Catalytic Hydrogenation of Soybean Oil with Rh(I) Dihydride Complexes As Catalysts

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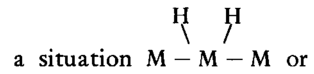
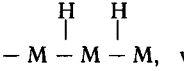
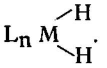
ABSTRACT

Cationic rhodium(I) complexes of the type $[NBD\ Rh\ L_2]^+[ClO_4]^-$ (NBD = norbornadiene and L = diphenylphosphinoethane or triphenylphosphine) have been studied as catalysts for the hydrogenation of soybean oil. These catalysts give a good yield of products with *cis*-configuration. Indeed, hydrogenation could be performed under mild conditions (30 C, 1 atm hydrogen pressure) to an iodine value of 80 with not more than 12% of *trans* monoenes and only 5% conjugated isomers formed. The results obtained are interpreted on the basis of the equilibrium $H_2RhL_n^+ \rightleftharpoons HRhL_n + H^+$. By the addition of acid ($HClO_4$) the bishydrido form of the catalyst could be studied. With this system only small amounts of *trans* monoenes were formed and no other *trans* isomers could be detected. By the addition of a base such as triethylamine, the monohydridic form of the catalyst could be studied. In contrast to the bishydrido complex, this system gave large amounts of *trans* monoenes, together with *cis-trans* and *trans-trans* forms of the 18:2 acid. With both forms of the catalyst system, conjugated isomers were formed.

INTRODUCTION

One consequence of interrupting the hydrogenation of vegetable oils before reaching completely saturated fatty acids is the formation of *trans* and other isomeric acids. In industrial operations these side reactions can in part be controlled and limited by reaction conditions such as temperature, pressure, agitating speed and the amount of catalyst (1). Certain additives can also be used to decrease the formation of *trans* acids (2). The recent discussion on the effects of *trans* acids on human health (3,4) has intitiated a new interest in finding methods for producing hydrogenated fats with a low content of *trans* acids. To reach this goal, coordination catalysts seem useful, as one can influence their activity in various ways by changing their constitution. Nishiguchi and coworkers (5,6) have examined various transition metal complexes as catalysts for hydrogen transfer reactions from different hydrogen donors to olefinic bonds. Good results were achieved with $RuCl_2(PPh_3)_3$ or $RuH_2(PPh_3)_4$ with isopropanol as the hydrogen source. With indolene as hydrogen source, on the other hand, $PdCl_2$ or $(NH_4)_2PdCl_4$ proved to be the best catalysts.

Another type of coordination catalyst with unique *cis*-producing properties is arene chromium tricarbonyl. This catalyst has been investigated in great detail by Frankel et al. (7,8,9,10). A common feature of $RuH_2(PPh_3)_4$ and arene chromium tricarbonyl is that in both cases a bishydrido complex, MH_2, takes part in the reaction. Fragale et al. (11) have used different Ir and Rh complexes as catalysts and tried to correlate the catalytic activity and selectivity to the number of phosphine ligands coordinated to the metal. They found that for Rh complexes the phosphine rich catalysts were highly active and produced the highest amount of *trans* isomers. $RhCl(PPh_3)_3$ was an exception, as this complex produced the lowest *trans* content although it gave the highest hydrogenation rate.

It may be of some interest in this connection that in heterogeneous catalysis, changes in process variables that increase the hydrogen concentration decrease the formation of *trans* isomers (12). An increase in hydrogen concentration will presumably lead to a situation  $M-\overset{H\ \ \ H}{\overset{\diagdown\ \diagup}{M}}-M$ or  $-\overset{H}{\overset{|}{M}}-\overset{H}{\overset{|}{M}}-M$, where the surface of the heterogeneous catalyst resembles a bishydrido coordination compound  $L_nM{<}^{H}_{H}$.

