 to 400 lb/in². The group has not yet finalised the reaction mechanism. The catalyst was formed in situ by reacting the 1,5-hexadiene complex of rhodium(III) with an optically active phosphine-based ligand such as methylphenyl-*N*-propylphosphine.