Hydrogenation Theory: Some Aspects

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ABSTRACT

The model of associate adsorption of olefinic groups to give the half-hydrogenated state suggested first by Horiuti and Polanyi, gives the simplest possible description of the hydrogenation process. By adding the requirement that a *cis* selective process is favored by preventing the free rotation around the C-C bond of olefinic parentage, one can rationalize many observations in fat hydrogenation. Examples given in the present paper show that this prevention is achieved if two coordination sites are available for an effective locking of the diene during the hydrogenation. From this very idea, it follows that the *trans* selectivity must increase when the iodine value has been reduced to such a point that the proportion of dienes is very small. Another indication of the usefulness of the presented ideas is the spectroscopic observation that poisoning of the sites on a metallic surface that make two coordination places available for olefin coordination increases the *trans*-selectivity. All in all, this review emphasizes the important contributions of coordination chemistry and spectroscopy to the understanding of the mechanism of hydrogenation processes on solid metal surfaces.

INTRODUCTION

In industrial practice, the hydrogenation of fatty oils is performed as a heterogeneous catalytic process with nickel or copper catalysts. Two major effects must be considered to describe or explain the rates and course of the reactions that proceed in such an operation. These two factors are what has been called the "hydrogen availability" and the "hydrogen demand" (1).

The first one describes mass transport effects, such as the complicated route for the hydrogen molecules from the bubbles through the liquid phase to the surface of the solid catalyst (Fig. 1). The diffusion of the reactants to – and of the products from – the active sites where the reaction takes place constitutes the mechanics of the hydrogenation reaction. These factors dominate the picture at high rates of conversion. They have been treated in some detail, e.g., by Schöön et al. (2).

At low rates, however, the chemistry of the surface reactions is decisive for the product pattern. Such reactions that demand high concentrations of hydrogen are favored if the hydrogen concentration is high at the surface and vice versa.

It is with this chemical part of the hydrogenation that this paper is concerned. The chemistry of the solid surface reactions has analogous counterparts in the reactions of homogenous catalysts and one of the main points will be to stress these similiarities.

Some Effects to be Considered

The purpose of the hydrogenation is to reduce the content of linolenic acid esters to a minimum and to avoid the formation of completely saturated acids – or rather, triglyceride esters.

During the reactions, isomeric products are formed, e.g., geometric isomers with *trans* configurations at the double bond and positional isomers with shifted position of the double bond. A special case of this latter type is the formation of conjugated double-bond systems. The state of knowledge of the hydrogenation reactions a decade ago was brilliantly summarized by Coenen (3). Some of his terminology will be used here.

To describe the result of a hydrogenation run, one often uses a set of selectivity parameters. Examples of such entities are the linoleic selectivity (S_I) describing the ratio of pseudo-first-order rate constants for hydrogenation of the linoleic ester (K_2) and that of the oleic ester (K_3); the linolenic selectivity (S_{II}) describing the analogous ratio K_1/K_2.

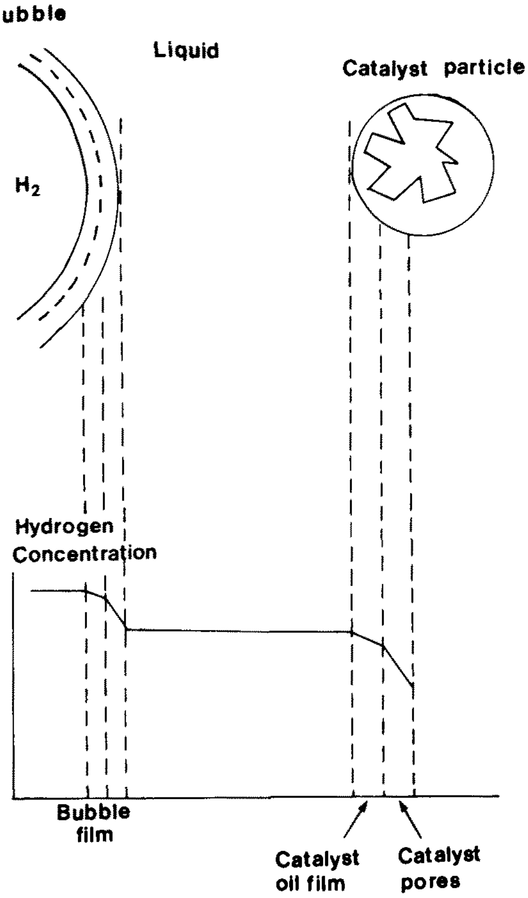


FIG. 1. Schematic view of mass transport effects.