As a consequence of the above observations we started to study other coordination catalysts known to form dihydrides. An interesting example of such complexes is the cationic rhodium(I) complex NBD $Rh^+(phosphine)_2$, where NBD = norbornadiene. This and similar complexes have been thoroughly investigated by Schrock and Osborn (13, 14,15) as hydrogenation catalysts for other substrates but not—to our knowledge—for fatty oils. Among the advantages of this system one can mention that the catalyst is active at low temperatures (30 C) and low hydrogen pressure (1 atm). It is also possible to heterogenize this type of complex by incorporating the phosphine ligand into polymeric matrices, either organic, as polystyrene (16), or inorganic, as silica. As the complex is cationic it ought, in theory, to be possible to use ion exchangers like zeolites for the same purpose. The possibility of heterogenizing the catalyst is important for industrial applications of the catalyst.

Also from the viewpoint of basic research this rhodium complex is interesting. Schrock and Osborn (13) have established that the catalyst under hydrogen exists in an equilibrium between mono- and dihydridic species (Eq. [I]).

$$L_nRh^+H_2 \overset{-H^+}{\rightleftharpoons} L_nRhH \qquad [I]$$

As can be seen from Eq. I, catalysis by both monohydrido and bishydrido complexes can be studied using the same metal and the same set of ligands only varying the pH. In this respect the system is rather unique (15).

This study was undertaken in order to gain some information on whether bishydrido complexes are important in the selective hydrogenation of polyunsaturated fats to *cis*-unsaturated products.

EXPERIMENTAL PROCEDURE

Chemicals

All solvents used were of analytical grade quality and used without further purification. Refined soybean oil was a gift from AB Karlshamns Oljefabriker, Karlshamn, and used as received. Rh NBD Cl_2 was purchased (Strem Chemical); Rh(NBD)acac, $[Rh\ NBD(PPh_3)_2]^+[ClO_4]^-$ and $[Rh\ NBD(diphos)]^+[ClO_4]^-$ were prepared according to reported methods (17). NBD = norbornadiene, acac = acetylacetonate, disphos = $(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}P(C_6H_5)_2$. We have found that if oxidizing agents (peroxide in tetrahydrofurane [THF] or hydroperoxides in soybean oil) are present the catalyst will be easily oxidized and destroyed.

Hydrogenations

The hydrogenation experiments were perfomed with the same type of apparatus and experimental procedure that was used in Ref. 13. For all the experiments, the results of which are given in the figures, we have used the following experimental conditions: temperature 32 C, total pressure 1 atm (no correction for vapor pressure of solvent was made), 1.0 ml soybean oil, acetone as solvent to a total volume of 10.0 ml, and catalyst concentration 7.2 mM. Perchloric acid $HClO_4$ or triethylamine NEt_3 was added as acetone solutions. The concentration of these additives are given in the figures. Samples were withdrawn and 1.0 ml n-hexane was added. These solutions were then passed through an Al_2O_3-column in order to remove the dissolved catalyst. The solvent was evaporated from the samples with nitrogen at room temperature. Methylations of the samples were done using sodium methoxide as catalyst.

Analysis

The gas liquid chromatography (GLC) procedure was similar to that used earlier to separate *cis* and *trans* isomers (18,19): methylated samples were analyzed using an OV 275 (15% on P AW-DMCS 70/80) column (600 cm x 1/8 in.) (Chrompack, Holland). The column temperature was 210 C, and the injector and detector temperature was 250 C. The flow rate of the carrier gas, nitrogen, was 20 ml/min. The gas chromatograms were evaluated by a peak triangulation procedure.

To check the *trans* content derived at on GLC analysis, some selected samples were subjected to infrared analysis of the *trans*-content (20). As the method (20) is not applicable to samples containing large amounts of conjugated esters we have preferred to use the *trans*-values found by GLC analysis when presenting the results (Figs. 2-4 and Table I). Because of the small amount of oil in each sample, the procedure in Ref. 20 was not followed exactly. Instead of weighing the oil to be analyzed, we have measured the absorption intensity of the C = O stretching vibration to determine the amount of oil in the CS_2-solution. This method proved to give an accuracy reasonably comparable to that of the GLC analysis.

