Modification of a Procedure for Analytical Hydrogenation of Edible Oils[1]

Z. TENE, ANINA YARON and **A. LETAN**, Department of Food and Biotechnology, Technion—Israel Institute of Technology, Haifa, Israel

ABSTRACT

Unsaturation, an important parameter in edible oils, can be determined by analytical hydrogenation. Recently Brown et al. (3-9) have proposed an "automatic" direct titration method for hydrogenation of various unsaturated organic compounds. Sodium borohydride, introduced through a pressure-actuated mercury valve, was utilized as hydrogen producing reagent, and both the hydrogen and the platinum catalyst were generated in situ. Application of the above method to determination of unsaturation in various edible oils was the subject of the present study. Several shortcomings inherent in the original procedure and apparatus have been overcome by introducing suitable changes. Isopropanol was used as a solvent for the borohydride; the buret was used at the operational stage in the near horizontal position; the end point manometer was filled with Brodie's solution; and the system was preliminarily flushed with hydrogen from an external source and was operated at a slight overpressure. As a result of those changes, the determined hydrogen iodine values were closer to the expected ones and the standard deviations were appreciably lowered. Gravimetric determinations have confirmed Brown's observation that the precipitated powder produced by reduction of chloroplatinic acid consists only of pure platinum. Microscopic examinations revealed that a finer structure and better dispersion is obtained when platinum was precipitated on activated carbon as support. This can be conceived with the observed higher over-all reaction rates achieved with the supported catalyst.

[1]Presented at the AOCS-ISF World Congress, Chicago, September 1970.

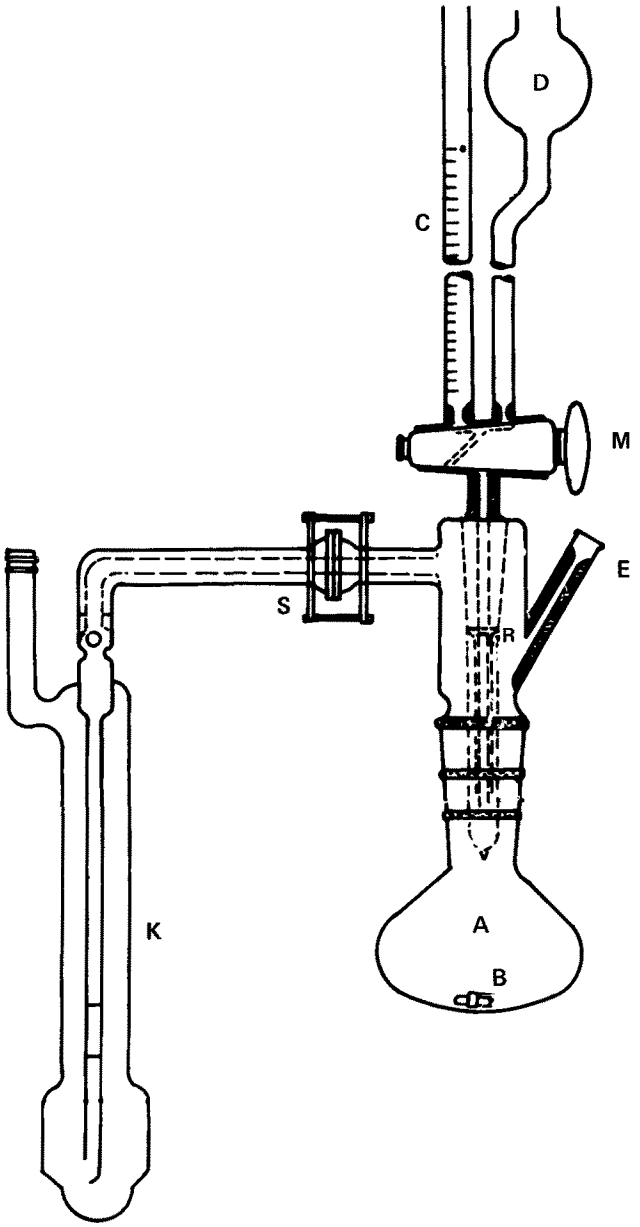

FIG. 1. Brown's hydroanalyzer (letter designations described under Experimental Procedure).

