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HOMOGENEOUS CATALYTIC HYDROGENATION: A RETROSPECTIVE ACCOUNT

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Introduction

Homogeneous catalytic hydrogenation has been a subject of intense research and application during the past several decades and continues to attract widespread attention. The monograph "Homogeneous Hydrogenation" by Brian R. James, published in 1973 [1], cites nearly two thousand literature references during the preceding twenty years. It is not unlikely that the volume of literature on the subject has doubled during the intervening period.

In view of this extensive interest and activity it is remarkable that the literature prior to 1953 contains only two documented examples of the homogeneous catalytic activation of molecular hydrogen by metal complexes *. The first of these dates back to 1938 when Calvin [2,3] reported that copper(I) salts, notably copper(I) acetate in quinoline solution, catalyzed the reduction by H_2, under homogeneous and relatively mild conditions, of substrates such as copper(II) and quinone according to the rate-law of eq. 1. Since the activation of H_2 had long been identified exclusively with heterogeneous catalysts and attributed to distinctive properties of solid surfaces, it is remarkable that the significance of this discovery does not appear to have been widely appreciated when it was first reported, nor was this early work repeated or followed up, until about fifteen years later.

$$-d[H_2]/dt = k_1[H_2][Cu^I]^2 \text{ (or } k'_1[H_2][(Cu^I)_2]) \qquad (1)$$

The other early example of homogeneous activation of H_2 pertains to the hy-

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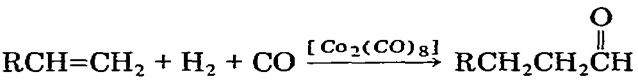
* Other reactions involving the homogeneous activation of H_2 undoubtedly had been observed but not identified at the time of observation as being homogeneous. For example, the absorption of H_2 by aqueous solutions of cobalt(II) chloride containing potassium cyanide, and hydrogenation activity connected with such systems, were reported by Iguchi as early as 1942 [4]. However, the system remained uncharacterized and the involvement of homogeneous reactions of H_2 was not identified until much later [5]. Similarly, it appears in retrospect, particularly in the light of our own studies, that *some* of the hydrogenation processes reported by Ipatieff, involving the precipitation of metals by reduction of dissolved metal salts [6], probably encompassed homogeneous reactions of H_2.

droformylation of olefins (Oxo process, eq. 2), and related hydrogenation reactions, catalyzed by cobalt carbonyl complexes. Discovered by Roelen, also in 1938 [7], this system has been and continues to be the theme of extensive studies, applications and modifications. Various observations, including the apparent insensitivity of the system to sulphur compounds which typically poison heterogeneous catalysts, led to early suggestions that the hydroformylation reaction was homogeneously catalyzed, probably through reactions between [$HCo(CO)_4$] and olefins [8—11]. However, at least in 1952 the kinetic and mechanistic aspects of this reaction were not well characterized and the homogeneous character of some of the hydrogenation reactions associated with hydroformylation continued to be disputed [12].



$$RCH{=}CH_2 + H_2 + CO \xrightarrow{[Co_2(CO)_8]} RCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H \qquad (2)$$

As elaborated below, my own association with this field, which began shortly after 1950, was quite unconnected with these earlier developments. My graduate and postdoctoral training were as a physical chemist and my earliest researches were concerned with kinetics and with the mechanistic aspects of organic reactions *. Following a stay as a postdoctoral fellow in the Department of Physical Chemistry of the University of Manchester, the exigencies of the academic marketplace led to my accepting in 1950 an appointment to the faculty of the Metallurgy Department of the University of British Columbia in Vancouver, a position that I held for six years before transferring to the Chemistry Department of the same university. The department that I joined initially was headed by the late Professor Frank A. Forward, a highly creative chemical and metallurgical engineer who was responsible for major contributions to extractive metallurgy, notably involving the utilization of redox and coordination chemistry in new approaches to the extraction of metals from ores and to the recovery of the metals from the resulting leach solutions. His offer of an appointment in his department to a chemist with no background (or apparent interest) in metallurgical science reflected an enlightened recognition of the desirability of adding a component of basic research to an academic department whose focus was primarily applied. I, in turn, found myself relatively free to pursue my own research interests in kinetics and mechanisms but at the same time, in view of my environment, it clearly seemed appropriate to redirect these interests to the study of reactions of metal ions. It was in this context that my interest and research career in inorganic chemistry had their origin. In retrospect, I consider these circumstances of my early career most fortunate since the field of inorganic kinetics and mechanisms was then still in a very underdeveloped state and the challenges and opportunities for important and exciting discoveries and contributions were enormous.

One of the initial lines of research that I undertook in this context was par-

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* It is a commentary on the state of many chemistry curricula at that time and on a situation that still has not much improved in many universities in this country, that neither as an undergraduate nor as a graduate student (both at McGill University) was I exposed to a course in inorganic chemistry.

ticularly rewarding and led, within a relatively short period, to a very active and fruitful research program encompassing many of the significant early developments relating to homogeneous catalytic hydrogenation. For the purpose of this particular article it seems appropriate to attempt to describe how this came about and to present a brief account of the initial decade of this research (spanning the period 1952 to 1962) during which the principal foundations of the field were laid.