RESULTS AND DISCUSSION

The first complex that we tested for the catalytic hydrogenation of soybean oil was the triphenylphosphine complex NBD $Rh^+(PPh_3)_2ClO_4^-$. The activity of this complex is very low. This observation stands in contrast to the findings of Fragale et al. (11), who used similar complexes, e.g., COD $Rh(PPh_3)_2^+$ BPh_4^- (COD - cyclooctadiene), to catalyze the hydrogenation of soybean oil. The main difference between these two complexes is the anion, since neither COD nor NBD are present in the active species. Schrock and Osborn (17) have, however, pointed out that such complexes with the tetraphenylborate anion have a "complicated solution behavior." In acetone solution, they claim (17), COD $Rh(PPh_3)_2^+$ BPh_4^- is converted to the two species Rh(COD)-BPh_4 and $Rh(PPh_3)_2BPh_4$, where one of the phenyl groups of the anion is coordinated to the metal atom via π-bonding. It is therefore not surprising that the BPh_4^- and ClO_4^- systems give different results.

We believe that the low rate we have found is caused by the formation of the complex $Rh(diene)_2PPh_3^+$. This diolefin complex reacts presumably only very slowly with H_2 or perhaps not at all. No attempts have been made, however, to isolate the diolefin complex or to identify it in solution by spectroscopic methods. The explanation suggested above is put forward by analogy, as it is known from the work of Schrock and Osborn (15) that 1-3-butadiene reacts to form $Rh(diene)_2PPh_3^+$, which adds hydrogen very slowly.

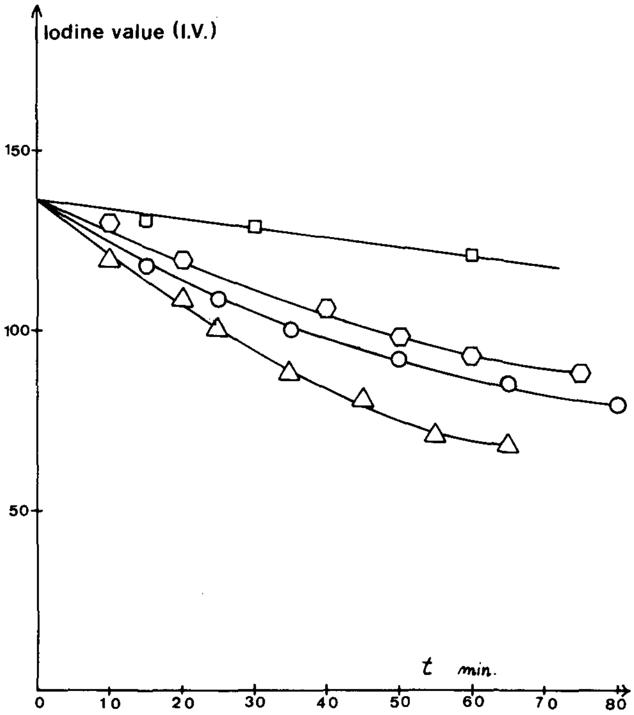


FIG. 1. Rate of reaction in hydrogenation of soybean oil (1.0 ml) catalyzed by NBD Rh diphos$^+$ ClO_4^- (7.2 mM) in acetone solution. Total volume 10.0 ml. Temperature 32.0 C. Key: △ = no additives; ○ = NEt_3 added $[NEt_3]$ = 2 mM; ○ = NEt_3 added $[NEt_3]$ = 10 mM; □ = $HClO_4$ added $[HClO_4]$ = 21 mM.

To prevent the formation of strong diolefin complexes Schrock and Osborn (15) have suggested the use of chelate forming ligands instead of monodentate ones. A drastic change in catalytic activity (about 10 times increase) was actually noted by us when $[NBD\ Rh\ diphos]^+[ClO_4]^-$ was used instead of the triphenylphosphine complex. We have therefore concentrated our study on this complex.