INTRODUCTION

Unsaturation is an important parameter in edible oils, usually determined either by the halogenation methods of Wijs or Hanus, or by analytical hydrogenation, using either a gasometric or a manometric technique. All these methods have disadvantages.

The results obtained with the above mentioned methods of halogenation closely approach theoretical values only for fats containing isolated double bonds. Even for those fats the halogenation by the Wijs method goes usually to about 98% of the stoichiometric value. The halogen containing reagents are unstable and difficult to keep as standardized solutions, being sensitive to light, heat and moisture. The addition reaction should be carried out in dark under standard conditions (10).

Methods of analytical hydrogenations also suffer from handicaps. The apparatus is usually of an elaborate design; it should be leak-proof and protected from possible explosion. The procedures are time consuming: for example, 2 hr are required for hydrogenation of edible oil by the method of Pack et al. (12). Catalyst should be protected from poisoning and it is necessary to have the gas burets thermostated. It is not surprising therefore that "little analytical use has been made of hydrogenation, even though various investigators have for considerable time called attention to its utility as a means of measuring total unsaturation" (10).

Brown and coworkers have developed a new and rapid procedure for quantitative determination of unsaturation in organic compounds (5,6,8,9). Sodium borohydride is utilized as an hydrogen producing reagent, and both the hydrogen and the carbon-supported platinum catalyst are generated in situ. The buret which contains a solution of the borohydride need not be thermostated.

According to the newer version of the method (8), an "automatic" direct titration of the sample takes place as the borohydric titrant enters the system through a pressure-

actuated mercury valve and reacts with the acid in the main vessel. Accuracy of 1.0-1.5% was reported in the determinations of unsaturation of a number of olefins and of samples of corn, olive, cottonseed and tung oils; the analyses required about 3 min each.

Miwa et al. (11) introduced many modifications in the earlier version of the Brown et al. method (5), and then adapted it for determination of unsaturation in various seed oils. These investigators used diglyme as solvent for the borohydride, carried out the determinations at an extremely high stirring rate and paid much attention to an elaborate adjustment of the end point pressure. They achieved a relative precision of 1% and found the method most useful for detecting unusual types of unsaturation, in oils in which the hydrogen iodine value differed much from the Wijs iodine value.

In this study we have tried to apply the newer version of the Brown et al. method (8) to determination of unsaturation in several representative vegetable oils. It was found that this procedure still suffered from several disadvantages: (1) the borohydric titrant was unstable, soon became turbid, and its concentration decreased considerably with time; (2) at the early stages of the operation the system was subject to a slow but a fairly prolonged drop in pressure (and this when the method calls for an operation at a constant pressure); (3) the manometric readings at the beginning and at the end of the titration were not the same (originally partly overcome by imposing limitation on the total unsaturation of the injected sample, to keep the difference in pressure within predetermined bounds); (4) standard deviations of the obtained values were appreciable.

The modifications made by us to overcome these shortcomings included changes both in the structural elements of the hydroanalyzer and in the procedure. With the modified method the system's pressure was stabilized and the end point readings could be taken at an unchanging pressure. Even injection of samples which differed considerably in total unsaturation was made possible; the results were closer to the expected values and their standard deviation was diminished.

The catalyst obtained by reduction of the chloroplatinic acid was also a subject of our study. Brown and coworkers described preparation of highly active catalysts for hydrogenation and compared their activities (3,7). They reported that the precipitate produced by the reduction of chloroplatinic acid was essentially pure platinum (3), and also found that carbon-supported catalysts possessed markedly enhanced activities (4,7).

In this investigation the activities of unsupported and of carbon-supported platinum catalysts have been compared. These catalysts have been also subjected to optical and electron microscope examination.

EXPERIMENTAL PROCEDURE

Determination of Iodine Values

Iodine values of three samples of oils--coconut, 2:1 mixture of olive and soybean, and safflower--were determined by each of the methods listed below.