Obviously, both S_I and S_{II} should have as large values as possible. To describe the formation of *trans* products, one can use the so-called specific isomerization index, S_i, describing the ratio of the number of *trans* double bonds formed per double bond eliminated (3), or analogously, the number of *trans* double bonds formed per unit rate of iodine value reduction (4).

There are now a number of observations that one must be able to explain in any model for hydrogenation: (a) The S_{II} selectivity is of the order of 2-3, excepting copper, where values up to 12 have been observed (3). (b) S_i increases with decreasing pressure and/or increasing temperature (4), i.e., under such conditions that the concentration of H_2 at the surface is low. (c) S_i increases strongly with decreasing iodine value (4). (d) S_i increases when part of the catalyst surface is poisoned with sulfur (5). (e) The formation of conjugation isomers increases under conditions where the hydrogen supply is low.

A CRUDE MODEL

In order to model the reactions leading to the various isomers and hydrogenation products, we can use a simple scheme such as that in Figure 2.

The first step undoubtedly involves the π-bonding interaction of the double bond and a metal atom very much like the one in the famous Zeise's salt (6). The next step can be written in analogy with what is believed (7) to occur in the case of simple coordination catalyst systems, e.g., the well known Wilkinson complex, $(Ph_3P)_3RhCl$. This means that a hydrogen atom from an M-H bond in the neighborhood is transferred to one of the carbons of the olefinic bond while this bond is simultaneously sliding off sideways so that a σ M-C bond is formed.

The resulting metal-bonded alkyl group has now various possibilities of reaction:

(I) There may be a reverse reaction to produce the original *cis*-configurated species. Thus nothing has really happened.

(II) There may occur a twisting or rotation around the C-C axis and thereafter a reverse reaction back to the π-bonded state and finally to the unbonded initial situation. This sequence produces a *trans*-configuration isomer.

(III) A hydride transfer from an M-H group to the metal-bonded carbon results in the liberation of the saturated species. The two M sites can thereafter take up a H_2 molecule which is split into two M-H groups.

(IV) A reversal as in points I and II may take place, but now involving the (M-)C-C bond on the other side of the metal-bonded carbon. This situation is illustrated in Figure 3. Depending on which of the two H-atoms are closest to an empty M-site, a *cis*- or a *trans*-olefin bond will be produced. If a diene system is considered that contains a bridging CH_2 unit, i.e., a 1,4-diene, a move of one of the double bonds in the direction of the other will create a conjugated system.

It must be stressed here that the double bond $C_b = C_c$ of Figures 2 and 3 could equally well be shifted to a $C_c = C_d$ position as the attack of hydrogen might have occurred at position "b" and the carbon at position "c" would then have been bonded to a metal site.

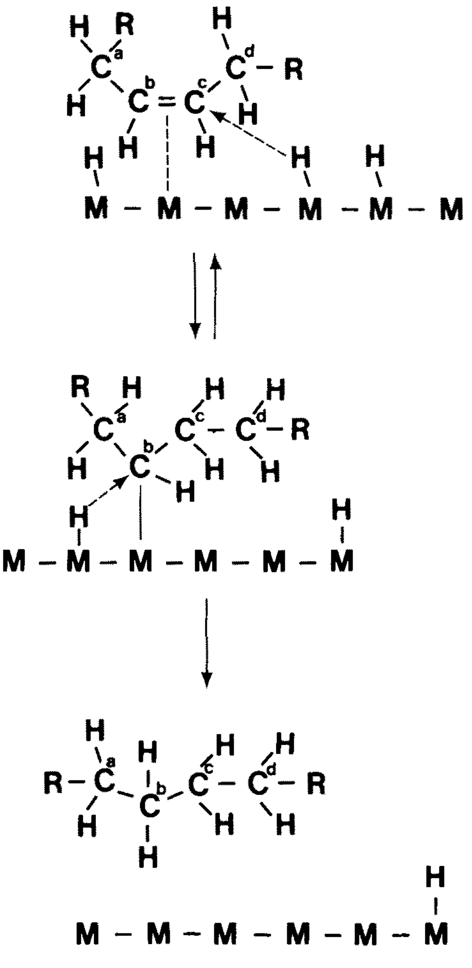


FIG. 2. Formation and reaction of the alkyl intermediate on a metal surface.