In order to compare the effect on the product distribution of the action of mono- and bishydrido catalysts a series of hydrogenation experiments was done at varying acidity. Perchloric acid was used to shift the equilibrium (Eq. I) towards the bishydrido side and triethylamine was used to shift it towards the monohydrido side. The results of these experiments are shown in Figures 1-4.

Product distribution. As stated in the introduction, the purpose of this study was to find out if the degree of formation of *trans*- and other isomers was dependent on the ratio between mono- and bishydrido catalysts. To discuss our results we refer to Figs. 2-4 and Table I. For the sake of clarity these figures have been divided into two parts. Part B represents the undesired products such as *trans* 18:1, nonconjugated *cis-trans* and *trans-trans* 18:2, and conjugated isomers. (In a separate test using a column separating conjugated from nonconjugated isomers but not differentiating *cis* and *trans*, we found one peak corresponding to 18:2 nonconjugated, the content of which was equal to the sum of the components designated as 18:2 *trans-trans*, 18:2 *cis-trans* and 18:2(*cis-cis*) in Fig. 4.) One notices that the product distribution curves for acid addition (Fig. 3) are about identical to those of the system with no additions (Fig. 2). This must mean that all rate parameters are changed to about equal degree—even if they are much smaller for the acid addition case (Fig. 1). This in turn, must mean that the same active intermediate is operating in both cases but that its concentration for some reason is decreased when acid is added. (The reason for the decreased rate will be discussed together with the catalytic activity in the following section.)

This active intermediate is probably the diene complex "A" formed by coordination of linoleic acid to Rh^+ diphos (Fig. 5). From this intermediate no dependence on acid addition would be expected. Such a dependence would be found, however, if either H_2Rh^+diphos or HRh diphos were the dominating species in solution. From A the reaction can proceed in two ways, either a reaction with H_2 which leads to saturation of one of the double bonds, or conjugation via an allylic rearrangement of the Rh^+ diene diphos complex prior to reaction with H_2. The concentration of conjugated isomers reaches a maximum of 16% at an iodine value of 110, whereafter it decreases (Figs. 2 and 3). The presence of such relatively large amounts of conjugated isomers in the reaction mixture means probably that unconjugated diene can substitute the conjugated isomer bound in species B. This in its turn means that the complex binding ability of the nonconjugated isomer does not differ much from that of the conjugated isomer. In this respect the diene present in soybean oil behaves differently from what has been found for other nonconjugated dienes, e.g., 1,4-cyclohexadiene (15). The conjugated isomer formed from 1,4-cyclohexadiene is only liberated after reaction with either H_2, leading to the monomer, or a phosphin, which leads to substitution.

One notices further from Figures 2 and 3 that the concentration of trans 18:1 begins to rise when the concentration of the conjugated acids starts to decrease. This probably means that the *trans* 18:1 to the main part originates from the conjugated isomers, either *trans-cis* or *trans-trans*.