Early studies on the homogeneous activation of H_2 by metal ions in aqueous solution

Some of my earliest independent research was concerned with the reduction by H_2 of metal salts in aqueous solution. The principal themes of this research involved kinetic and mechanistic studies but the work also had some significant technological applications. Shortly after arriving at the University of British Columbia I developed, in collaboration with Frank Forward (and in response to the discovery in Canada of large deposits of uranium ores which could not be treated effectively by existing technology), a new process for recovering uranium from pitchblende ores by oxidative extraction with aqueous carbonate solutions followed by reduction of the dissolved uranyl carbonate complex with H_2, leading to precipitation of the uranium as UO_2 according to eq. 3 [13—16].

$$[UO_2(CO_3)_3]^{4-} + H_2 \xrightarrow{Ni} UO_2 + CO_3^{2-} + 2\ HCO_3^- \qquad (3)$$

Not unexpectedly, this reaction required the addition of a hydrogenation catalyst such as metallic nickel powder, in the presence of which reduction and precipitation of UO_2 proceeded readily under relatively mild conditions (ca. 100°C, 10—50 atm H_2). A similar procedure, also involving the use of a conventional heterogeneous hydrogenation catalyst such as nickel, was found to be effective for the reduction of vanadate and precipitation of V_2O_3 from aqueous solutions according to eq. 4 [17].

$$2\ VO_3^- + 2\ H_2 \xrightarrow{Ni} V_2O_3 + 2\ OH^- + H_2O \qquad (4)$$

Our interests at this time extended also to the precipitation of metals (for example Ni which is now produced commercially by this procedure) from aqueous solution by reduction of their salts with H_2 [18]. In the case of Ni (eq. 5) and Co, this procedure did not require the addition of a catalyst since, following nucleation, the precipitated metal itself provided the catalytic surface necessary for further reduction by H_2 to proceed.

$$Ni^{II} + H_2 \rightarrow Ni + 2\ H^+ \qquad (5)$$

Among the metals that were found to undergo precipitation by such reduction of their salts in aqueous solution with H_2 under relatively mild conditions was copper. This observation surprised me since, unlike nickel and cobalt, metallic copper was not known to exhibit significant activity as a heterogeneous hydrogenation catalyst. Accordingly, it occurred to me that copper(II) might, instead, be reacting with H_2 homogeneously in solution and I proposed in 1952 to R.G. Dakers, one of my first graduate students (who joined me shortly after my arrival at U.B.C. to work toward an M.Sc. degree; our department did not yet have a Ph.D. program at the time), an investigation directed at examining this possibility.

The system that we chose to study involved the reduction by H_2 of copper(II) acetate in aqueous solution, leading to the formation of cuprous oxide according to eq. 6. The reaction was found to proceed readily under relatively mild conditions (ca. 100°C, 10 atm H_2). A careful kinetic study demonstrated unequivocally that the initial reaction of H_2 with Cu^{II} proceeded homogeneously according to the rate law of eq. 7 where $k_7 = 6 \times 10^{11}$ exp-[$-24200/RT$] M^{-1} sec^{-1}. The results thus suggested a homogeneous bimolecular rate determining reaction between H_2 and Cu^{II}. This investigation was completed in 1953 [19] and the results were first described in a communication in the Journal of Chemical Physics [20]. It was in the course of preparing this communication that I first became aware of the prior work by Calvin [1,2] on the reduction of copper(II) acetate by H_2 in quinoline solution. Shortly thereafter several further papers appeared describing the duplication and extension of Calvin's earlier studies [21—26].

$$2\ Cu(OAc)_2 + H_2 + H_2O \rightarrow Cu_2O + 4\ HOAc \tag{6}$$

$$-d[H_2] = k_7[H_2][Cu^{II}] \tag{7}$$

Our system [19,20,27], involving the first demonstration of the homogeneous activation of H_2 by a metal complex in aqueous solution, differed from Calvin's in several important respects, notably: (1) whereas Cu^I apparently was responsible for the activation of H_2 in quinoline solution and Cu^{II} was inactive (resulting in autocatalytic reduction of the latter), the opposite was the case in aqueous solution; (2) the first order kinetic dependence of the Cu^{II} concentration (i.e., eq. 7) implied a process involving the activation of H_2 at a single metal center. By contrast, the two other examples then known of homogeneous activation of H_2 both involved the interaction of H_2 with two metal centers (2 Cu^I or $Co_2(CO)_8$). The simultaneous involvement of two metal centers in the activation of H_2 (i.e., one for each of the H atoms) seemed to be a conceptually more attractive result, and one more readily reconciled with prevailing views concerning the mechanism of the heterogeneous catalytic activation of H_2 (i.e., through two-site dissociative chemisorption) on metallic surfaces. Accordingly, our unprecedented claim to have demonstrated the homogeneous activation of H_2 at a single metal center encountered a somewhat skeptical initial reception. Repeated suggestions were advanced (a) that our system might not be truly homogeneous, traces of colloidal metal being responsible for the activation of H_2, or (b) that binuclear, rather than mononuclear, complexes might be responsible for the activation of H_2. In the latter context it is of some interest that shortly thereafter we identified another system involving the catalytic activation of H_2, namely by copper(I) heptanoate in heptanoic acid where, indeed, an equilibrium between mononuclear and binuclear copper(I) complexes was identified and quantitatively characterized [28]. However, contrary to the prevailing prejudice it turned out that the catalytic activity was due exclusively to the mononuclear complex, the binuclear species being completely inactive. This experience seems worth recalling in the context of developments associated with the recent interest in "cluster catalysis" and with some of the rationales and claims that have been advanced in respect of the potential of metal cluster catalysts.