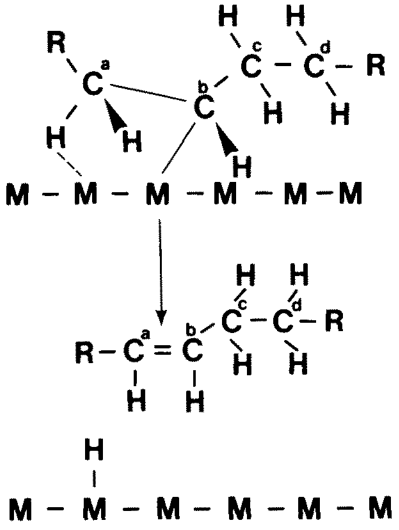


FIG. 3. Bond shift resulting from reaction of the alkyl intermediate.

Similar schemes have been produced by, e.g., Coenen (3). These, as well as the one given above, emphasize that the shift of double-bond positions must occur easily under conditions with low hydrogen coverage of the surface. (cf. point "e" of the list of observations to explain.) There is, however, one further way of describing the shift of double-bond positions that does not need the presence of M-H groups at all. This was originally proposed by Davies for homogeneous systems (8) and contained the appearance of a metal-carbene intermediate. For a metal surface, the analogous reaction will be as described in Figure 4.

DEDUCTIONS

It is a common observation (3,9) that hydrogenation of multiply unsaturated fatty acids (esters) proceeds via conjugated species. This means in the scheme above that the rates at which the reverse reactions occur are much higher than that of the addition of a second H atom to the metal-alkyl group.

It further must hold that the rate of hydrogenation of the conjugated species must be large compared to that for an isolated olefinic bond.

These conditions can be very clearly observed experi-

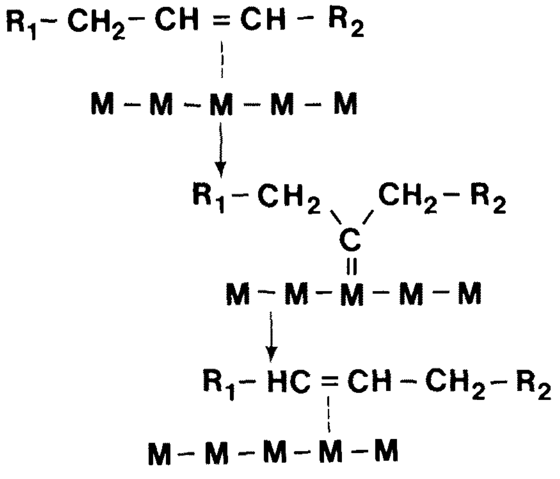


FIG. 4. Bond shift via a carbene intermediate.

mentally for copper systems, e.g. (9), where the rates of hydrogenation of dienes and conjugated dienes are much lower with the corresponding nickel systems. One observes (Fig. 1 of Ref. 9) that the concentration of conjugated dienes is rapidly decreasing when the average number of double bonds comes near the value one.

The hydrogenation rates of isolated double bonds in dienes (or trienes) and especially of monenes were extremely low, resulting in monoenes as the final product. This reflects the generally low activity for hydrogenation of copper as hydrogenation catalyst (10).

This mechanism with a conjugated intermediate, just described, implies a selectivity $S_{II} > 2$. This follows from the twice greater chance of a 9,12,15-triene to give a conjugated system than there is for a 9,12-diene; cf. Figure 5.

As most metals give a value S_{II} of about 3, the remaining double bond in, say, a 10,12,15-triene must infer a somewhat larger reactivity to the conjugated group than for the case of a conjugated diene. Possibly this effect is extremely strong in the case of copper.

By comparing results for Cu and Ni, respectively, (11) and (12), e.g., the product pattern for hydrogenation of linoleate, one finds indeed very similar results. Especially for the *trans* monoenes formed, one notices peak values for the 10- and 11- positions. This must mean that the same mechanism of conjugation is operating.

The question, however, why exactly those conjugated species are reacting faster than the nonconjugated dienes is not easily answered. It is not because of a low hydrogen atom coverage of the surface. That may explain the fact that bond shift does take place — but not more. Otherwise, the conditions are equal.

The detailed explanation must probably await quantum-chemical calculations on olefin hydrogenation in general.