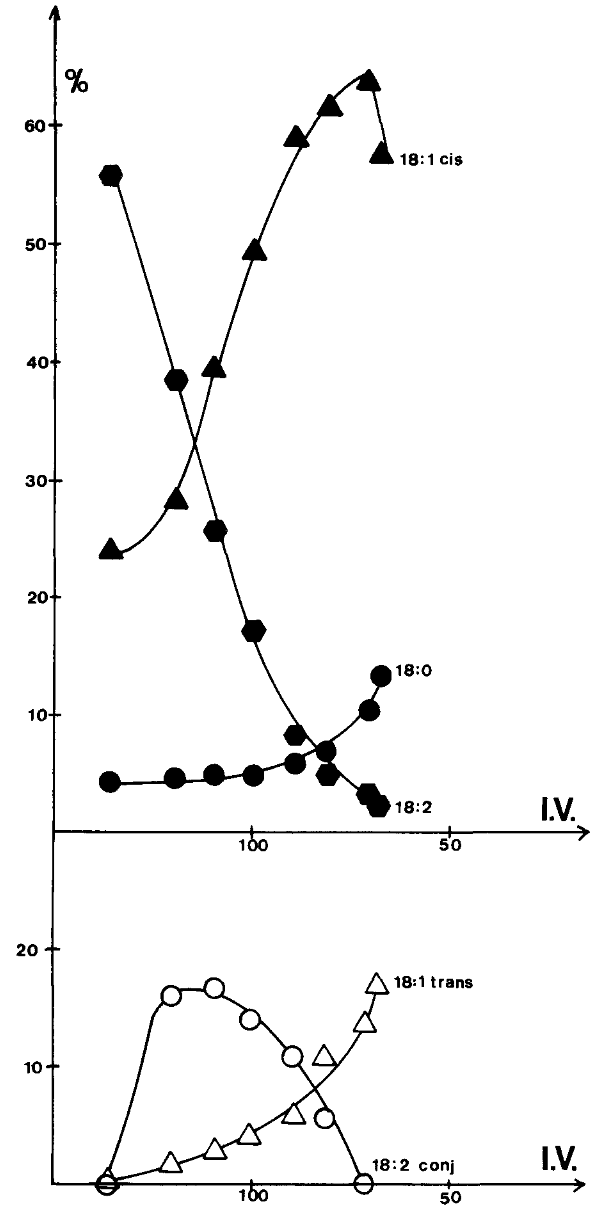


FIG. 2. Composition of the hydrogenated soybean oil at different iodine values. No additives. Conditions as in Figure 1. The 18:3 component in the starting mixture was converted so rapidly that it was not possible to detect.

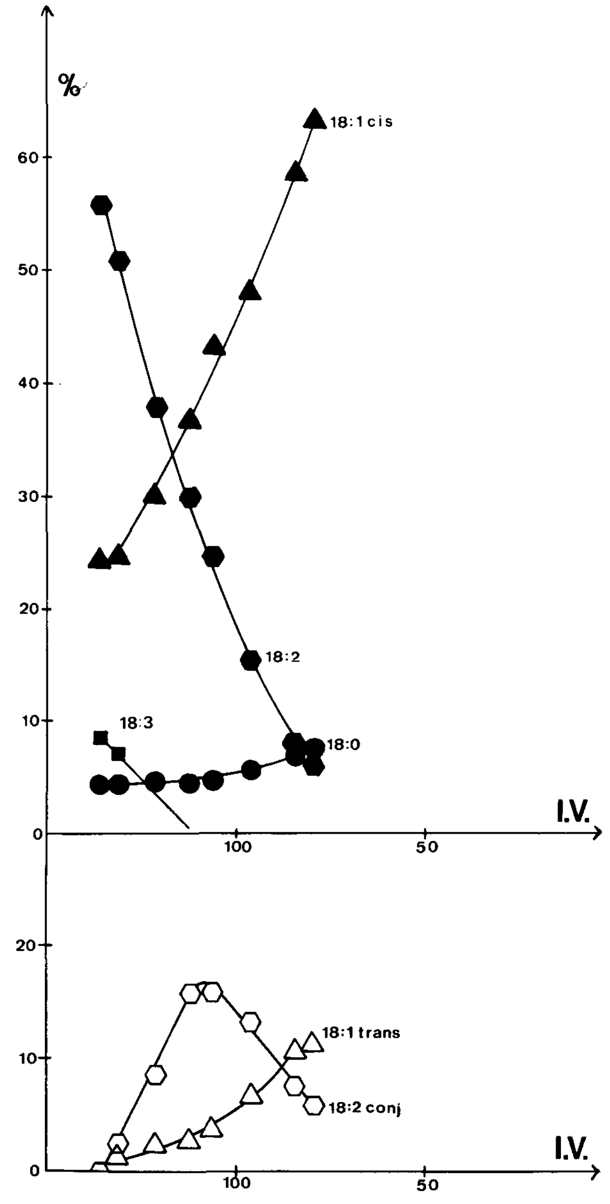


FIG. 3. Composition of the hydrogenated soybean oil at different iodine values ($HClO_4$ added) [$HClO_4$] = 21 mM. Conditions as in Figure 1.