Our initial work on the activation of H_2 by copper(II) acetate in aqueous solution was followed rather quickly by several further developments in my laboratory, including (a) the demonstration that in the presence of an oxidizing agent such as chromium(VI), the activation of H_2 by Cu^{II}, while exhibiting the same rate-law (i.e., eq. 7), proceeded catalytically as a result of rapid reoxidation of Cu^{I} by the oxidant [29], (b) the demonstration that other copper(II) salts including the aquocopper(II) ion were effective in the catalytic activation of H_2 (the catalytic activity depending on the ligands) [30,31], and (c) the demonstration that a number of other metal ions and complexes including those of silver(I) [32], mercury(I) and mercury(II) [33], as well as the permanganate ion [34], reacted homogeneously with H_2 in aqueous (as well as other) solvents [35,36]. These studies were conducted by my first Ph.D. students, E. Peters, J.G. Korinek, A.H. Webster and A.J. Chalk and the results published during 1954—1959. During this period I was also joined by several postdoctoral fellows from Britain, notably P.E. Potter, J.F. Harrod and B.R. James, who extended these studies to the Group VIII metals and demonstrated the homogeneous catalytic activation of H_2 by Pd^{II} [37], Rh^{III} [38], Ru^{III} and Ru^{II} [39—43]. By 1960 the catalytic activation of H_2 by metal complexes had been identified for a large and diverse range of systems and, as elaborated below, significant progress also had been made toward a mechanistic understanding of the chemistry of these systems [44].

Mechanistic aspects: role of hydridometal complexes

The kinetics initially observed for the metal ion-catalyzed oxidation of H_2, for example eq. 1 for the Cu^{I}-catalyzed oxidation of H_2 by Cu^{II} or quinone or eq. 7 for the Cu^{II}-catalyzed oxidation of H_2 by Cr^{VI}, typically exhibited dependencies on H_2 and on the catalyst but not on the oxidizing substrate. This implied a multistep mechanism in which the rate-determining reaction between H_2 and the catalytic metal ion led to the formation of an undetected intermediate (or intermediates) which reacted rapidly with the substrate to regenerate the catalyst.

The nature of these intermediates was first revealed by our studies on the Cu^{2+}-catalyzed oxidation of H_2 by $Cr_2O_7^{2-}$ [45]. The rate-law for this reaction (eq. 8) provided convincing evidence for the mechanistic sequence of eq. 9—11, involving the heterolytic splitting of H_2 in the rate-determining step to form the hydridocopper complex CuH^+. Additional evidence for reaction 9 and for analogous reversible processes in the case of other metal ions (e.g., for Ag^+ and $RuCl_6^{3-}$ according to eq. 12 and 13, respectively) was subsequently provided by observations of H_2—D_2O exchange accompanying such reactions in D_2O solution [46,32,41]. On the basis of such evidence analogous hydridometal complexes, e.g., CuH, AgH, AgH^+ (later identified by EPR in frozen solutions [47]), $HRuCl_5^{3-}$, $HPdCl_3^{2-}$, etc., were deduced to be intermediates in the homogeneous catalytic activation of H_2 by other metal ions and complexes [44].

$$\frac{-d[H_2]}{dt} = \frac{k_9 k_{10}[H_2][Cu^{2+}]^2}{k_{-9}[H^+] + k_{10}[Cu^{2+}]} \tag{8}$$

$$Cu^{2+} + H_2 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} CuH^+ + H^+ \tag{9}$$

$$CuH^+ + Cu^{2+} \xrightarrow{k_{10}} 2\ Cu^+ + H^+ \tag{10}$$

$$2\ Cu^+ + 2/3\ Cr^{VI} \xrightarrow{\text{fast}} 2\ Cu^{2+} + 2/3\ Cr^{III} \tag{11}$$