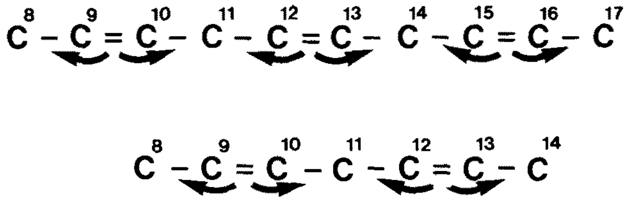


FIG. 5. Schematic view of the possibilities of bond shifts in a 9,12,15-triene and a 9,12-diene.

Such studies are at their infancy, beginning with the simplest possible system, ethene (13-15). In the meantime, one might possibly use empirical relations between hydrogenation activity and frequencies of C-H deformation vibrations of the reacting olefins. This latter approach was suggested by the present author as part of a discussion on vibrational resonance in catalytic processes (16).

Now let us return to the problem of *cis/trans* isomerization. It follows from the scheme in Figures 2 and 3 that, if one wants to avoid the formation of *trans* isomers, one should ideally prevent the formation of the alkyl group that is the "pièce de resistance" of the schemes. It is in that group that a twisting around the C-C bond of olefin parentage takes place. If one could fix or lock the π-bonded olefinic group (Fig. 2) so that it could not so easily slide in a sideways direction, this goal is achieved.

If one then has two M-H units available, each of which could more or less simulatenously attack the two ends of the C=C bond, hydrogenation — or the reverse of the reaction — would result in the initial *cis* isomer. Such a situation can be found in some homogeneous systems of coordination compounds. We will therefore consider such systems in the following paragraph.

COORDINATION CATALYSTS

One of the drawbacks of the early investigated coordination compounds as hydrogenation catalysts for fat hardening, e.g., $Co(CN)_5H^{3-}$ (17) or $Cl_3Sn\text{-}PtCl_2H^{2-}$ (18), was that a considerable amount of *trans* isomers was formed. This was explained in terms of the metal-alkyl formation that is implicit in Figure 2.

One noticeable exception was discovered, though. That was the class of complexes carrying the group $Cr(CO)_3$, e.g., arene $Cr(CO)_3$ (19). It could be shown that, for already conjugated dienes, a 1,4-hydrogen addition took place. This resulted in a 2,3-*cis* configuration of the end product. The mechanism proposed (19) contains a model of free coordination sites of the chromium atom where the two double bonds can coordinate with two hydrogen atoms (Fig. 6).

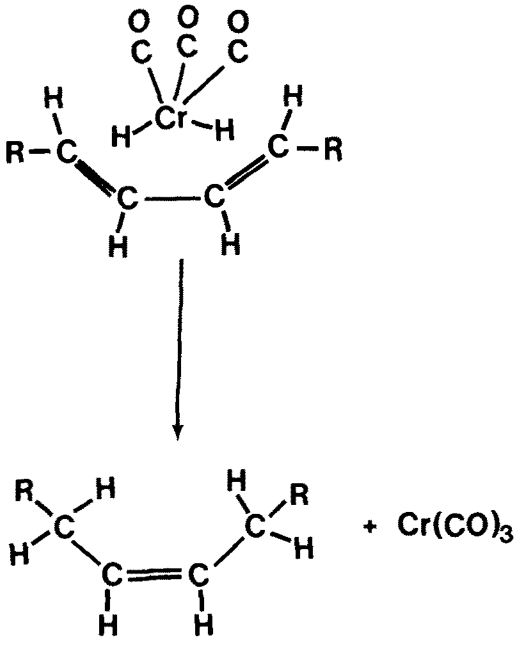


FIG. 6. 1,4-addition at a conjugated diene catalysed by $Cr(CO)_3$.

This means that, even if the two conjugated double bonds have *trans* configurations, the very coordination act gives rise to a *cis*-like arrangement around the chromium atom. When the two Cr-H bonded hydrogen atoms are transferred in 1,4-positions, one gets a *cis*-configurated 2,3-monoene as the end product (20).

We meet here an example of a mechanically rigid arrangement that keeps the C=C bond fixed in respect to sideways movement. Such a system was suggested above as necessary for avoiding the *trans*-generating alkyl intermediate. Admittedly, the two hydrogen atoms are not transferred to the same olefinic group, but they are nevertheless transferred more or less concertedly (19).

