[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Mechanisms of Reductions at Metal Surfaces. I. A General Working Hypothesis

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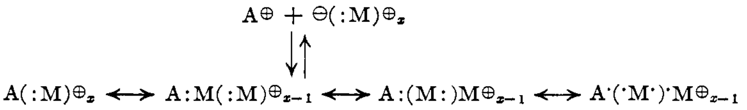
It is postulated that reductions at metal surfaces occur with the formation of resonance-stabilized chemisorption complexes as intermediates. It is suggested that a hydrogen chemisorption complex is the active reducing agent at electrodes of low hydrogen overvoltage and in catalytic hydrogenation (indirect reduction). Reduction at electrodes of high hydrogen overvoltage or by means of active metals appear to involve organic chemisorption complexes as key intermediates (direct reduction). Detailed ionic mechanisms for the direct and indirect reduction of ketones are presented.

The course of chemical, catalytic or electrolytic reduction at a metal surface appears to be determined by the structure of the reducible substance, the availability of protons in the solvent and the hydrogen overvoltage of the metal.[1] Reductions at a low overvoltage cathode resemble those at the surface of a hydrogenation catalyst[1,2a]; reductions at a high overvoltage cathode are similar to those produced by an active metal.[1,2b]

The hypothesis that chemisorption[3] of a reducible substance (A) or of molecular hydrogen at a metal surface involves the formation of a resonance-stabilized complex such as I(A)[4] permits a mechanistic correlation of these facts. A high hydrogen overvoltage would result if I(H) formed slowly or reacted slowly with protons[3b,5] (and other reducible substances). In either case, I(H) would be an improbable intermediate in fast reactions at high overvoltage surfaces but a possible intermediate at low overvoltage surfaces.



$$\begin{array}{c} A^{\oplus} + \ominus(:M)^{\oplus}_{x} \\ \downarrow\uparrow \\ A(:M)^{\oplus}_{x} \longleftrightarrow A{:}M(:M)^{\oplus}_{x-1} \longleftrightarrow A{:}(M{:})M^{\oplus}_{x-1} \longleftrightarrow A^{\cdot}(^{\cdot}M^{\cdot})^{\cdot}M^{\oplus}_{x-1} \end{array}$$

I

I(H); A = H, derived from a proton or molecular hydrogen
I(R); A = an organic molecule or ion

The catalytic hydrogenation of olefins,[6] acetylenes[6] and of aromatic hydrocarbons and acids[7] over noble metal catalysts appears to occur by *cis* addition of hydrogen to that side of a molecule which can most easily engage in close-in broadside attack on the catalyst surface.[6-9] These results indicate that some sort of surface hydride,[10] such as I(H), is an actual intermediate at low overvoltage surfaces. As these reductions appear to require an intermediate in the transfer of electrons from a cathode or from molecular hydrogen to the reducible substance, they will be termed indirect reductions.

The evidence[11] which served to overthrow the "nascent hydrogen" theory of reductions by active metals indicates that an intermediate such as I(H) is not involved in reductions at high *hydrogen* overvoltage surfaces. The present hypothesis that an *organic* chemisorption resonance hybrid I(R) is formed at such surfaces achieves a reconciliation of the theories of Willstätter[12] and of Burton and Ingold.[13] Here, electrons are pictured as being transferred directly from the *massive* metal to the reducible substance *via* essentially covalent bond formation (direct reduction); protons are acquired by the reducible substance either before or after the electron transfer. This picture differs from the earlier ones chiefly in assigning important steric and resonance-stabilizing effects to the solid metal itself.

The formulation of I(A) as a hybrid of cationic, radical, anionic and covalent forms serves to point up the potential ability of a metal to behave as a cathode at one point and an anode at another point on its surface. Physical significance is thus attached to the fact that both chemical and catalytic reductions can be duplicated at suitable cathodes. The utility of this approach is seen in the fact that it suggests that chemisorption of a substance at one point on a surface should alter both the amount and the type of chemisorption possible at other points on the surface.[4] This provides a simple interpretation of the ability of compounds with unshared electron pairs (unsaturated compounds, N, P, O and S compounds, and ions of heavy metals[14]) to modify the activity of hydrogenation catalysts. This behavior would produce an apparent inhomogeneity of the catalyst surface; the necessity for the somewhat indefinite concept of special active centers is thereby removed.