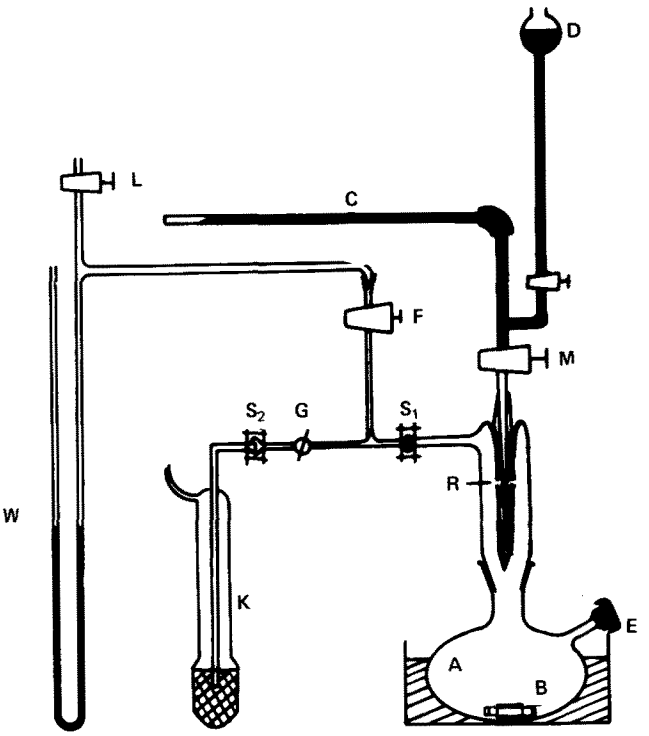

FIG. 2. The modified hydroanalyzer (letter designations described under Experimental Procedure).

Wijs: values were determined according to the Cd 1-25 (revised 1956) method of AOCS (1).

Gas chromatography: methyl esters were obtained as described in the Ce-2-66 method of AOCS (2). Separation was carried out in a Packard Model 7821 gas chromatograph equipped with a No. 811 hydrogen flame detector. The glass column (8 ft x 1/4 in.) was filled with 10% EGSS-X on Chromosorb W-AW 60-80 mesh (Applied Science Laboratories). The temperatures of injection, column and detector were 210, 175 and 190 C respectively. Nitrogen was used as carrier gas at 40 ml/min; hydrogen and air were supplied to the detector at 40 and 400 ml/min respectively. Detector voltage was 500 v, and amplifier sensitivity was set at 10^{-9} ampere. The volume of the injected samples was 1 μliter (10% solution in carbon disulfide). Under these conditions detector response was linear. Peak areas were determined with the aid of a Packard Model 565 disc integrator. The composition of the injected monoesters and the iodine values of the oils were calculated from the chromatographic data.

Brown's hydroanalysis (original): values were determined according to the procedure described by Brown et al. (8). The hydroanalyzer was supplied by Delmar Scientific Laboratories, Maywood, Ill. (Fig. 1). (The letter designa-

TABLE I

Iodine Values[a] of Edible Oils and of Alkene Standards Determined by Different Methods

Method	Edible oils			Alkenes	
	Coconut[b]	Olive-soybean 2:1	Safflower	Cyclohexene[c]	1-Octene[d]
Brown's hydroanalysis (original)	14.5 ± 0.5	103.1 ± 1.3	146.2 ± 3.3	305.0 ± 7.0	227.0 ± 5.2
Brown's hydroanalysis (modified)	14.3 ± 0.1	102.0 ± 0.8	145.0 ± 0.7	304.0 ± 0.8	228.0 ± 0.9
Wijs	13.2 ± 0.3	99.8 ± 1.8	140.0 ± 1.0	307.0 ± 1.0	224.5 ± 0.5
Gas chromatography	13.0 ± 0.2	101.2 ± 0.1	144.7 ± 0.5	---	---

[a]Each Figure represents the mean of 10 determinations and the standard deviation.

[b]Contains traces of soybean oil.

[c]Calculated iodine value: 310.

[d]Calculated iodine value: 227.

TABLE II

Changes in Concentration[a] of Sodium Borohydride in Different Solvents

Time, days	Diglyme[b]	Diglyme-isopropanol 1:10[b]	Isopropanol[c]	
0	87.0	85.0	84.3	74.0
3	85.4	83.1	84.0	73.6
7	81.0	81.9	83.6	72.5
14	78.5	80.5	82.5	72.0
20	76.3	79.2	81.9	71.9

[a]Milligram moles per liter.