An even more interesting example can be found in the cationic complex $Rh(PR_3)_2^+$, studied first by Schrock and Osborn (21). The hydrogenated species $H_2Rh(PR_3)_2^+$ enters into a rather unique redox equilibrium (21):

$$H_2Rh(PR_3)_2^+ \rightleftharpoons HRh(PR_3)_2 + H^+$$

In acidic media, the bishydrido complex is dominating. In basic media the monohydride dominates and – from our model described above – gives rise to *trans* products. The two remaining sites in the bishydrido complex make possible the coordination of two olefinic bonds, conjugated or not.

This complex has recently been tested for hydrogenation of linoleate esters and similar systems. van der Plank and coworkers (22) studied isolated methyl esters and performed a thorough analysis of the positional isomers formed. Andersson and Larsson (23) tested the complex directly on soybean oil. Both investigations were carried out at about atmospheric pressure of hydrogen and ambient or slightly higher temperature. The results are essentially the same; the hydrogenation proceeds to part via a conjugation mechanism that leaves both *cis*- and *trans*-18:1 esters and via a direct hydrogenation of one of the two double bonds, leaving the other intact as *cis*. One can notice, e.g., from Figure 7, that the significant rise of 18:1 *trans* starts first when all 18:2 components are consumed, i.e., there is no longer any possibility to get a mechanically fixed array of two (more or less directly linked) double bonds coordinated to the same metal atom.

Whereas our investigation (23) was performed with "diphos", $Ph_2P\,CH_2CH_2\,P\,Ph_2$, as the ligand, the Dutch group (22) investigated three different complexes with phosphine ligands of gradually increasing base strength. The less basic one, $L = P(C_2H_5)_2C_6H_5$, gave a monoene product pattern for the hydrogenation of the *cis*-9, *cis*-12 ester, as shown in Figure 8, very similar to that found for metallic copper (11). The difference is that, in the present case, the proportion of *trans* species was quite small. Quite strikingly, van der Plank et al. (22) found that this complex gave almost exactly the same product pattern after a "preconjugation" of the olefin.

The most basic ligand, $L = PMe_3$, on the other hand, was characterized as a bad conjugation catalyst and gave a product pattern for the hydrogenation of *cis*-9, *cis*-12 that was strikingly similar to what has been reported for metallic nickel catalysts (12). Also in this case there was a very low proportion of *trans* components (see Fig. 9).

The authors (22) draw the conclusion, inter alia, that for this latter-mentioned complex "the direct hydrogenation of one of the double bonds predominates over the conjugation route."

It is tempting to interpret this finding in terms of a model excluding the formation of freely rotating (twisting) alkyl groups. Indeed, the authors do exactly this (22,24). In a paper describing an extremely selective hydrogenation of methyl linoleate (24), they point out that, in most cases, the simultaenous coordination of two olefinic groups joined