The generally accepted mechanism (above) for the hydrogenation of olefins and aromatic hydrocarbons cannot be used to explain the reduc-

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(1) C. L. Wilson, *Trans. Electrochem. Soc.*, **75**, 353 (1939).

(2) (a) *Cf.* F. Fichter, "Organische Elektrochemie," Steinkopf, Dresden, 1942, pp. 270-288; (b) pp. 233-251.

(3) (a) *Cf.* S. Glasstone, "Textbook of Physical Chemistry," 2nd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, pp. 1201-1204; (b) p. 1017.

(4) For a refined treatment of this concept, see M. Boudart, THIS JOURNAL, **74**, 1531, 3556 (1952).

(5) *Cf.* J. N. Agar, *Ann. Repts. Chem. Soc.*, **44**, 5 (1947); J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948); J. O'M. Bockris and E. C. Potter, *J. Electrochem. Soc.*, **99**, 169 (1952).

(6) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 837 (1942).

(7) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. H. Whetstone, THIS JOURNAL, **64**, 1985 (1942).

(8) C. R. Waldeland, W. Zartman and H. Adkins, *ibid.*, **55**, 4234 (1933).

(9) Labile *cis* hydrogenation products are isomerized to *trans* products by nickel catalysts, especially at high temperatures, N. D. Zelinsky and E. I. Margolis, *Ber.*, **65**, 1613 (1932); **69**, 1710 (1936). The sometimes apparently anomalous reductions of phenols and anilines appear to result from the formation of ketones and imines as intermediates; G. Vavon and co-workers, *Bull. soc. chim.*, [4] **37**, 296 (1925); [4] **41**, 1638 (1927).

(10) *Cf.* P. Sabatier, *Ber.*, **44**, 1984 (1911).

(11) Reviewed by K. N. Campbell and B. K. Campbell, *Chem. Revs.* **31**, 77 (1942), and A. J. Birch, *Quart. Rev.*, **4**, 69 (1950).

(12) R. Willstätter, F. Seitz and E. Bumm, *Ber.*, **61**, 871 (1928).

(13) H. Burton and C. K. Ingold, *J. Chem. Soc.*, 2022 (1929).

(14) See, E. B. Maxted, in "Advances in Catalysis," Vol. III, Academic Press, In., New York, N. Y., 1951, pp. 129-177.

tion of cyclohexanones to equatorial alcohols in neutral medium and to axial (polar) alcohols in acid medium.[15] This mechanism assigns no role to solvent protons; on steric grounds, this mechanism would be expected to produce axial alcohols (see Fig. 1) in both neutral and acidic medium.

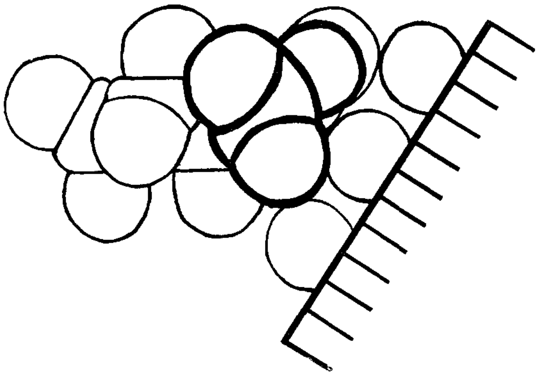

Fig. 1.—Simultaneous *cis* addition of hydrogen atoms from a metal surface to 2-methylcyclohexanone. Note that if the catalyst surface be aligned parallel to the carbon–oxygen double bonds, *cis*-2-methylcyclohexanol must result. A close-in broad-side approach to the other side of this double bond is prohibited by the puckering of the ring.

The present formulation of the "surface hydride" as I(H) suggests that ketones might be able to accept a proton from the solvent and the equivalent of a hydride ion from the catalyst, in distinct steps. The bulky metal surface would be expected to assume an equatorial conformation in the last named step. The reduction of a ketone in neutral medium would, then, produce chiefly the equatorial alcohol (see Fig. 2); reduction of the reactive protonated form of a ketone would produce chiefly the axial alcohol (see Fig. 3), in agreement with experiment.[15] As might be expected, these effects are more pronounced in the rigid steroids (Figs. 4 and 5).