$$Ag^+ + H_2 \rightleftharpoons AgH + H^+ \tag{12}$$

$$[RuCl_6^{3-}] + H_2 \rightleftharpoons [RuHCl_5^{3-}] + H^+ + Cl^- \tag{13}$$

When the evidence cited above first led us in 1955 to recognize the role of CuH^+ as an intermediate in Cu^{2+}-catalyzed reactions of H_2, such hydridometal complexes were virtually without precedent. The only reasonably well defined "molecular" transition metal hydrides then known were the carbonyl hydrides, i.e., $[HCo(CO)_4]$, $[H_2Fe(CO)_4]$, etc., whose structural features (including the bonding of the H atoms to the metal) still remained to be elucidated. However, at about the same time a major breakthrough that led to the opening up of an extensive new era of hydrido-transition metal chemistry occurred through the discovery and characterization of the complexes, $[HRe(C_5H_5)_2]$ [48] and [*trans*-$HPtCl(PEt_3)_2$] [49], followed by many other transition metal hydrides containing apparently stabilizing ligands such as phosphines and cyclopentadienyls [50]. The parallels between such stable hydrides and the hydridometal complex intermediates in our hydrogenation reactions were immediately apparent and, indeed, hydrido-transition metal chemistry has continued to play a major role in the subsequent evolution of homogeneous catalytic hydrogenation and related catalytic chemistry.

Our studies on metal ion-catalyzed oxidation reactions of H_2 revealed, in addition to the heterolytic path for the splitting of H_2, exemplified by eq. 9, 12 and 13, another path involving homolytic splitting by reaction of H_2 with two metal centers. Ag^+ was found to react with H_2 by both paths, the first (favored at high temperatures) depicted by eq. 12 and the second (exhibiting the third-order rate law, $-d[H_2]/dt = k_{14}[H_2][Ag^+]^2$ and favored at lower temperatures) depicted by eq. 14 [32]. A few other examples of such homolytic splitting of H_2 (e.g., by $[Co(CN)_5]^{3-}$ according to eq. 15) have subsequently been identified [51,52].

$$2\ Ag^+ + H_2 \xrightarrow{k_{14}} 2\ AgH^+ \tag{14}$$

$$2[Co^{II}(CN)_5]^{3-} + H_2 \rightarrow 2[Co^{III}H(CN)_5]^{3-} \tag{15}$$

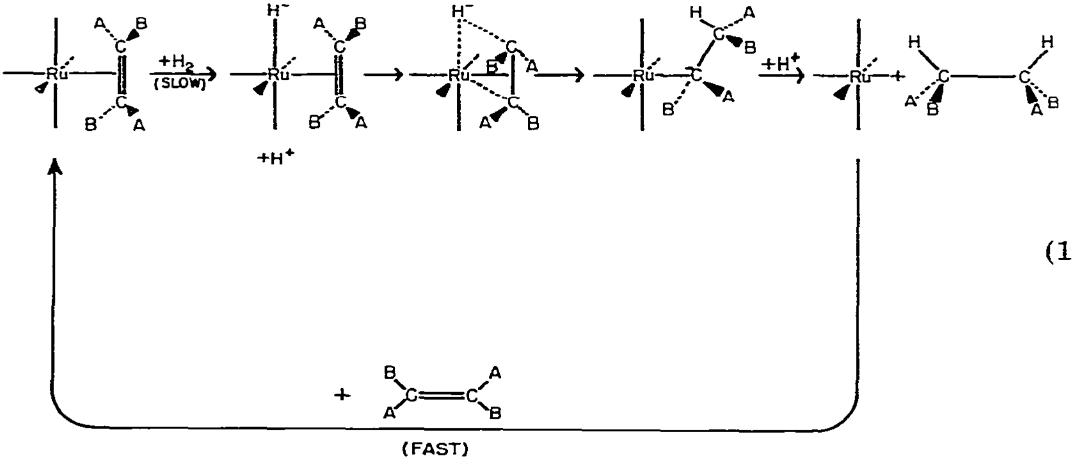
More recently, one further mode of activation of H_2, involving homolytic splitting at a single metal center (oxidative addition) has been identified [53,54]. This process, exemplified by eq. 16, is most commonly encountered for four coordinate low-spin d^8 complexes, notably of Rh^I [55,56] and Ir^I [53,57].

$$[Rh^I Cl(PPh_3)_3] + H_2 \rightarrow [Rh^{III} H_2 Cl(PPh_3)_3] \tag{16}$$

All three modes of activation of H_2 by metal complexes identified above, i.e., heterolytic splitting (or electrophilic attack), homolytic splitting (or two-center oxidative addition) and one-center oxidative addition, lead to the formation of hydridometal complexes as the initial products and such complexes are involved as intermediates in virtually all homogeneous hydrogenation reactions. These three processes are the only modes of activation of H_2 by metal complexes that have been identified to date.

