The Selective Homogeneous Hydrogenation of Soybean Methyl Esters[1]

JOHN C. BAILAR, JR., Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

Abstract

Soybean methyl esters are homogeneously, selectively hydrogenated in the presence of a variety of catalysts, of which $[Pt(Pph_3)_2Cl_2]$ + $SnCl_2 \cdot 2H_2O$ and $[MoCl_2(CO)_3(Pph_3)_2]$ + $SnCl_2 \cdot 2H_2O$ are typical. Many variations can be made in these catalysts without destroying their selectivity. All of the catalysts bring about isomerization of the substrate molecules. The role of the solvent and the mechanism of the reaction are discussed.

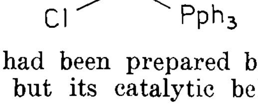
The work described in this paper, most of which was detailed in earlier papers (1–9), was undertaken at the suggestion of the Northern Regional Research Laboratory and has been financed largely by that Laboratory. Our liaison with the Laboratory has been E. N. Frankel, who has taught us a good deal about edible oils.

The object of this research was to convert the linolenic ester in soybean methyl esters to linoleic ester or, failing that, into other dienoic or to monoenoic esters with no formation of saturated (stearic) ester. This is not a new problem, and several catalysts have been developed for the selective hydrogenation of polyenes to monoenes (10).

Cramer et al. (11) showed that a mixture of chloroplatinic acid and tin (II) chloride is an active catalyst for the hydrogenation of ethylene, although the former alone is only moderately active, and the latter is not active at all. Since this bimetallic catalyst is unusual in both composition and properties, we hypothesized that it might show a selective activity. This expectation was fulfilled, even in the first experiment. A mixture of benzene and methanol was used as the solvent for the hydrogenation, and the solution was treated with hydrogen under a pressure of 500 psi at 90 C. Complete removal of triene and nearly complete removal of diene resulted with no increase in the concentration of stearate in the mixture (2). Doubling the time of exposure to the hydrogen and increasing the pressure did not result in further uptake of hydrogen.

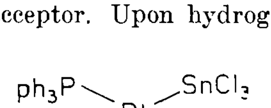
The product of this hydrogenation is a mixture of monoenic esters. In most of the molecules, the double bond is near the middle of the chain, but in others it occurs at widely different positions, being found from the 3 to the 16 position in the chain (12). Migration of the double bond is essential to the hydrogenation, since reaction takes place only when the double bonds are sterically well situated.

Early in the program, the catalyst was modified by substituting bis-diphenylphosphine dichloroplatinum (II) for chloroplatinic acid (2). This new catalyst gave a slightly higher selectivity and, with modifications to be described later, resulted in a more active catalyst. The presence of tin chloride is also essential here. A bimetallic complex containing a platinum-tin bond is formed in the H_2PtCl_6–$SnCl_2$ mixture as confirmed by x-ray studies (13) as well as by other observations (14). The structure of the $PtCl_2(Pph_3)_2$–$SnCl_2$ complex is as follows.



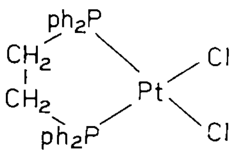
(I)

This compound had been prepared before we began our work (14), but its catalytic behavior had not been studied. The trichlorostannato group is now well recognized as a strong π-accepting, weakly σ-donating ligand, and it is this property that gives the complex its unique catalytic properties. A σ-donating ligand (here, the $SnCl_3^-$ group) shares a pair of its outer electrons with the central atom (here the Pt). However, the tin (II) atom can also accept a pair of electrons from the platinum, thus expanding its outer electron shell. It is thus a π-electron acceptor, or simply a π-acceptor. Upon hydrogenation, (I) is converted to



which is thought to be the actual catalytic specie.

Although the phosphine molecules in [I] are in *trans* positions in the complex, this is not an essential feature. The complex



(II)

with added tin (II) chloride, is equally effective.

The formation of the platinum-tin bond is reversible, and the best catalytic effect is obtained when a 10-fold excess of tin chloride is present. Addition of a greater excess of tin chloride decreases the catalytic activity, supposedly through the formation of bis-triphenylphosphine-bis-trichlorostannato-platinum (II) (6).