[b]Appearance of solutions after 20 days: uniform turbidity.

[c]Appearance of solutions after 20 days: clear with slight fine precipitate on bottom.

tions are the same as described for the modified hydroanalyzer under Apparatus and Hydrogenation Procedure).

Brown's hydroanalysis (modified): the materials and methods recommended by Brown et al. (8) were used in the first series of experiments. On the basis of the observed performance and results, modifications were introduced both in the structural elements of the apparatus (Fig. 2) and in the hydrogen procedure (as indicated below).

Apparatus and Hydrogenation Procedure

The modified hydroanalyzer is shown in Figure 2. The flask (A) was of 100 ml capacity; its side neck was closed by the silicone septum (E), which could be pierced with a hypodermic needle. The buret (C) was filled with the sodium borohydride titrant and connected to the system through a flexible joint; at the operational stage it was used in the near horizontal position, but it could be turned to vertical for the purposes of priming.

The bubbler (K) was filled with mercury and served as a one way valve, permitting escape of hydrogen at a pressure of about 20 mm Hg above atmospheric. The manometer (W) was filled with Brodie's solution. The modified apparatus was also provided with a number of additional stopcocks and joints. The mercury valve (R) was almost the same as in the Brown's original apparatus (Fig. 1), but the mercury level was lower, the remaining space being filled with titrant.

To generate in situ the carbon-supported platinum catalyst, 250 mg of Darco K-B activated carbon and 1 ml of 0.05 M solution of chloroplatinic acid in isopropanol were delivered to the flask (A). A teflon-coated stirring rod (B) was inserted and the apparatus was assembled. The flask (A) was placed in a 25 C thermostatic bath mounted on a stirrer drive. The reservoir (D), the buret (C) and the upper part of valve (R) were filled with a 0.05-0.10 M solution of sodium borohydride in isopropanol. The septum (E) was pierced with a hypodermic needle and the system was thoroughly flushed with high purity hydrogen from a small cylinder, to remove even traces of air. At this stage the stopcocks (M), (F) and (L) were closed and (G) was open. [Isopropanol vapors left the system through the bubbler (K)]. After the flushing, stopcock (M) was opened and 15 ml of the borohydric solution were added from the buret (C) (in the vertical position) to the reaction flask, to reduce the chloroplatinic acid. Stopcock (M) was closed, stirring was started and after one min 1 ml of concentrated HCl (10 N) was injected through the septum E–to destroy the excess of borohydride and to take part later in generation of additional amounts of hydrogen by reacting with the borohydride introduced during the titration. The syringe was withdrawn, washed immediately with large amount of water and dried to prevent corrosion of the needle.

Stopcock (G) was then closed and (L) opened, after which (F) was opened and (L) immediately closed. The buret was refilled, restored to its usual near horizontal position and the stopcock (M) was reopened. When the system gained equilibrium, it was primed by injection of 1 ml of a solution of edible oil in ethyl acetate (containing 100-400 mg oil). After this, when equilibrium was regained, stopcock (M) was closed, the buret again refilled to the zero mark and the stopcock (M) was reopened.

At this stage the investigated sample of oil (also in ethyl acetate) was injected and the "automatic" titration took place. (The borohydric titrant was drawn through the buret's open stopcock each time when there was a drop in the system's pressure, owing to hydrogen's consumption during the reduction of the unsaturated sample.)

The difference in the titrant's readings in the buret was recorded and the unsaturation was calculated from:

$$\text{I.V.} = \frac{2 \times 126.9 \times \text{mmoles } H_2}{10 \times \text{grams of sample}};$$

and

$$\text{mmoles } H_2 = (4 \times M \times V) + \frac{(V + Vs) \times 273 \times P}{22.4 \times (T + 273) \times 760};$$

(M and V = molarity and volume of titrant, ml; Vs = volume of injected sample, ml; P = absolute pressure in system, mm Hg; and T = temperature, C).

The capacity of the reaction flask sufficed for 15 successive titrations, and those could be performed with a single batch of catalyst; the buret had to be refilled after 2-3 titrations.