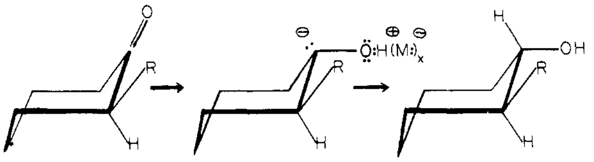

Fig. 2.—Hydrogenation of a 2-alkylcyclohexanone in neutral medium.

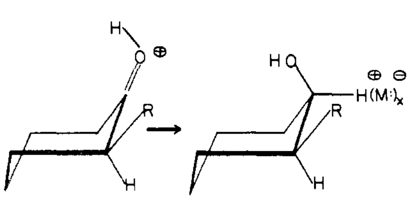

Fig. 3.—Hydrogenation of a 2-alkylcyclohexanone in acid medium.

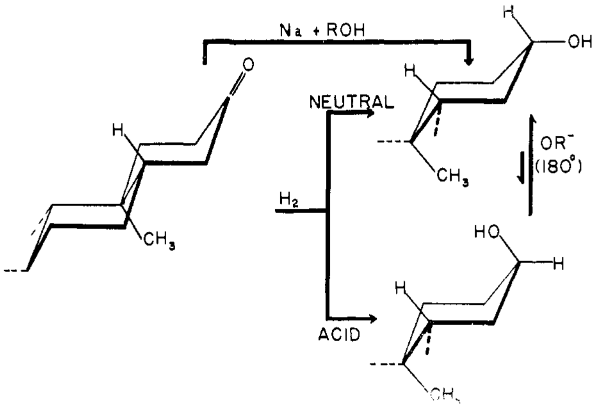

Fig. 4.—Reductions of cholestanone.

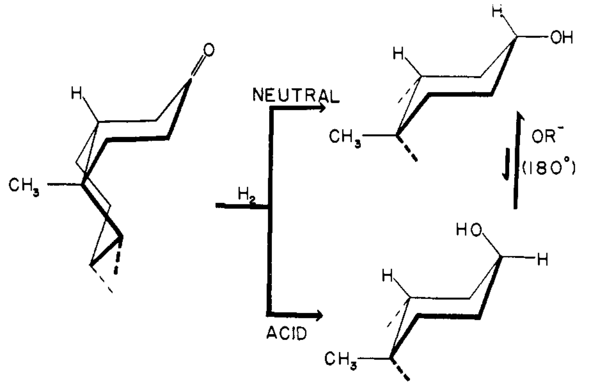

Fig. 5.—Reductions of coprostanone.

By contrast with catalytic and metal hydride reductions, reductions with active metals commonly produce bimolecular products. A number of reductions with active metals are carried out in the absence of proton donors, hydrolysis being a separate step.[11] Evidence for the direct intervention of the metal in such reductions has been presented by many workers.[11,12] Organometallics have been found as by-products in the electrolysis of ketones at cathodes of lead[16] and mercury.[17] These facts suggest the formation of an organic complex, I(R), at high overvoltage surfaces, perhaps by default of formation of I(H). Like I(H), this complex could dimerize, react with reducible organic substances or abstract a proton from the solvent. This concept permits a simple interpretation of the active metal reductions of ketones, which produce alcohols in neutral or alkaline protonic solvents, pinacols in aprotic and acidic solvents and hydrocarbons under the special conditions of the Clemmensen reduction.[18]

The chemisorption of a ketone on a metal surface could result in bonding at either the carbon or oxygen atom to produce I(R) complexes in which II, III, IV and V would be important resonance forms. Of these, II and III would be sterically

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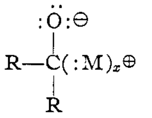
(15) A. Skita, *Ann.*, **431**, 1 (1923); A. Skita and W. Faust, *Ber.*, **64**, 2878 (1931). The configurations of important alcohols in this series have been established in many ways. See, G. Vavon, *Bull. soc. chim.*, [4] **49**, 937 (1931); L. N. Owen and co-workers, *J. Chem. Soc.*, 326 (1949), 408 (1953); H. L. Goering and C. Serres, THIS JOURNAL, **74**, 5908 (1952); D. S. Noyce and D. B. Denny, *ibid.*, **74**, 5912 (1952); S. Siegel, *ibid.*, **75**, 1317 (1953). Data on the reduction of steroidal ketones is summarized in L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 3rd Edition, 1949, pp. 98-99 and 635-643.