Other phosphines than triphenyl can be used (even triethylphosphite is effective) and some of them are superior to the triphenyl derivative. One of the most active which has been found is dimethylphenyl phosphine, $P(CH_3)_2ph$, which forms a complex that causes the hydrogenation of soybean methyl esters to proceed several times as fast as does the one containing triphenylphosphine. The catalyst containing methyldiphenylphosphine, $P(CH_3)ph_2$, is not as effective, but is still superior to that made from triphenylphosphine. Trimethylphosphine, however, is a poor

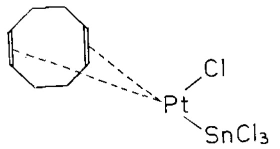
---

[1] One of 10 papers to be published from the Symposium "Hydrogenation," presented at the AOCS Meeting, New Orleans, April 1970.

catalyst. It has been suggested that at least one phenyl group must be present to act as a hydrogen transfer agent.

Triphenylarsine gives a more active catalyst than triphenylphosphine, but it is thermally less stable, and the use of arsenic compounds in materials which are to be used in the preparation of human food is undesirable. The catalyst made from triphenylstibine is selective, but not particularly active (4). Diphenylsulfide and diphenylselenide also give selective catalysts, but these have not been studied extensively (7).

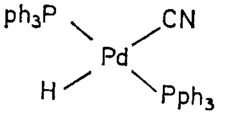
Quite a different variation in catalyst composition is introduced by the use of a molecule of 1,5-cyclooctadiene in place of the two molecules of triphenylphosphine to form the complex



It is more active than $PtCl(SnCl_3)(Pph_3)_2$, but less active than $PtCl(SnCl_3)(PCH_3ph_2)_2$.

$PbCl_2$ or $GeCl_2$ in place of $SnCl_2$ give catalysts which show some selectivity, but these are quite inferior to the ones made with $SnCl_2$.

Platinum (II) bromide or iodide can be used in the original preparation instead of the chloride, but, in general, they offer no advantages. Palladium (II) cyanide is a selective catalyst and no tin chloride need be added (3). The cyano group, like the trichlorostannato group, is a strong π-acceptor and weak σ-donor. The active catalyst is thought to be



Other metals than platinum can be used in the construction of these catalysts. Several palladium compounds have been studied and have been found to be catalytically more active but thermally less stable than the corresponding platinum compounds (3). Their use seems to offer no advantage. Bis-triphenylphosphine dichloro- and dibromo-nickel (II) complexes show little catalytic activity, but the diiodo complex $[NiI_2(Pph_3)_2]$ is active and selective (5). It is much less active than the platinum compound, however. The addition of tin chloride effects no change in catalytic activity, for the iodo- group, like the trichlorostannato and cyano groups, is a π-acceptor and σ-donor.

Under mild conditions (40–60 C and pressures as low as atmospheric) these hydrogenation catalysts bring about migration of the double bonds in the soybean esters, and convert them largely to the *trans* form, but do not bring about hydrogenation. The migration of the double bonds leads, eventually, to the formation of conjugated systems. The catalyst must be in the hydrido form (≥Pd-H) to effect this transformation; the chloro complex cannot be used (6).

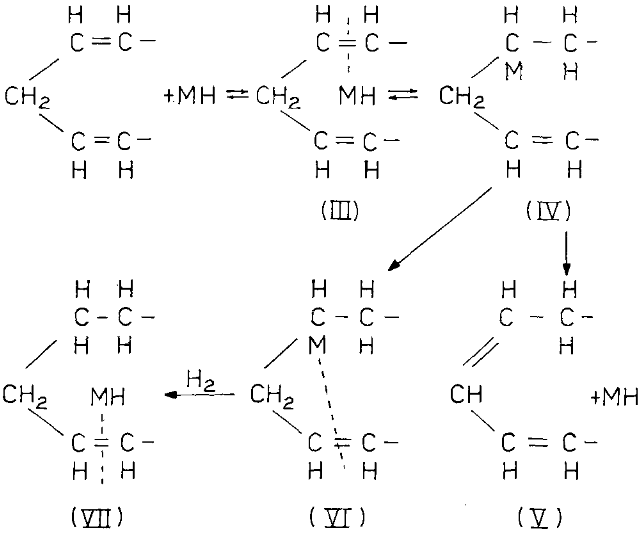
In studying the isomerization reaction, we found that under high temperature and pressure, hydrogenation is effected by the methanol in the solvent, with the concomitant formation of formaldehyde

$$\geqq Pd - Cl + CH_3OH \rightarrow \geqq Pd - H + HCHO + HCl \quad (3).$$

This reaction is not surprising in view of Chatt and Shaw's observation that chloro complexes of the platinum metals are converted to hydrido-complexes by alcohols (15).