From the simplified reaction scheme given in Figure 5 one can say that in order to avoid formation of conjugated isomers the rate of reaction with H_2 (K_1) must be much higher than the rate of conjugation (K_2). This might be possible to achieve by using a bulky ligand which by steric influence makes the allylic rearrangement more difficult.

The reaction possibilities depicted in Figure 5 correspond to the path C described by Osborn et al. (15), i.e., olefin coordination before reaction with H_2. If, however, the equilibrium $MH_2^+ \rightleftharpoons MH + H^+$ is shifted strongly towards the left side no further change in product distribution on addition of acid can be observed. Therefore, the presence of the dihydride route (path B) cannot be excluded.

In the scheme given by Schrock and Osborn the only way to convert the system to the monohydride is to shift the equilibrium $M^+H_2 \rightleftharpoons MH + H^+$. The drastic change of the product distribution pattern found upon adding the base to the solution (Fig. 4) indicates a conversion of the system to the monohydride. Thus, only small amounts of the dihydride exists in solution. The *trans* 18:1 acid reaches values close to 50% and the hydrogenation proceeds to the saturated acid 18:0. Also the formation of nonconjugated *cis-trans* 18:1 and *trans-trans* 18:2 can be noted. This pattern has all the characteristics of a single M-H attack on an isolated olefin bond. We suggest that the action of the base (triethylamine) is two-fold: (a) A shift of equilibrium 1 towards the right side to form the L_n RhH complex. (b) Blocking some of the coordination sites of the metal atom. This second effect will be discussed more when dealing with the catalytic activity.

Catalytic activity. The highest activity was obtained (Fig. 1) when the complex was used without additives. The addition of $HClO_4$ to the system results in a lowering of the activity. Thus the addition of acid ($HClO_4$) causes a decrease of the overall reaction rate but retains the product distribution pattern. This is in contrast to the reports of Osborn et al. (13). They found a distinct difference in the production of isomers parallel to that of the rate decrease on addition of $HClO_4$. This effect was found for monoenes, however, (13). For dienes no pronounced variation in either reaction rate or product pattern was found on acid addition (15). The decrease in rate of hydrogenation that we have found in this investigation (Fig. 1) is probably caused by a decrease in the concentration of species A (Fig. 5). Actually at higher acid concentration the rate is lowered even more. One way by which the concentration of species A can be decreased is by oxidation of Rh(I) to Rh(III). It is possible that the oxidizing acid ($HClO_4$) could produce hydroperoxides or perhaps more likely epoxides from the unsaturated acids originally present in the soybean oil. These products can act as catalyst poisons or perhaps even oxidize Rh(I) to Rh(III) and destroy the active intermediate. This explanation is put forward on the basis of hydrogenation experiments done with oxidized oils: Oils with peroxide values of 4 were not hydrogenated with the present system.

Another possible explanation is the effect that arises from specific interaction of protons on the more or less negatively charged carbon atoms π-bonded to the transition metal atom. Hence—and because of the positive charge of this metal atom—repulsion takes place that decreases the stability of the species A.