Homogeneous catalytic hydrogenation of olefins and related substrates

The metal complexes on which we carried out our earliest studies (i.e., those of Cu^{II}, Cu^{I}, Ag^{I}, Hg^{II}, etc.), although capable of activating H_2, proved ineffective as catalysts for the hydrogenation of substrates such as olefins. Apparently, competition from back-reaction or oxidation of the intermediate hydrides (exemplified by eq. 9 and 10, respectively) won out in competition with transfer of hydrogen from the hydride to such relatively unreactive substrates. It occurred to me that the prospects of achieving such a transfer might be improved by effecting the activation of H_2 through mechanisms similar to those that we had already identified but with a metal complex containing a coordinated olefin. This would result in a species containing both a hydride and an olefin ligand coordinated to the same metal ion thereby enhancing the prospect of reaction between them. This approach proved fruitful and led to the first characterized examples of homogeneous catalytic hydrogenation of olefinic substrates, i.e., the hydrogenation of activated olefins such as maleic or fumaric acid by ruthenium(II) chloride in aqueous solution. A detailed examination of this reaction encompassing kinetic, isotopic tracer and stereochemical studies, led to deduction of the mechanism described by eq. 17. These studies, involving the collaboration of J.F. Harrod and B.R. James, were completed in 1961 [40,58,43].



(17)

The mechanistic scheme encompassed by eq. 17 contains most of the features that have been identified in the many other homogeneous catalytic hydrogenation reactions of olefins that have subsequently been discovered and characterized, i.e., hydridoolefin intermediates, migratory insertion of an olefin into a metal—hydride bond, etc. Identification of this reaction scheme also served to call attention to important parallels between the mechanistic aspects of homogeneous and heterogeneous catalytic hydrogenation [58].

Modelling of hydrogenase

Another challenge that confronted us during this period was that of contributing to an understanding of the nature and mode of action of the hydrogen-activating enzyme hydrogenase [59]. Only recently has this enzyme been isolated in pure form and the nature of the active site (an iron-sulfur cluster of the $[Fe_4S_4(SR)_4]^{n-}$ type) identified [60]. In 1959 [61] virtually nothing was know about the constitution of the enzyme although the involvement of iron (and possibly molybdenum) as an active component was suspected. Indications about the mode of action of the enzyme were largely indirect, based on recognition of the reactions catalyzed by it (exchange of H_2 with D_2O, oxidation of H_2 by substrates such as methyl viologen and liberation of H_2 by reduction of water) and on the response of the enzyme to various inhibitors (reversible inhibition by oxidizing agents, etc.). One important mechanistic conclusion had been deduced by Rittenberg [62,63] on the basis of studies of the H_2—D_2O exchange reaction, namely that the splitting of H_2 by the enzyme was heterolytic, i.e., analogous to the processes depicted by eq. 9, 12 and 13. This and other characteristic features of the behaviour of this enzyme system are depicted schematically in Figure 1.

Utilizing various features of the redox chemistry of ruthenium chlorides and of their reactions with H_2 we succeeded in constructing a reaction scheme, depicted in Figure 2, which successfully models virtually all of the pertinent redox, inhibition and H_2-activating features of the hydrogenase enzyme system [39,41,59(b)]. It is remarkable that after nearly 20 years, during which extensive progress has been made in our knowledge and understanding both of homogeneous catalytic hydrogenation processes and of the hydrogenase enzyme system, this remains the only successful hydrogenase "model". In this connection it is especially surprising that hydrogen-activating ability has not thus far been demonstrated for protein-free iron-sulfur clusters (i.e., hydrogenase active site analogues) nor, indeed, for any inorganic iron compounds.

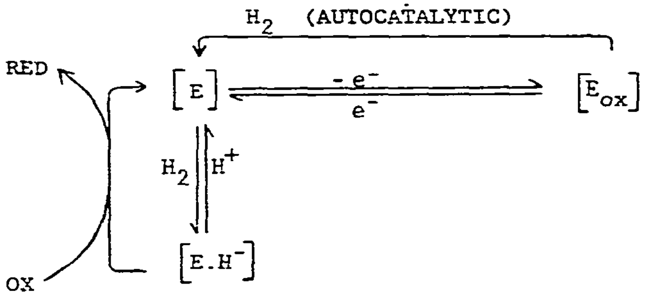


Fig. 1. Schematic representation of hydrogenase system.

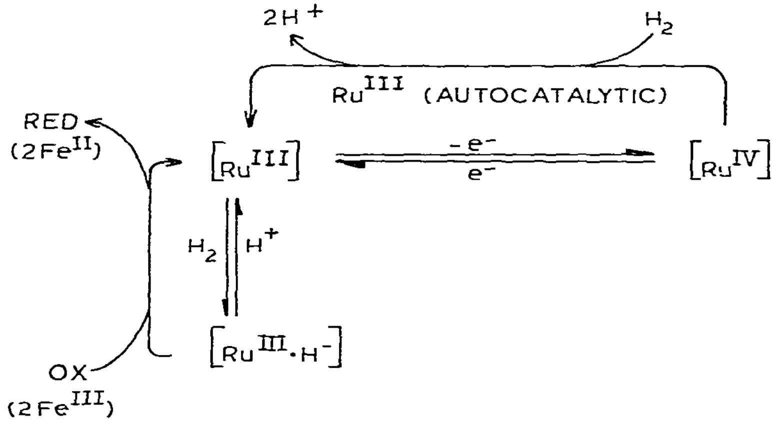


Fig. 2. $RuCl_n$ "model" for hydrogenase.