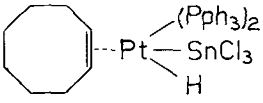
Platinum (II) usually shows a coordination number of four, but since it has 10 electrons less than the next rare gas (radon), it can coordinate five donor atoms. The use of the fifth coordination position is necessary to its catalytic action, for it is at that position that the substrate molecule is attached and activated. It is essential, therefore, that no strongly coordinating groups be present to compete with the substrate molecule. Methanol is not a particularly strong complexer, but it has enough coordinating ability that when it is present as the solvent, it competes with the ethylenic bonds in the soybean methyl esters. It has been found that although chlorinated hydrocarbons, such as methylene chloride, are poor solvents for the catalyst, they allow the hydrogenation reaction to proceed about five times as fast as does the methanol-benzene solvent. Acetone is not as good as methylene chloride, but is better than methanol-benzene. Pyridine, which is a strong coordinator, blocks the reaction completely (7).

Although the mechanism of the hydrogenation reaction is not completely worked out, we believe that it proceeds in the following way (7) (MH represents a mole of $[Pt(Pph_3)_2(SnCl_3)H]$ or similar catalyst).

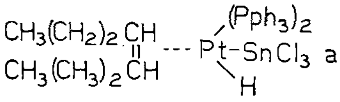


The first step is the formation of a π-bond with one of the double bonds of the unsaturated ester (III) which is quickly transformed into the σ-bonded compound (IV). The original substrate molecule and MH may be readily regenerated by reversal of these reactions. However, it is equally easy to generate the isomer (V). The metal atom in (IV), although attached to a carbon atom, may still form a coordinate bond with a properly situated ethylenic group to form (VI) which is stabilized by ring formation. Upon hydrogenation, the σ-metal-carbon bond is broken to give (VII). If the substrate chain contains another double bond, the process may be repeated, but when only one double bond remains, a structure such as (VI) is impossible and no hydrogenation can take place. Migration of double bonds is so facile that conjugation will take place even if the double bonds are far apart (as in the 9,15-octadecadienoic acid).

Some credence is given to this postulate by the isolation of some of the proposed platinum-olefin complexes (6). These include

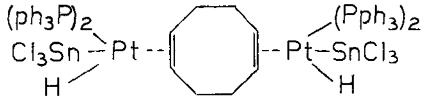


(VIII)



and

(IX)



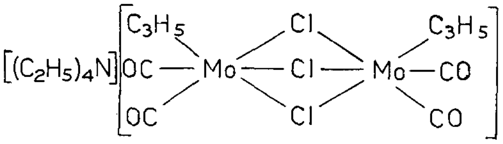
(X)

We have recently found that certain molybdenum and tungsten complexes will also selectively hydrogenate soybean methyl esters (unpublished work). Thus far, two types of such compounds have been found:

$MoX_2(CO)_3(Qph_3)_2$ (X = Cl or Br, Q = P or As) (16)

(XI)

and



(17)

(XII)

The triphenylphosphine complex XI is not as active as the arsine complex.

The work on molybdenum and tungsten catalysts has not progressed very far, and only a preliminary account of it can be given here. Compound XI is catalytically active when 4 to 10 moles of tin (II) chloride are present in the solution for each mole of molybdenum. The addition of tin chloride to XII is not essential. Neither of these catalysts is active below 150 C, and they achieve good catalytic activity only at 180 C. Probably they are decomposed into simpler substances at these temperatures, and the decomposition products are the actual catalysts. The molybdenum and tungsten catalysts are far more effective in chlorinated hydrocarbons than in other solvents.

Both of the molybdenum catalysts are sensitive to air, but the dark colored oxidation products are also catalytically active, perhaps because they are reduced to the original materials again. There is some spectral evidence that the aerial oxidation of XI gives the molybdenyl complex $MoOCl_2(CO)_3(Asph_3)_2$.

