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NOTES

Homogeneous Hydrogenation with a Soluble Nickel Borohydride Catalyst

Treatment of nickel acetate with sodium borohydride in aqueous or ethanolic solution produces a black colloidal material—nickel boride—which is a well-known hydrogenation catalyst exhibiting a remarkably low tendency to isomerization (*1*). However, if an appropriate solvent is applied or ligand is added, the interaction between nickel acetate and sodium borohydride may result in the formation of a borohydride complex. In liquid ammonia, for example, an isolatable complex $Ni(NH_3)_6(BH_4)_2$ is formed (*2*). Recently, the preparation of hydridoborohydrido(tricyclohexylphosphine) nickel (II) has been described (*3*). To our knowledge, little research has been done on the catalytic activity of nickel borohydride complexes, although a rhodium borohydride complex prepared from tris(pyridine) $Rh^{III}Cl_3$ and $NaBH_4$ in dimethylformamide solution has recently been shown to be an active hydrogenation catalyst (*4*). In this paper, some properties of a nickel catalyst prepared from $NiCl_2$ and $NaBH_4$ in dimethylformamide (dmf) solution are reported.

In particular the hydrogenation of vegetable oils and their polyunsaturated fatty acid components have been studied.

A serious difficulty connected with the selective hydrogenation of polyunsaturates to monounsaturates is the geometric and positional isomerization of the remaining double bonds. This may lead to an intolerably high melting point of the hydrogenated oil due to the presence of high melting *trans* products.

The catalyst was produced by adding 0.44 mmole $NaBH_4$ to a stirred solution of 0.4 mmole $NiCl_2$ in 100 ml dmf at 25°C. When the color had become deep-brown, hydrogen was admitted up to a total pressure of 78 cm Hg and hydrogenation was started by introducing 25 mmole of alkene with a hypodermic syringe.

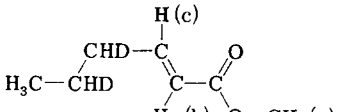
The initial hydrogenation rates of this catalytic system showed a wide spread. The rate with 1-hexene was rather high (*ca.* 90 ml/min), lower with 1,3-cyclohexadiene and methyl sorbate (*ca.* 10 ml/min), and extremely low with cyclohexene and methyl oleate. As with colloidal nickel boride, the latter system causes a remarkably low degree of isomerization. During the reduction of 1-hexene, at most 2% of *trans* and traces of *cis*-2-hexene are formed.

The products from linoleate (methyl *cis*-9,*cis*-12-octadecadienoate) hydrogenated at 25°C and 20 atm were analysed as 10% methyl stearate and 90% monoenoic ester containing *ca.* 15–20% *trans* unsaturates. The reaction rate slows down considerably when all methyl linoleate has been converted into monoenoic esters. At a partial hydrogenation, the linoleate fraction contained *ca.* 95% *cis–cis* and *ca.* 5% *cis–trans* conjugatable diene. Only traces of conjugated isomer were present. Oleate is only slightly reactive, not only in hydrogenations but also in isomerizations. The *trans* double bond of isomerized oleate is still mainly located at the Δ-9 position.

The hydrogenation of refined soybean oil at 25°C and 40 atm, resulted in products with low *trans* contents ($<10\%$) at an I.V. of about 80 while the stearate content had increased to about 12%.

The hydrogenation of methyl sorbate yielded 80% 2-hexenoate, 5% 3-hexenoate and 15% capronate. The results of deuterium tracer studies showed that the reduction proceeds by a 1,2- addition of hydrogen. Proton NMR and IR analyses indicated that the major product formed from catalytic deuterated methyl sorbate was 4,5-dideuterio-2-hexenoate.

Proton NMR. The signal in the alkene region shows that the major component—possessing alkene protons—present in the reaction product must be:



(a) 3.73 ppm singlet
(b) 5.73 ppm doublet of doublets (J 15.5; 1.5)
(c) 6.79 ppm broad doublet of doublets (J 15.5; 6.5)

Infrared. One fairly strong peak at 2150 cm^{-1} due to C–D stretching vibrations is observed. No absorptions are found at 2196 cm^{-1} and 2102 cm^{-1} reported for CD_2 asymmetric and symmetric stretching vibrations (*5*). An absorption at 2180 cm^{-1}, which has been tentatively assigned to CHD flanked by one alkene and one carbonyl group (*6*), could not be observed. Strong absorption appeared at 1658 cm^{-1} and 990 cm^{-1} characteristic of a *trans* double bond conjugated with a carbonyl group (*7*). These results provide direct evidence that a 1,2- hydrogen addition is indeed the dominant reduction mechanism.