Concluding remarks

The account that I have presented of research on homogeneous catalytic hydrogenation during the period 1952 to 1962 has emphasized the work of my own laboratory at the University of British Columbia. While this is in keeping with the spirit of the article that I was invited to contribute to this volume, it also reflects the fact that during this seminal period of development of the subject, our laboratory was the major center of research in this field. Nevertheless, it would be highly inappropriate not to make at least passing reference to several other important concurrent developments and contributions. These include studies conducted by several groups on (a) cobalt carbonyl catalyzed hydroformylation and hydrogenation reactions [64] and, in particular, the important mechanistic suggestions concerning this system advanced by Heck and Breslow [65,66], (b) activation of H_2 by copper(I) acetate and other systems related to that originally discovered by Calvin [21—26], and (c) reactions of H_2 catalyzed by cobalt(II) cyanide complexes [67—72,51].

By 1962 the homogeneous activation of H_2 by metal complexes, only a few isolated examples of which had been identified prior to a few years earlier, had come to be recognized as a widespread phenomenon with significant applications to inorganic, organic and biochemical systems. A considerable degree of understanding of the mechanistic aspects of such systems also had been achieved. At about this time interest in the subject expanded very dramatically and the field began to attract a large number of other research workers.

Much of the subsequent research in this field has been directed, with conspicuous success, at extending the range of catalysts and substrates for homogeneous hydrogenation [1,73]. For the most part, however, such extensions have continued to be accommodated by the mechanistic concepts and insights already yielded by our earlier work. Perhaps the most important advances subsequent to 1962 are associated with the introduction of a much wider range of ligands, notably phosphines, into the design of homogeneous hydrogenation catalysts and catalyst precursors, thereby greatly extending the accessible range of catalyst stability, catalytic activity and catalyst types. Striking illustrations of these extensions are provided by the important developments associated with rhodium phosphine complexes as hydrogenation [55,73] and hydroformylation [74] catalysts. An important consequence of the incorporation of phosphine and related ligands into hydrogenation catalysts also has been the opportunity thereby afforded for the systematic variation and "fine tuning" of steric and electronic factors to regulate catalytic activity and selectivity. Perhaps the most significant achievement along these lines, and surely the most impressive accomplishment in catalytic selectivity to date, is the recent use of rhodium complex catalysts containing chiral phosphine ligands to effect the asymmetric hydrogenation of prochiral olefins with essentially quantitative optical yields [75].

Following my move to the University of Chicago in 1962, my own research interests have largely shifted to other areas of coordination and organometallic chemistry with an increasing emphasis on bioinorganic themes. At the same time I have continued to maintain a modest research effort in the area of homogeneous catalytic hydrogenation. Our own most recent research on this subject has continued to focus on relatively simple systems with a view to identifying new mechanistic features (for example, free radical mechanisms of catalytic hydrogenation [76—79]) and to elucidating the mechanisms of catalytic hydrogenation in greater detail and at the most fundamental level [80]. The latter task is a challenging one because of the complexity of such catalytic systems (which often encompass several consecutive and simultaneous steps involving a large number of species) and because of the difficulty of intercepting and characterizing highly labile and short-lived catalytic intermediates in solution. We have been gratified by the progress that has been achieved along these lines but much remains to be accomplished. As an illustration of this theme, attention is directed to the widespread role that hydridoalkylmetal intermediates (generally postulated to form by insertion of an olefin into one of the metal—hydrogen bonds of a dihydride complex) have played in the mechanisms in terms of which most homogeneous catalytic hydrogenation reactions of olefins have been interpreted for many years. Yet it is only during the past year that we have succeeded in actually intercepting and characterizing the first example of such an intermediate [81].

Other significant current challenges include the extension of some of the chemistry associated with the catalytic activation of H_2 and with homogeneous catalytic hydrogenation to the activation of other inert molecules, notably saturated hydrocarbons, and to the hydrogenation of highly unreactive substrates such as carbon monoxide and dinitrogen. Only very modest beginnings have been made in these directions and the present state of these tasks is reminiscent of the earliest stages of development of homogeneous catalytic hydrogenation which I have described in this account. I have every expectation that the challenges and potentials of these fields will be realized with comparable success.

Acknowledgments

I wish to express my appreciation, for their contributions to the research that I have described, particularly to the following students and postdoctoral fellows who were associated with me at the University of British Columbia during the period 1952—1962; A.J. Chalk, S. Ciccone, R.G. Dakers, A.C. Harkness, J.F. Harrod, B.R. James, J.G. Korinek, E.R. Macgregor, J.B. Milne, E. Peters, P.E. Potter, and A.H. Webster. Grateful acknowledgment also is made for support of our research on homogeneous catalytic hydrogenation over the years by the National Research Council of Canada, the National Science Foundation, the National Institutes of Health and the donors of the Petroleum Research Fund administered by the American Chemical Society.