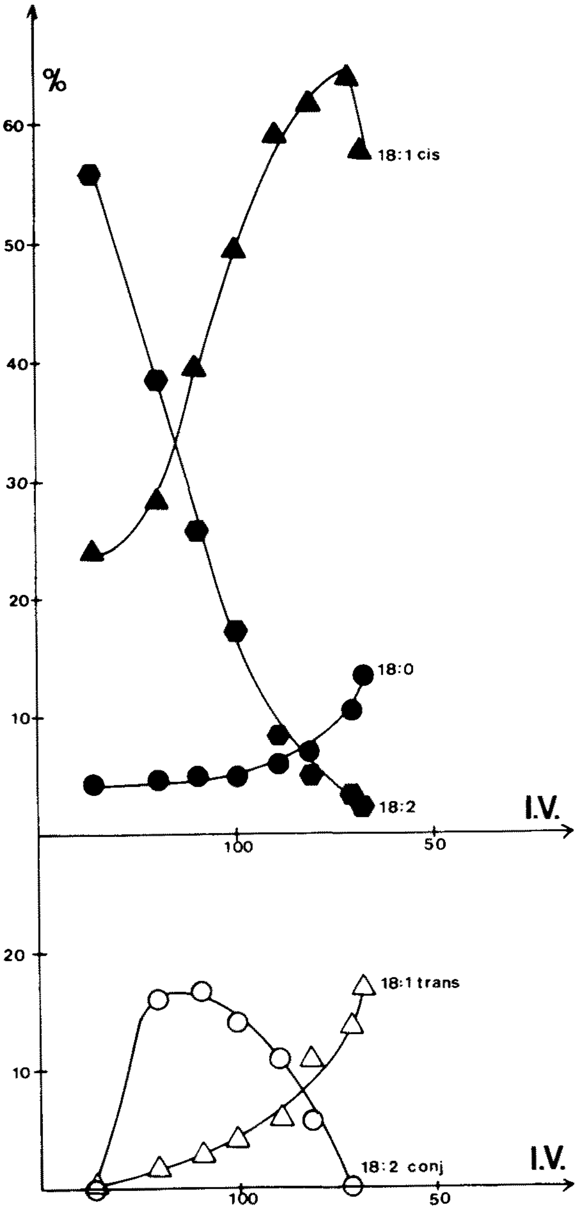


FIG. 7. Product pattern from the hydrogenation of soybean oil with Rh diphos⁺ complex (from Ref. 23).

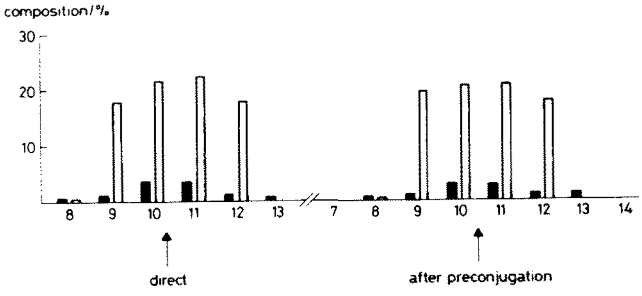


FIG. 8. Product pattern from the hydrogenation of methyl linoleate with RhL_2^+, $L = P\,Et_2\,Ph$ (from Ref. 22).

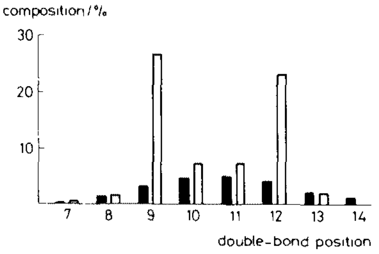


FIG. 9. Product pattern from the hydrogenation of methyl linoleate with RhL_2^+, L = PMe_3 (from Ref. 22).

by one methylene group is made impossible because of the strain introduced in the system in such a case. For such ligands, however, where this strain is already present or compensated for, e.g., in norbornadiene, a π,π coordination is possible.

But, the authors point out (24), if a metal-carbon σ bond is established simultaneously with a hydrogen transfer, as in Figure 2, the strain is released. In this way, we have precisely the type of rotationally locked metal-alkyl that will lead to hydrogenation or to the reversal of the original *cis* configuration. In a simplified manner, the main points of the model are represented in Figure 10.

In the case studied by van der Plank and van Oosten (24), viz., Pd^{n+} on a resin, very little positional isomerization was found to be caused by the route via the intermediate just described. However, in some cases, depending on the availability or coordination sites, etc., one might expect a reversal of the reaction of Figure 10 in the sense that it is one of the hydrogen atoms of the hydrogen atoms of carbon 11 that is accepted by the metal atom. In this way, one gets a conjugation of the 1,4-diene without the intermediate of a free-rotatable alkyl group. Such a process might be thought to occur in the case of those Rh^+ complexes (22,23) where one observes an extremely small part of *trans,trans* diene during the reaction.

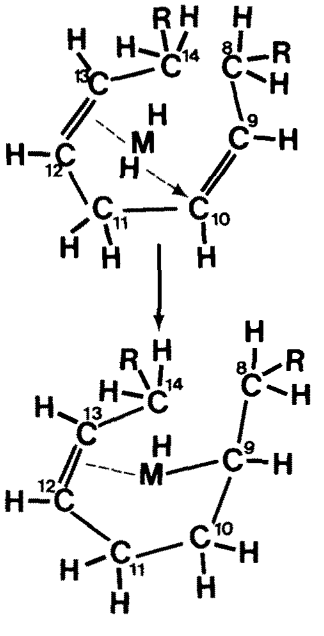


FIG. 10. Schematic description of the binding of the 9,12-diene with an ethylene bridge according to Ref. 24.

To conclude this section, it seems very likely that the locking of two olefinic bonds via the availability of two coordinating sites on a metal atom is a prerequisite for preventing the formation of *trans* isomers.

SPECTROSCOPIC INFORMATION

In the last decade, a great number of spectroscopic methods for studying clean surfaces and/or species adsorbed on a surface have been developed or improved. In this section, some results that are relevant to the topic of fat hydrogenation will be indicated.

