Pure & Appl. Chem., Vol. 60, No. 8, pp. 1285–1290, 1988.
Printed in Great Britain.

Mechanisms of homogeneous stoichiometric, catalytic and photocatalytic dihydrogen formation using thiocomplexes

D. Katakis

Inorganic Chemistry Laboratory, Department of Chemistry,
University of Athens, Athens 106 80, Greece

Abstract - In neutral aqueous solutions (pH 7.5-8.5), with cysteine as a ligand and vanadium (II) or chromium (II) as reductants two electrons are transferred to the solvent and there is formation of dihydrogen. The role of cysteine is essentially catalytic. It is postulated that the reaction proceeds via a dissociative proton oxidative addition rate determining step. Estimated thermodynamics for this and subsequent steps are favorable. Electron transfer to the solvent may be prevented by paths which are competitive to the formation of the hydride. Two systems are described, in which the electrons end up on the thioligand: one involving reductive scission of a carbon-sulfur bond and desulfurization, the other reductive scission of a sulfur-sulfur bond, proceeding by parallel one- and two-electron paths. Dihydrogen formation in acid solutions using metal ions of low valence is relatively slow. The reasons are kinetic rather than thermodynamic, and are related to positive-positive repulsions in the critical hydride formation step. If, however, the conditions allow negative charge accumulation on the metal ion (e.g. via an excess of a negatively charged ligand) the reaction is accelerated. This is the case in the formation of dihydrogen from chromium (II) in concentrated HCl, with the couple $Mo_2Cl_8^{4-}/Mo_2(\mu\text{-}H)(\mu\text{-}Cl)_2Cl_6^{3-}$ acting catalytically. Catalytic dihydrogen formation also takes place using dithiolenes. The mechanisms investigated include the transfer of the electrons from the free radical of N,N'-dimethyl-4,4'-dipyridine ($MV^{\overset{+}{\cdot}}$) to water.

INTRODUCTION

The first mechanistic observations on the formation of "iflammable air", as Pristley called dihydrogen, are perhaps those referring to "nascent hydrogen", i.e. to hydrogen at the moments of its birth. "Nascent hydrogen" was found to be more reactive than molecular hydrogen itself and early observers even noticed that the reactivity depends on the origin.

These observations led to the conclusion that the species responsible for the enhanced activity were not always the same, and the hypothesis that "nascent hydrogen" was atomic, was soon abandoned.

At the time, even the concept of the mechanism had not yet been formulated, and a persuasive alternative to the atomic hydrogen hypothesis could not be offered.

The specificity of the reactive intermediates in the path towards dihydrogen formation is, of course, also related to the overvoltage in the electrolytic preparation.

Early observations, however, refer to heterogeneous systems. Reports on more convenient for mechanistic deductions homogeneous aqueous systems appeared much later. One such system, based on cyanonickel (I)

$$Ni_2(CN)_6^{4-} + 2CN^- + 2H_2O \rightarrow 2Ni(CN)_4^{2-} + 2OH^- + H_2$$

was studied by Llopis and Sanchez (ref. 1), by Vlček (ref. 2), and later by Bingham and Burnett (ref. 3). Another system based on polyamine ligands was reported by Taube and co-workers (ref. 4), and Shilov and co-workers (ref. 5) and Schrauzer and Palmer (ref. 6) reported still another homogeneous system based on pyrochatechol. More recently, several other systems were studied and they will be reviewed here. It is noted in this connection that there is an enormous amount of work on homogeneous hydrogenation reactions often in non aqueous solutions, where dihydrogen evolution is competitive to its activation. There are also many cases of dehydrogenations of organic molecules. Here we will not deal with such cases. We will deal with the homogeneous formation of H_2 from water, using thiocomplexes.

Generally speaking, dihydrogen can be formed from atoms, but this requires high activation and becomes important only under energy rich conditions, e.g. in Radiation Chemistry and UV Photochemistry.

A second general path to dihydrogen is through hydride formation. In fact, the early observations on "nascent hydrogen" already indicate that this path is by no means rare.