Even the addition of NEt_3 to the system caused a decreased activity, compared to the activity of the system without additives (Fig. 1). This can be explained if one takes into account that triethylamine is not only a Brønsted base that can shift the proton equilibrium (Eq. II), but also a Lewis base that can coordinate to the metal. By coordination of NEt_3 to the metal (Eq. 3), coordination sites on the

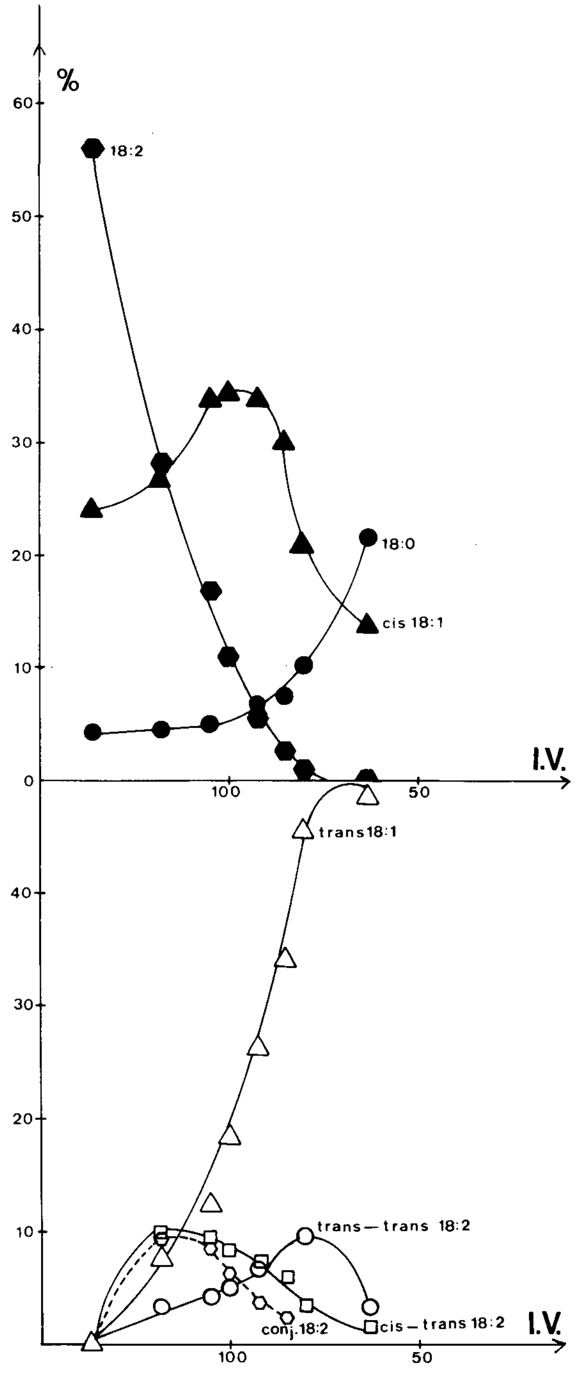


FIG. 4. Composition of the hydrogenated soybean oil at different iodine values NEt_3 added. [NEt_3] = 2 mM. Conditions as in Figure 1. As in the experiment with no additives it was not possible to detect the 18:3 component.

TABLE I

Composition of the Hydrogenated Oil at Some Selected Iodine Values. Data from the run without additives.

IV	18:0 %	*cis* 18:1 %	*trans* 18:1 %	*cis* 18:2 %	conj isomers %
100	4.8	48.2	4.0	16.8	13.6
80	6.8	61.2	10.4	5.2	4.8

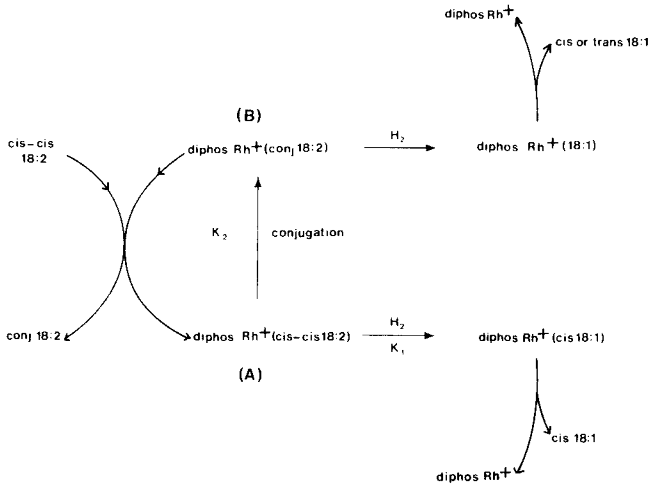


FIG. 5. Reaction scheme suggested for the hydrogenation of linoleic acid esters.