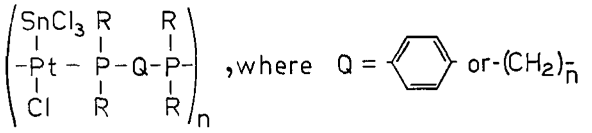
The results of an experiment with compound XII are shown in Table I.

TABLE I

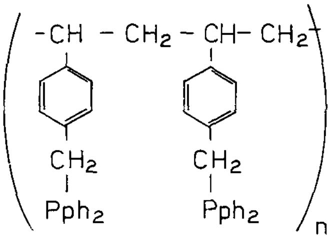
Hydrogenation of Soybean Methyl Esters Using $[Et_4N][Mo_2(CO)_4(C_3H_5)_2Cl_3]$; CH_2Cl_2 solvent; 150 C; 500 psi H_2; 5 hr

Ester	Palmitate	Stearate	Monoene	Diene	Triene
Initial	11.08	5.8	30.6	46.6	5.4
Final	14.08	5.6	47.3	31.6	0.7

Currently, we are making further studies on the molybdenum and tungsten catalysts and are also trying to develop selective, heterogeneous platinum catalysts. Our efforts in the latter connection are directed toward the preparation of catalysts which contain nonchelating diphosphines:



or



Our goal is to prepare catalysts which are stable, highly active, of reasonable cost, not readily poisoned and convenient to use.

REFERENCES

1. Bailar, Jr., J. C., and Hiroshi Itatani, "Proceedings of the Symposium on Coordination Chemistry," Hungarian Academy of Sciences, Tihany, Hungary, 1965.
2. Bailar, Jr., J. C., and Hiroshi Itatani, JAOCS *43*, 337 (1966).
3. Itatani, Hiroshi, and J. C. Bailar, Jr., Ibid. *44*, 147 (1967).
4. Bailar, Jr., J. C., and Hiroshi Itatani, J. Amer. Chem. Soc. *89*, 1592 (1967).
5. Itatani, Hiroshi, and J. C. Bailar, Jr., Ibid. *89*, 1600 (1967).
6. Tayim, Hassan, and J. C. Bailar, Jr., Ibid. *89*, 3420 (1967).
7. Tayim, Hassan, and J. C. Bailar, Jr., Ibid. *89*, 4300 (1967).
8. Adams, R. W., G. E. Batley and J. C. Bailar, Jr., Inorg. Nucl. Chem. Letters *4*, 455 (1968).
9. Adams, R. W., G. E. Batley and J. C. Bailar, Jr., J. Amer. Chem. Soc. *90*, 6051 (1968).
10. Zajcew, M., JAOCS *37*, 130 (1960); R. R. Allen, Ibid. *39*, 457 (1962); Yoshio Tajima and Etsuo Kunioka, J. Org. Chem. *33*, 1689 (1968); L. H. Slaugh, Tetrahedron *22*, 1741 (1966); Jack Kwiatek, Catal. Rev. *1*, 37 (1967); Jack Kwiatek and J. K. Seyler, Adv. Chem. Series *70*, 207 (1968); E. N. Frankel, T. L. Mounts, R. O. Butterfield and H. J. Dutton, Ibid. *70*, 177 (1968).
11. Cramer, R. D., E. L. Jenner, R. V. Lindsey, Jr. and U. G. Stolberg, Ibid. *85*, 1691 (1963).
12. Frankel, E. N., E. A. Emken, Hiroshi Itatani and J. C. Bailar, Jr., J. Org. Chem. *32*, 1447 (1967).
13. Lindsey, Jr., R. V., G. W. Parshall and U. G. Stolberg, Inorg. Chem. *5*, 109 (1966).
14. Cramer, R. D., R. V. Lindsey, Jr., C. T. Prewitt and U. G. Stolberg, J. Amer. Chem. Soc. *87*, 658 (1965).
15. Chatt, J., and B. L. Shaw, J. Chem. Soc. *1962*, 5075.
16. Colton, R., and I. B. Tompkis, Aust. J. Chem. *19*, 1143, 1519 (1966).
17. Murdoch, H. D., J. Organometal. Chem. *4*, 119 (1965).

[Received May 13, 1970]