First, however, an in relation to what has just been said, one can recall the not-so-novel observation that one can assign the infrared (IR) spectra of carbon monoxide adsorbed on a metal surface to the different species $M\text{-}C{\equiv}O$ and $^{M}_{M}{>}C{=}O$ (25).

This is done by strict analogy to what is known for simple coordination compounds. A study by Garland (26) has shown that when a nickel surface is poisoned by sulfur (CS_2), only one of the two CO bands can be observed for adsorbed carbon monoxide. The band that is absent corresponds to the sites where carbon monoxide is adsorbed to two metal atoms.

Thus one can conclude that sulfur poisoning affects the nickel surface in such a way that only single-atom sites are left. This means in our simple model (Fig. 2) that no restrictions would exist on the twisting and rotation of the intermediate alkyl species that would appear should the nickel surface have been used for hydrogenation. It is, therefore, not surprising that sulfur poisoning is reported (5) to increase the amount of *trans* isomers (cf. point "d", above). It is also noteworthy in this connection that sulfur poisoning of a nickel catalyst strongly decreases the 1,2-addition in the hydrogenation of 1,3-butadiene as well as strongly favoring the *trans*-isomer formation (27).

Recent spectroscopic results apply to the very first step of olefin activation. For technical reasons, most of these studies have been applied to the simplest possible system: ethylene. Both IR and electron energy loss spectroscopy (ELS) have been used as well as ultraviolet photoelectron spectroscopy (UPS).

In Table I, a collation of some of the results is given, although with no claim for completeness. One can notice that many different species are supposed to exist and that various spectroscopic methods do not always agree.

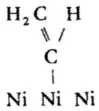
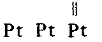
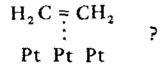
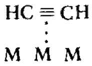
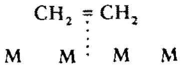
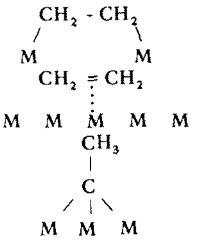
One thing seems to be rather well established: at low temperatures the primary adsorbed form is the π-bonded $CH_2 \underset{\underset{M}{\vdots}}{=} CH_2$ species (31,33,34).

For many of the group VIII metals that catalyse the hydrogenation of ethylene, catalysis is so effective that the reaction proceeds readily at very low temperatures (37). It is thus reasonable that in such circumstances the first step of the reaction is one between π-adsorbed ethylene and metal-hydride groups (as shown in Fig. 2).

Actually, in a recent investigation, Soma (30) followed the reaction catalysed by Pt/Al_2O_3 at 203 K by measuring the IR absorption of π-adsorbed ethylene (1205 cm^{-1}) and that of the Pt-H vibrations at 2120 cm^{-1}. One of the interesting observations can be especially mentioned: it is the IR-active, easily desorbed hydrogen that takes part in the hydrogenation reaction, not the bridged type of greater adsorption strength. This agrees with the resonance model

TABLE 1

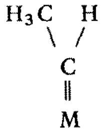
Some Spectroscopic Indications of the Structure of Adsorbed Ethylene

Temperature	Metal	Structure	Method	Reference
T = 150 K	Ni (111)		ELS	Ibach et al. (28)
T > 500K	Pt	$CH_3 \cdot CH$ dehydrogenates		
260K < T < 500K			ELS	Ibach et al. (29)
T < 260 K				
T = 203 K	Pt	π - adsorbed	IR	Soma (30,31)
T = 298 K	Pt, Ag Ni, Pd		IR	Ito et al. (32, 33)
T < 200 K				
T = 100 K	Ni (111) Ni (110) Pd (111) Pt (111)	π-adsorbed "very weak distortions"	UPS	Demuth (34)
T = 293 K	Pt Pd		IR	Sheppard et al. (35,36)

proposed for this type of reaction (16).

However, most authors and most spectroscopic techniques agree that at room temperature, or slightly above, the adsorbed ethylene no longer exists as a π-adduct. Rather, a drastic rehybridisation takes place. The precise nature of the species formed may vary from metal to metal. Furthermore, the analysis is strongly dependent on a delicate use of group theory and the special selection rules that hold close to a metal surface (35).