Stability of the Borohydric Titrant

Sodium borohydride (analytical grade powder, Alfa Inorganics, Beverly, Mass.) was dissolved in either diglyme (diethylene glycol dimethyl ether), in isopropanol, or in their 1:10 v/v mixture–to give solutions between 0.05-0.10 M. All the solvents have been pretreated to remove peroxides (by refluxing with stannous chloride) and traces of water (by refluxing with calcium hydride). They were stored in dark glass bottles under dried nitrogen. The solutions of borohydride in these solvents were stored under the same conditions.

The concentrations and appearance of the borohydric solutions were checked every 3-7 days over a 3 week period; before each standardization a 5 ml aliquot was filtered through Wnatman No. 1 paper and treated with an excess of 0.15 N hydrochloric acid. The excess acid was subsequently titrated with 0.1 N sodium hydroxide.

Nature and Performance of Catalyst

The catalyst was generated according to the procedure of Brown et al. (8), by reduction of 0.1-4.0 ml (usually 1.0 ml) of 0.05 M chloroplatinic acid in isopropanol with 15 ml of 0.05-0.10 M solution of sodium borohydride in isopropanol–either in the presence of 250 mg of the Darco K-B activated carbon, or without it. This was followed by addition of 1 ml of concentrated (10 N) hydrochloric acid.

The precipitates obtained without carbon were carefully washed with water and dried. Their weights were recorded and compared with the calculated platinum content in the chloroplatinic acid reagent.

The precipitates of both types were viewed and photographed under an optical microscope using the immersion technique, and under JEM 7 electron microscope by transmission, with each specimen carbon-coated.

The influences of the amount of precipitated catalyst and of the carbon support on the time required for completion of hydrogenation of several standard samples were also recorded.

RESULTS AND DISCUSSION

The results of the iodine value determinations of three

TABLE III

Main Dissimilarities Between the Original[a] and Modified Methods of Hydroanalysis

Variable	Method	
	Original	Modified
Solvent, for $NaBH_4$	Diglyme-isopropanol 1:10	Isopropanol
Titration buret	Vertical	Near horizontal
End point manometer	Mercury	Water, Brodie's solution
Operating pressure	Slight underpressure	Slight overpressure
Total unsaturation of injected samples	Should be almost the same	May differ
Additional requirements		Thorough flushing with hydrogen

[a] Brown et al. (8).

representative vegetable oils and also of two alkene standards are given in Table I.

For the triglycerides, the values obtained by the modified method were nearer to the results calculated from the gas chromatographic determinations and to those determined by the Wijs method, than the values obtained by the original method (8).

For both the triglycerides and the alkenes, the standard deviations of the values determined by the modified method were appreciably lower than the deviations of the results obtained by the original method (8).

Table II reflects the changes in concentration vs. time of the borohydric reagent in different solvents. The strength of the borohydric solutions in diglyme and in diglyme-isopropanol decreased by 8-12% over the 3 week storage period. Moreover these solutions became uniformly turbid and difficult to filtrate.

The solutions in pure isopropanol remained clear, while the slight precipitate which collected at the bottom of the flask could be easily separated by decantation. Over the same observation period their concentration decreased by only 3%. Accordingly the use of isopropanol as solvent seems to be justified.

The main modifications introduced in the original method are summarized in Table III and commented upon below.

Pretreated pure isopropanol was used as a solvent for the borohydride for the reasons already explained.

The near horizontal adjustment of the buret eliminated the fluctuations in the system's pressure which had been caused by the variations in the titrant's level in the vertical buret. In the modified apparatus the buret has been connected to the system by a flexible joint, and it was used in the original vertical position only at the priming stage. At the operational stage the buret was used in the near horizontal position. The advantage of this modification is obvious: when the modified apparatus is used a change in the titrant's volume in the buret will not cause a change in the titrant's hydrostatic pressure, and will not influence the system's end point pressure. The modified method can therefore dispose with the original requirement for a similar total unsaturation of the injected samples (these will require similar volumes of the titrant, and will therefore induce similar changes in the end point pressure). Calculations show that with a hydroanalyzer of the original type (equipped with the vertical buret), an error of about 2% may be expected in analysis of a 100 mg sample with iodine value of 100, owing to a change in the system's pressure (caused by the difference in the titrant's level in the buret before and after titration). It was observed that the standard deviations of the values obtained by the original method (8) were indeed within that range (Table I).