References

1 B.R. James, Homogeneous Hydrogenation, John Wiley and Sons, New York, 1973.

2 M. Calvin, Trans. Faraday Soc., 34 (1938) 1181.

3 M. Calvin, J. Amer. Chem. Soc., 61 (1939) 2230.

4 M. Iguchi, J. Chem. Soc. Japan, 63 (1942) 634, 1752.

5 For a review, see Ref. 1, Chapt. 10.

6 For example, V.N. Ipatieff and W. Werchowsky, Chem. Ber., 42 (1909). 1954, 2078; V.N. Ipatieff and F.N. Ipatieff and F.N. Ipatieff, Jr., Chem. Ber., 60 (1927) 1982; 62 (1929) 386.

7 O. Roelen, U.S. Patent 2327066 (1943).

8 H. Adkins and G. Krsek, J. Amer. Chem. Soc., 70 (1948) 383; 71 (1949) 3051.

9 G. Natta and R. Ercoli, Chimica e Industria (Milan), 34 (1952) 503.

10 I. Wender, H.W. Sternberg and M. Orchin, J. Amer. Chem. Soc., 75 (1953) 3041.

11 M. Orchin, L. Kirch and J. Goldfarb, J. Amer. Chem. Soc., 78 (1956) 5450.

12 C.L. Aldridge and H.B. Jonassen, J. Amer. Chem. Soc., 85 (1963) 886.

13 F.A. Forward and J. Halpern, Trans. Canad. Inst. Min. Met., 56 (1953) 344.

14 J. Halpern and E. Peters, Trans. Canad. Inst. Min. Met., 56 (1953) 350.

15 F.A. Forward and J. Halpern, Trans. Canad. Inst. Min. Met., 56 (1953) 354.

16 F.A. Forward and J. Halpern, J. Metals, 6 (1954) 1408; U.S. Patent 2727806 (1955).

17 R.N. O'Brien, F.A. Forward and J. Halpern, Trans. Canad. Inst. Min. Met., 56 (1953) 359.

18 For a review see: F.A. Forward and J. Halpern, Trans. Inst. Min. Met. (London) 66 (1957) 190; Zhurnal Prikladnoi Khimii, 30 (1957) 3.

19 R.G. Dakers, The Kinetics of the Reactions between Cupric Acetate and Molecular Hydrogen in Aqueous Solution, M.Sc. Thesis, The University of British Columbia, Vancouver, 1953.

20 J. Halpern and R.G. Dakers, J. Chem. Phys., 22 (1954) 1272.

21 S. Weller and G.A. Mills, J. Amer. Chem. Soc., 75 (1953) 769.

22 L.W. Wright and S. Weller, J. Amer. Chem. Soc., 76 (1954) 3345.

23 L. Wright, S. Weller and G.A. Mills, J. Phys. Chem., 59 (1955) 1060.

24 W.K. Wilmarth and M.K. Barsh, J. Amer. Chem. Soc., 75 (1953) 2237.

25 M. Calvin and W.K. Wilmarth, J. Amer. Chem. Soc., 78 (1956) 1301.

26 W.K. Wilmarth and M.K. Barsh, J. Amer. Chem. Soc., 78 (1956) 1305.

27 R.G. Dakers und J. Halpern, Canad. J. Chem., 32 (1954) 969.

28 A.J. Chalk and J. Halpern, J. Amer. Chem. Soc., 81 (1959) 5846, 5849.

29 E. Peters and J. Halpern, Canad. J. Chem., 33 (1955) 356.

30 E. Peters and J. Halpern, J. Phys. Chem., 59 (1955) 793.

31 E. Peters and J. Halpern, Canad. J. Chem., 34 (1956) 554.

32 A.H. Webster and J. Halpern, J. Phys. Chem., 60 (1956) 280; 61 (1957) 1239.

33 G.J. Korinek and J. Halpern, Research, 7 (1954) 561; J. Phys. Chem., 60 (1956) 285; Canad. J. Chem., 34 (1956) 1372.

34 A.H. Webster and J. Halpern, Trans. Faraday Soc., 53 (1967) 51.

35 A.J. Chalk, J. Halpern and A.C. Harkness, J. Amer. Chem. Soc., 81 (1959) 5854.

36 J.B. Milne and J. Halpern, Proc. Second Intern. Cong. Catalysis, Ed. Technip, Paris (1961), p. 445.

37 J. Halpern, J.F. Harrod and P.E. Potter, Canad. J. Chem., 37 (1959) 1446.

38 J.F. Harrod and J. Halpern, Canad. J. Chem., 37 (1959) 1933.

39 J.F. Harrod, S. Ciccone and J. Halpern, Canad. J. Chem., 39 (1961) 1372.

40 J. Halpern, J.F. Harrod and B.R. James, J. Amer. Chem. Soc., 83 (1961) 753.

41 J. Halpern and B.R. James, Canad. J. Chem., 44 (1966) 671.

42 J. Halpern, B.R. James and A.L.W. Kemp, J. Amer. Chem. Soc., 88 (1966) 5142.

43 J. Halpern, J.F. Harrod and B.R. James, J. Amer. Chem. Soc., 88 (1966) 5150.

44 For reviews of this period of our research see: J. Halpern, Quarterly Revs. Chem. Soc. (London), 10 (1956) 473; Advan. Catalysis, 9 (1957) 302; J. Phys. Chem., 63 (1959) 398; Advan. Catalysis, 11 (1959) 301.