Of the results of interest in the present context, one can quote that Ibach and colleagues (29) find reason to report a carbene-like intermediate



If such species are formed also for more long-chained olefinic systems at the temperatures where fat hydrogenation takes place (5), they would open a path for double-bond shift other than the formation of an alkyl intermediate. One must recall in this connection the suggestion of a similar route for bond migration in homogeneous systems by Chatt and Davies (8) referred to above.

These examples will indicate the potentialities of spectroscopic techniques to increase the understanding of the details of hydrogenation processes. In passing one can also include the powerful technique of X-ray photoelectron spectroscopy (XPS, ESCA) that gives information, inter alia, on the electronic properties of a metal surface. Using this method, Okamoto and coworkers (37) have studied poisoning and selectivity effects for a series of nickel hydrogenation catalysts with different degree of surface modification.

REFERENCES

1. Stingley, D.V., and R.J. Wrobel, JAOCS 38:201 (1961).
2. Bern, L., M. Hell and N.-H. Schöön, Ibid. 52:182 (1975).
3. Coenen, J.W.E., Proceedings of a seminar held at Dijon University, Leiden, edited by E.J. Brill, 1970.
4. Puri, P.S., JAOCS 55, 865 (1978).
5. Allen, R.R., Ibid. 58:166 (1981).
6. Wunderlich, J.A., and D.P. Mellor, Acta Crystallogr. 7:130 (1954).
7. Dolcetti, G., and N.W. Hoffman, Inorg. Chim. Acta 9:269 (1974).
8. Davies, N.R., Nature 201:490 (1964).
9. Koritala, S., R.O. Butterfield and H.J. Dutton, JAOCS 47:266 (1970).
10. Schuit, G.C., and L.L. van Reijen, Adv. Catal. 10:242 (1958).
11. Koritala, S., JAOCS 47:269 (1970).
12. Coenen, J.W.E., H. Boerman, B.G. Linsen and B. de Vries, 3rd International Conference on Catalysis, Amsterdam, 1964.
13. Åkermark, B., M. Almemark, J. Almlöf, J.-E. Bäckvall, B. Roos and Å Støgård, J. Am. Chem. Soc. 99:4617 (1977).
14. Swope, W.C., and H.F. Schaefer, III, Mol. Phys. 34:1037 (1977).
15. Kitaura, K., S. Sakaki and K. Morokoma, Inorg. Chem. 20: 2292 (1981).
16. Larsson, R., Chem. Scr. 12:78 (1977).
17. Mabrouk, A.F., H.J. Dutton and J.C. Cowan, JAOCS 41:153 (1964).
18. Bailar, J.C., Jr., and H. Itatani, Ibid. 43:337 (1966).
19. Frankel, E.N., and R.O. Butterfield, J. Org. Chem. 34:3930 (1969).
20. Frankel, E.N., JAOCS 47:11 (1970).
21. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 98:2134 (1976).

22. van der Plank, P., A. van der Ent, A. Onderdelinden and H. van Oosten, JAOCS 57:343 (1980).
23. Andersson, C., and R. Larsson, Ibid. 58:54 (1981).
24. van der Plank, P., and H.J. van Oosten, Ibid. 56:54 (1979).
25. Eichens, R.P., and W.A. Pliskin, Adv. Catal. 10:1 (1958).
26. Garland, C.W., J. Phys. Chem. 63:1423 (1959).
27. George, M., K.B. Moyes, D. Romanaras and P.B. Wells, J. Catal. 52:486 (1978).
28. Lehwald, S., and H. Ibach, Surf. Sci. 89:425 (1979).
29. Ibach, H., H. Hopster and B. Sexton, Appl. Surf. Sci. 1:1 (1978).
30. Soma, Y., J. Catal. 75:267 (1982).
31. Soma, Y., Ibid. 59:239 (1979).
32. Ito, M., and W. Suëtaka, Surf. Sci. 62:308 (1977).
33. Ito, M., Y. Mari, T. Kato and W. Suëtaka, Appl. Surf. Sci. 2: 543 (1979).
34. Demuth, J.E., Surf. Sci. 84:315 (1979).
35. Pearce, H.A., and N. Sheppard, Ibid. 59:205 (1976).
36. Prentice, J.D., A. Lesiunas and N. Sheppard, J. Chem. Soc. Chem. Commun. 1976:76.
37. Okamoto, Y., Y. Nitta, T. Imanaka and S. Teranishi, J. Catal. 64:397 (1980).