(16) J. Tafel, *Ber.*, **44**, 327 (1911).

(17) C. J. Haggerty, *Trans. Amer. Electrochem. Soc.*, **56**, 421 (1929).

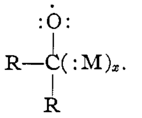
(18) This topic is considered in the following papers.

strained; IV and V would be less strained and, if derived from phenyl ketones, would be stabilized by additional resonance. The *simplest* mechanism for the formation of an alcohol in a protonic but non-acidic solvent would be one in which V abstracted a proton from the solvent to form a surface alkoxide. This picture is in accord with the fact that cyclohexanones are reduced to equatorial alcohols by active metals.[15,19]



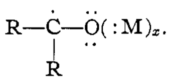
$$\mathrm{R-\underset{\displaystyle R}{\overset{\displaystyle :\ddot{O}:^{\ominus}}{C}}(:M)_x^{\oplus}}$$

II



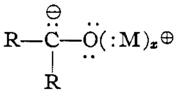
$$\mathrm{R-\underset{\displaystyle R}{\overset{\displaystyle :\dot{O}:}{C}}(:M)_x.}$$

III



$$\mathrm{R-\underset{\displaystyle R}{\dot{C}}-\ddot{O}(:M)_x.}$$

IV

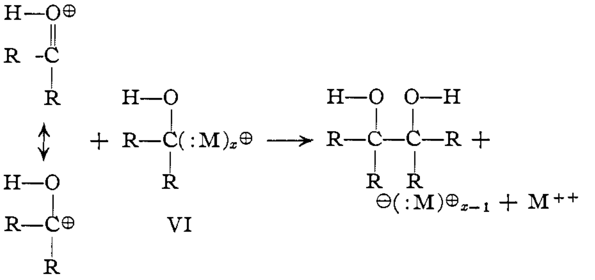


$$\mathrm{R-\underset{\displaystyle R}{\overset{\ominus}{\ddot{C}}}-\ddot{O}(:M)_x^{\oplus}}$$

V

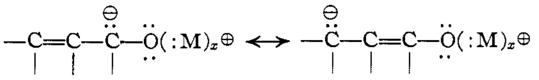
In aprotic medium a pinacol could most easily be formed by dimerization of IV or by reaction of V with a dissolved ketone. Again, as in the formation of alcohols, more complex mechanisms would be required if either II or III were to serve as intermediates. The separation from the metal surface of dianions or of ion radicals cannot at present be excluded as possible steps; such processes would lead to more complex pathways of reaction.

In acidic medium, the protonated form of the ketone would be available, in low concentration, as an intermediate highly sensitive to nucleophilic attack.[20] The *electronically* most favored mode of reaction of such an intermediate would produce the complex VI. For steric reasons, VI could not couple with itself; it might be capable of suffering electrophilic displacement at the carbonyl carbon atom by a molecule of the protonated ketone[21] (equation 1). The rapid formation of VI, rather than V, is offered as an explanation of the fact that alcohols are generally not important products in acid medium (V would surely form an alcohol under such conditions). It should be noted that phenyl ketones and sterically hindered ketones would, on the present picture, be more prone to form V than would unhindered alkyl ketones (see part III).



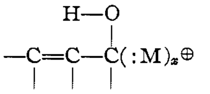
$$\left\{\begin{matrix}\mathrm{R-\underset{\displaystyle R}{\overset{\displaystyle H-O^{\oplus}}{\overset{\|}{C}}}} \\ \updownarrow \\ \mathrm{R-\underset{\displaystyle R}{\overset{\displaystyle H-O}{C^{\oplus}}}}\end{matrix}\right\} + \underset{\text{VI}}{\mathrm{R-\underset{\displaystyle R}{\overset{\displaystyle H-O}{C}}(:M)_x^{\oplus}}} \longrightarrow \mathrm{R-\underset{\displaystyle R}{\overset{\displaystyle H-O}{C}}-\underset{\displaystyle R}{\overset{\displaystyle O-H}{C}}-R} + {}^{\ominus}(:\mathrm{M})^{\oplus}_{x-1} + \mathrm{M}^{++}$$

The monomolecular and bimolecular reductions of α,β-unsaturated aldehydes and ketones[22] are described easily in terms of the mechanisms outlined above, using the resonance hybrid VII in depicting reductions in neutral and aprotic medium and the isomers VIIIa and VIIIb for reductions in acidic medium.