45 J. Halpern, E.R. Macgregor and E. Peters, J. Phys. Chem., 60 (1956) 1455.
46 H.E.A. von Hahn and E. Peters, J. Phys. Chem., 75 (1971) 571.
47 R.S. Eachus and M.C.R. Symons, J. Chem. Soc. (A), (1970) 1336.
48 (a) J. Birmingham and G. Wilkinson, J. Amer. Chem. Soc., 77 (1955) 3421; (b) M.L.H. Green, L. Pratt and G. Wilkinson, J. Chem. Soc., (1958) 3916.
49 J. Chatt, L.A. Duncanson and B.L. Shaw, Proc. Chem. Soc., (1957) 343.
50 See, for example: H.D. Kaesz and R.B. Saillant, Chem. Revs., 72 (1972) 231.
51 N.K. King and M.E. Winfield, J. Amer. Chem. Soc., 83 (1961) 3366.
52 J. Halpern and M. Pribanic, Inorg. Chem., 9 (1970) 2616.
53 L. Vaska, Acta. Chem. Res., 1 (1968) 186.
54 J. Halpern, Accts. Chem. Res., 3 (1970) 386 and references therein.
55 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc., (1966) 1712.
56 J. Halpern and C.S. Wong, J. Chem. Soc. Chem. Commun., (1973) 629.
57 L. Vaska and J.W. Diluzio, J. Amer. Chem. Soc., 84 (1972) 679.
58 J. Halpern, Proc. Third Intern. Cong. Catalysis, Amsterdam, 1964, North Holland Publishing Co., Amsterdam, 1965, p. 146.
59 For recent reviews see (a) L.E. Mortenson and J.S. Chen, in J.B. Nielands (Ed.), Microbial Iron Metabolism, Academic Press, New York, 1974, Chapt. 10; (b) R.H. Holm in A.W. Addison, W.R. Cullen, D. Dolphin and B.R. James (Eds.), Biological Aspects of Inorganic Chemistry, John Wiley and Sons, New York, 1977, p. 71.
60 W.O. Gillum, L.E. Mortenson, J.S. Chen and R.H. Holm, J. Amer. Chem. Soc., 97 (1975) 463.
61 J. Halpern, Advan. Catalysis, 11 (1959) 301 and references cited therein.
62 (a) A.I. Krasna and D. Rittenberg, J. Amer. Chem. Soc., 76 (1954) 3015; (b) D. Rittenberg and A.I. Krasna, Disc. Faraday Soc., 20 (1955) 185.
63 D. Rittenberg, Proc. Intern. Symp. Enzyme Chem., Tokyo and Kyoto, 2 (1957) 256.
64 For example, Refs. 9—11.
65 R.F. Heck and D.S. Breslow, Proc. Second Intern. Cong. Catalysis, Paris, 1960, Ed. Technip, Paris (1961), p. 671.
66 D.S. Breslow and R.F. Heck, Chem. Ind. (London), (1960) 467.
67 M.E. Winfield, Revs. Pure Appl. Chem. (Australia), 5 (1955) 217.
68 J. Bayston, N.K. King and M.E. Winfield, Advan. Catalysis, 9 (1957) 312.
69 N.K. King and M.E. Winfield, J. Amer. Chem. Soc., 80 (1958) 2060.
70 G.A. Mills, S. Weller and A. Wheeler, J. Phys. Chem., 63 (1959) 403.
71 B. de Vries, J. Catalysis, 1 (1962) 489.
72 J. Kwiatek, I.L. Mador and J.K. Seyler, J. Amer. Chem. Soc., 84 (1962) 304.
73 B.R. James. Advan. Organometal. Chem., 17 (1979) 319 and references cited therein.
74 P. Pino, F. Piacenti and M. Bianchi, In I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. 2, John Wiley and Sons, New York, 1977, p. 136.
75 For reviews see: (a) W.S. Knowles, M.J. Sabacky and B.D. Vineyard, Adv. Chem. Ser., 132 (1974) 132; (b) H.B. Kagan, Pure Appl. Chem., 43 (1975) 401.
76 L.Y. Wong and J. Halpern, J. Amer. Chem. Soc., 90 (1968) 6665.
77 H.M. Feder and J. Halpern, J. Amer. Chem. Soc., 97 (1975) 7186.
78 R.L. Sweany and J. Halpern, J. Amer. Chem. Soc., 99 (1977) 8335.
79 J. Halpern, Pure Appl. Chem., 51 (1979) 2171.
80 J. Halpern, Trans. Amer. Cryst. Assoc., 14 (1978) 59.
81 A.S.C. Chan and J. Halpern, J. Amer. Chem. Soc., 102 (1980) 838.