An additional sensitive water-filled manometer (W) (actually filled with Brodie's solution) was introduced to enable indication of even slight changes in the system's

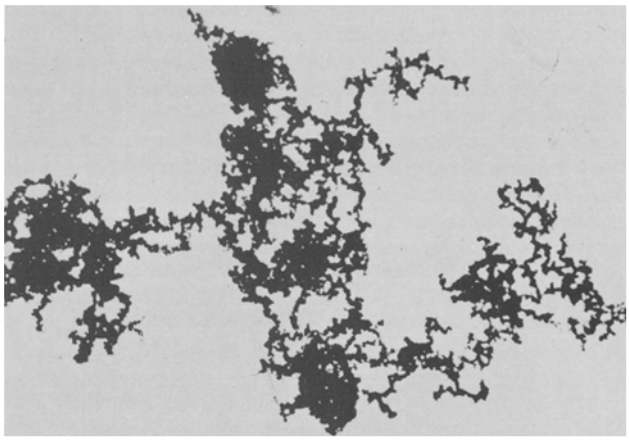

FIG. 3. An agglomerate of platinum (x 23,000).

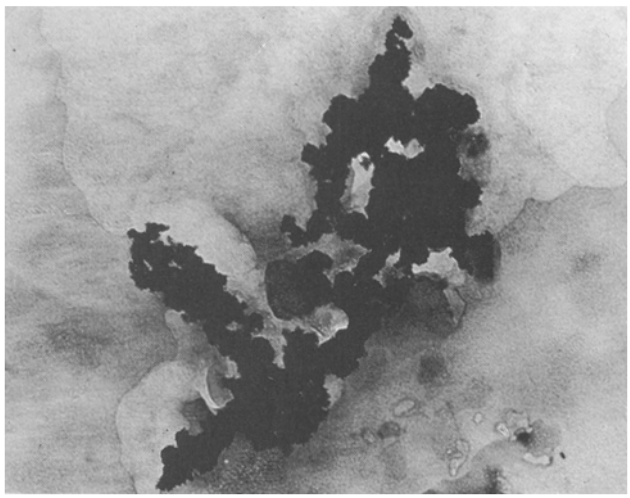

FIG. 4. A particle of platinum (x 150,000).

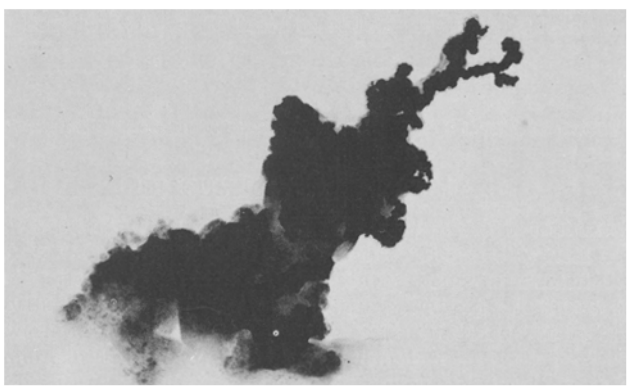

FIG. 5. A particle of platinum on activated carbon (x 62,500).

TABLE IV

Time Required for Complete Hydrogenation of 100 mg Samples of Edible Oils and of 1-Octene[a]

Type of catalyst	Weight of platinum, mg	Reaction time		
		Mixture of olive and soybean oils 2:1[c]	Safflower oil[c]	1-Octene[d]
Pt	9.4	> 15 min	> 15 min	> 10 min
Pt/C[b]	1.3	> 30 min	> 30 min	4 min, 15 sec
	9.4	100 sec	100 sec	95 sec
	25.0	102 sec	100 sec	95 sec

[a]In presence of unsupported and of carbon-supported platinum catalysts.

[b]In each experiment, 250 mg of activated carbon were used as support.

[c]In ethyl acetate.

[d]In isopropanol.

pressure. In the modified apparatus the mercury-filled bubbler (K) was used only in the preliminary stages of the operation, as a one-way valve for building up an atmosphere of hydrogen in the system and for maintaining the required overpressure.