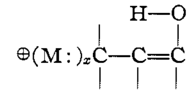
$$\mathrm{-\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{\ominus}{\ddot{C}}}-\ddot{O}(:M)_x^{\oplus}} \longleftrightarrow \mathrm{-\underset{|}{\overset{\ominus}{\ddot{C}}}-\underset{|}{C}=\underset{|}{C}-\ddot{O}(:M)_x^{\oplus}}$$

VII



$$\mathrm{-\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{\displaystyle H-O}{C}}(:M)_x^{\oplus}}$$

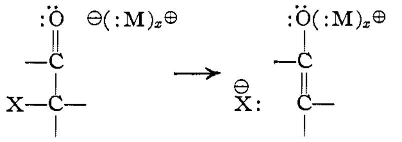
VIIIa



$$\mathrm{{}^{\oplus}(M:)_x\underset{|}{\overset{|}{C}}-\underset{|}{C}=\underset{|}{\overset{\displaystyle H-O}{C}}}$$

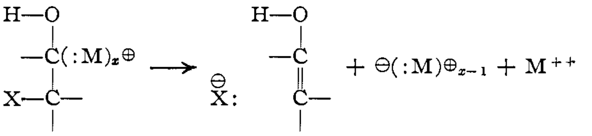
VIIIb

α-Halogen, hydroxy and amino groups generally are replaced by hydrogen in the reduction of ketones by active metals[23] (see part II). Using the present mechanisms, such processes can be pictured as concerted nucleophilic displacements (equation 2) in neutral medium and as concerted eliminations (equation 3) in acidic medium.



$$\mathrm{X-\underset{|}{C}-\overset{\displaystyle :\ddot{O}\quad {}^{\ominus}(:M)_x^{\oplus}}{\overset{\|}{C}}-} \longrightarrow \overset{\ominus}{\mathrm{X}:}\quad \mathrm{\underset{|}{C}\overset{\|}{}-\overset{\displaystyle :\ddot{O}(:M)_x^{\oplus}}{C}-} \qquad (2)$$

(2)



$$\mathrm{X-\underset{|}{C}-\overset{\displaystyle H-O}{C}(:M)_x^{\oplus}} \longrightarrow \overset{\ominus}{\mathrm{X}:}\quad \mathrm{\overset{\displaystyle H-O}{C}=\underset{|}{C}-} + {}^{\ominus}(:\mathrm{M})^{\oplus}_{x-1} + \mathrm{M}^{++} \qquad (3)$$

(3)

W. Lafayette, Indiana

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(19) See D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953), for a review.

(20) *Cf.* P. D. Bartlett, in H. Gilman, "Organic Chemistry, an Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 91–121.

(21) The protonated solvent is the other important electrophilic reagent in such a system. The electrophilicity of the proton is largely satiated by bonding with the solvent. It seems reasonable to assume that most proton transfer reactions involve *nucleophilic displacement on hydrogen*. So long as the carbonyl carbon atom of VI is tetracovalent that carbon atom is not a nucleophilic center.

(22) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, pp. 5–10. *Cf. e.g.*, R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928); J. F. J. Dippy and R. H. Lewis, *Rec. trav. chim.*, **56**, 1000 (1937); Z. C. Glacet and co-workers, *Compt. rend.*, **226**, 923 (1948), and earlier papers.

(23) *Cf.* L. S. Birnbaum and G. Powell, *J. Org. Chem.*, **4**, 139 (1939); S. Jenkins, This Journal, **54**, 1155 (1932), for references to much of the earlier literature. See also V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947); M. Stoll and coworkers, *ibid.*, **30**, 1815, 1822 (1947).