We have succeeded in establishing that the reduction of 1,4-diunsaturated systems such as methyl linoleate takes place without an initial conjugation step. The double bond in the isomeric monoenes from reduced linoleate is mainly located at the Δ-9 or Δ-12 position in both the *cis* (52% Δ-9 and 45.5% Δ-12) and the *trans* fraction (40% Δ-9 and 34% Δ-12). This distribution is consistent with that for a reduction of the methyl linoleate by 1,2- addition, which shows a slight selectivity towards the Δ-12 double bond. Further evidence for the absence of conjugation during the reduction of linoleate was obtained from the double bond distribution in the monoene fraction from reduced conjugated linoleate, which was more or less equally distributed between Δ-8 and Δ-13. The same distribution might be expected if the reduction of linoleate had proceeded via conjugation. After deuteration of linoleate and conjugated linoleate, the NMR spectra indicated the presence of four methylene protons—α to the double bond—in the monoene fraction from reduced linoleate and of only three in the monoene fraction from conjugated linoleate. This is only consistent with a 1,2- addition of the 1,4-diunsaturated system.

Although methyl oleate is not completely inert for hydrogenation and isomerization reactions, its reactivity is very poor in comparison with linoleate. The much greater activity of linoleate cannot be explained by assuming that reactive 1,3-conjugated systems are involved as intermediates. The double bond distribution in the monoenes from reduced linoleate as well as the number of deuterium atoms α to the remaining double bond clearly indicate that conjugation does not take place. It seems to us that there are two explanations for the greater reactivity of linoleate. It may be that a 1,4-alkadiene–nickel complex is formed. A 1,2- addition of hydrogen will then indeed produce an alkene with its double bonds essentially located at the Δ-9 or Δ-12 position. Another possibility is that one of the double bonds attaches to the metal center to form a π complex which then rearranges to a σ-alkyl complex. The second double bond is subsequently coordinated and a σ-alkyl–π-alkene complex is formed. This stabilizes the σ-alkyl bond making attack by hydrogen possible. The monoene complex thus obtained subsequently exchanges with free diene.

A similar mechanism has been suggested previously (*8*) for the selective reduction of conjugated dienes to monoenes. The same mechanism may be operating here because

σ-alkyl–π-alkene complexes with two or three carbon atoms between the σ-alkyl and the π-alkene bond have been described (*9*).

Like methyl oleate, other internal alkenes such as cyclohexene and methyl-3-hexenoate are only slightly reactive. On the other hand, alkenes having a terminal double bond are hydrogenated quite easily. Terminal alkenes have the possibility to form a linear alkyl in the half-hydrogenated state whereas oleate must form a secondary alkyl. Steric requirements are probably less stringent for linear alkyl than for secondary alkyl formation. The low isomerization tendency of 1-hexene could also point in the direction of highly favored linear alkyl formation. Although for linoleate the same steric restrictions hold as for oleate, hydrogenation is here promoted by the formation of a 1,4-alkadiene or a σ-alkyl–π-alkene complex. Indeed, isolinoleate (with more than two carbon atoms between the double bonds) is not hydrogenated.

It seems to us that the most interesting property of this catalytic system is the ability to combine a good selectivity with a low positional isomerization tendency. The *trans* double bond in hydrogenated linoleate and isomerized oleate is still mainly located at the original Δ-9 or Δ-12 and the Δ-9 position respectively.

The catalyst is not indefinitely stable, slower rates being observed upon reintroduction of alkene after a complete hydrogenation run. In some cases, a slight deposition of a black material is formed, causing destruction of the catalytic properties. The nature of the active complex remains to be established. By analogy with its rhodium counterpart, one would be tempted to formulate the active catalyst as $(\mathrm{dmf})_3\mathrm{NiCl}(\mathrm{BH}_4)$. On the other hand, the color of the catalytic mixture resembles that of soluble Ziegler-type catalysts. It is generally accepted that these contain metal in a reduced form, solubilized and stabilized by solvent and reducing agent.

We have made a few attempts to isolate a complex from the solution, but these have proved unsuccessful so far.

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On the Existence of Hydroxyl Nests in Acid-Extracted Mordenites

The nature of catalytic action in zeolites is a matter of debate, although there seems to be consensus that activity derives from the existence of tetrahedrally or trigonally coordinated aluminum ions in the lattice. A useful approach to this problem is the possibility of varying the silica:alumina ratio in a zeolite of a given type, along