When the original procedure was used, pressure instability was observed in the system already at the priming stage. The pressure dropped asymptotically over an interval of about 20 min, to about 10 mm Hg below the set level. This phenomenon was eliminated by a preliminary thorough flushing of the system with hydrogen from an external source. The success of this additional step was owing to the complete removal of even the traces of air, and to preventing in this way the platinum-catalyzed reaction of oxygen with hydrogen (13-15).

The modified procedure also calls for operation at a slight overpressure, rather than at a slight underpressure (as originally specified), to prevent even traces of the atmospheric air from entering the system.

As regards the nature of the catalyst, the amounts of the obtained precipitate corresponded exactly to the platinum content in the chloroplatinic acid, with the conclusion that the catalyst consists of pure platinum, in agreement with the earlier observations of Brown and Brown (3).

Ordinary and electron microphotographs of the catalyst obtained by reduction of chloroplatinic acid (Fig. 3-5) show that agglomerates are formed when the catalyst is precipitated without carbon support, in contrast to the much finer structure and dispersion obtained in the presence of the carbon (when the metal particles adhere to the carbon's surface).

As seen from Table IV, the performance of the carbon-supported catalyst was much better than that of the unsupported platinum. This is in agreement with the observations of Brown and Brown (4,7) who found that platinum showed higher catalytic activity when precipitated on supports which had large surface areas. (The best results were actually obtained with activated carbon.) With 9.4 mg of the unsupported catalyst (and also with the supported variant with the lowest platinum content, 1.3 mg) the reaction times required to achieve complete hydrogenation of the samples were fairly long, despite the high catalyst-substrate ratios (almost 10% for the unsupported catalyst and over 1% for the supported variant). It seems worth mentioning that in all the experiments the alkenes were reduced more rapidly than the triglycerides.

When supported by the carbon, the same amount of 9.4 mg of platinum sufficed for complete hydrogenation of all the 100 mg substrates in less than 2 min, a minimum which could not be improved upon by further increase in the platinum content (to 25 mg). Since the hydrogen-substrate contact is undoubtedly improved as the metal content increases, mass transfer of the reactants towards the catalyst seems to have been the limiting factor. The same conclusion was reached by Brown and Brown (7), who found that varying the amount of the Pt/C catalyst does not result in a proportionate change in the hydrogenation rate, "presumably because of the importance of diffusion control with these highly active catalysts." This conclusion is also sustained by the observation that in the presence of sufficient amounts of the supported catalyst, there were no significant differences in the times required for hydrogenation of the three substrates, which differed either in the degree of unsaturation or in chemical classification.

REFERENCES

1. AOCS Official and Tentative Methods (method Cd 1-25, revised in 1956), Third Edition, Chicago, 1966.
2. AOCS Official and Tentative Methods (method Ce 2-66), Third Edition, Chicago, 1966.
3. Brown, H.C., and C.A. Brown, J. Am. Chem. Soc. 84:1493 (1962).
4. Brown, C.A., and H.C. Brown, Ibid. 84:2827 (1962).
5. Brown, H.C., K. Sivasankaran and C.A. Brown, J. Org. Chem. 28:214 (1963).
6. Brown, H.C., and C.A. Brown, Ibid. 31:3989 (1966).
7. Brown, H.C., and C.A. Brown, Tetrahedron 1966(8)(I):149.
8. Brown, C.A., S.C. Sethi and H.C. Brown, Anal. Chem. 39:823 (1967).
9. Brown, C.A., Ibid. 39:1882 (1967).
10. Mehlenbacher, V.C., "The Analysis of Fats and Oils," The Garrard Press Publishers, Champaign, Ill., 1960.
11. Miwa, T.K., W.F. Kwolek and I.A. Wolff, Lipids 1:152 (1966).
12. Pack, F.C., R.W. Planck and F.C. Dollear, JAOCS 29:227 (1952).
13. Ponec, V., J. Catalysis 6:362 (1966).
14. Reed, R.M., "Hydrogen," in Kirk and Othmer's "Encyclopedia of Chemical Technology," Second Edition, Vol. 11, Wiley and Sons, N.Y., 1966, p. 343.
15. Tomezoko, E.S.J., and G.T. Furukawa, J. Catalysis 8:386 (1967).

[Received December 30, 1970]