catalyst are blocked and the activity lowered:

$$H_2Rh\ diphos^+ + NEt_3 \rightleftharpoons H\ Rh\ diphos + H^+NEt_3 \quad [II]$$

$$H_2Rh\ diphos^+ + xNEt_3 \rightleftharpoons H_2Rh(diphos)(NEt_3)_x^+ \quad [III]$$

The suggested explanation is supported by the following: If the concentration of added NEt_3 is reduced, and consequently less blocking of rhodium occurs, the catalytic activity as reported in Figure 1 is increased. The number of amine molecules that can add to the complex (i.e. x in Eq. III) is most probably greater than one. Therefore, it is quite reasonable that the blocking effect (Eq. III) of NEt_3 is more concentration-sensitive than the mere buffering action (Eq. II). Further support to this interpretation is the observation by Schrock and Osborn (13) that acetonitrile is not a suitable solvent because of the formation of a strong complex. $H_2Rh(PPh_3)_2(NC{\cdot}CH_3)_2^+$.

The model of hydrogenation suggested in the present paper conforms to our reported observations and to those of earlier investigators (13-15,17). In order to substantiate the reasoning, further work should include spectroscopic studies on the interaction of protons with π-bonded metal-diene complexes and on how ligand basicity and ligand bulkyness influence the reaction. A study using nonoxidizing, noncoordinating acid, like HBF_4, could also give valuable information.

ACKNOWLEDGMENT

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REFERENCES

1. Allen, R.R., and J.E. Covery, Jr., JAOCS 47:494 (1970).
2. Dutch Pat. Unilever N.V.P. appl. 7813005-1.
3. JAOCS 53:466A-468A Abstracts 146-164 (1976).
4. Sqoutas, D., and F.A. Kummerow, Am. J. Clin. Nutr. 23:111 (1970).
5. Nishiguchi, T., T. Tagawa, H. Imai and K. Fukuzumi, JAOCS 54:144 (1977).
6. Tagawa, T., T. Nishiguchi and K. Fukuzumi, Ibid. 55:332 (1978).
7. Frankel, E.N., and F.L. Little, Ibid. 46:256 (1969).
8. Frankel, E.N., and R.O. Butterfield, J. Org. Chem. 34:3030 (1969).
9. Frankel, E.N., JAOCS 47:11 (1970).
10. Awl, R.A., E.N. Frankel and J.P. Friedrich, Ibid. 55:577 (1978).
11. Fragale, C., M. Gargano, T. Gomes and M. Rossi, Ibid. 56:498 (1979).
12. Puri, P.S., Ibid. 55:865 (1978).
13. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 98:2134 (1976).
14. Schrock, R.R., and J.A. Osborn, Ibid. 98:2143 (1976).
15. Schrock, R.R., and J.A. Osborn, Ibid. 98:4450 (1976).
16. Strukul, G., M. Bonivento, M. Graziani, E. Cernia and N. Palladino, Inorg. Chim. Acta 12:15 (1975).
17. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 93:2397 (1971).
18. Smith, L.M., W.L. Dunkeley, A. Franke and T. Dairike, JAOCS 55:257 (1978).
19. Dittmar, K.E.J., H. Heckers and F.W. Melcher, Fette, Seifen Anstrichm. 80:297 (1978).
20. "Official and Tentative Methods of the American Oil Chemists' Society", Vols. 1&2, 3rd ed., 1973, AOCS, Champaign, IL, Method Cd 14-61.

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