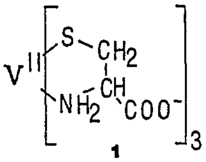
The homogeneous systems to be described belong in this second category and are either stoichiometric or catalytic. They can also be photocatalytic, but with photons of relatively low energy.

DISSOCIATIVE PROTON OXIDATIVE ADDITION

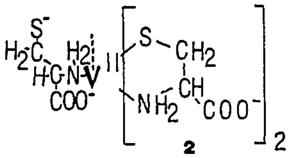
It is well known that in ordinary acid-base reactions the proton jumps from one site to another with no activation other than what might be required for diffusion. It is perhaps less well known that oxidative proton reactions like that represented by eq. (1).

$$M^n + H^+ \rightarrow M^{n+2} - H \qquad (1)$$

may be quite slow indeed, requiring considerable reorganization. An example is provided (ref. 7) by the proton oxidative addition to 1.



1



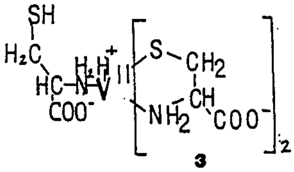
2

overall charge on 1 and 2 : -4

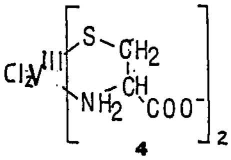
In the pH range between 7.5 and 8.5 this addition is independent of hydrogen ion concentration, which is consistent with a partial ring opening rate determining step (ref. 8) yielding 2. The activation for this process is 54 kJ/mole, resulting from a combination of the energy needed for breaking the V-S bond and the energy gained by the protonation of the sulfur. In non-complexed cysteine, protons are removed either from $-NH_3^+$ or -SH at pH 8.3 to 8.8 .

With Cr(II) instead of V(II) the activation energy (at pH 9.3) is only ca. 21 kJ/mole. The overall reaction is diffusion controlled (ref. 9).

The rate determining step is followed by fast proton addition to 2 yielding 3 or the corresponding Cr(II) species (eq. 2). Data for constructing a Born-Haber cycle for this reaction are not available. Nevertheless, an acceptable



3



4

overall charge
-2 on 3
-3 on 4

$$2(aq)+H_3O^+(aq) \rightarrow 3(aq)+H_2O \qquad (2)$$

estimate can be obtained (ignoring entropy contributions) using the following data: 430 kJ/mole for the enthalpy of hydration of H_3O^+, 694 kJ/mole for the proton affinity of water (ref. 10), and 42 kJ/mole for the enthalpy of vaporization of water. We also need the difference in the hydration energies of 2 and 3, which we assume to be approximately equal to the hydration energy of a singly charged cation (ca. 330 kJ/mole). For the proton affinity of **2** we assume a value of 840 kJ/mole, close to the value determined for neutral organometallic complexes (ref. 11), which is not very sensitive to the nature of the metal ion and the ligand. For anionic species the values are much higher (ref. 12) but it is safer to use lower values because the negative charge on **2** is spread out over the molecule. Even with this conservative choice of proton affinity, however, it is estimated that reaction (2) is indeed thermodynamically favored.

On the other hand our results indicate that there is no activation energy either.

Similar arguments can be advanced for reaction (3):

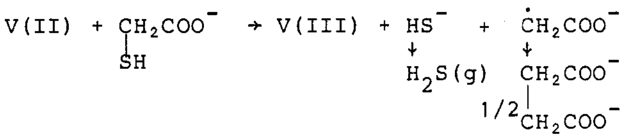
$$\mathbf{2}(aq)+H_2O \rightarrow \mathbf{3}(aq)+OH^-(aq) \qquad (3)$$

With V(II) the opening of the ring in **2** is irreversible. The ring eventually breaks up completely and the final product in the presence of Cl^- is **4**.

COMPETING PATHS TO HYDRIDE FORMATION

In the intermediate **2** there is enough negative charge accumulation on the metal to facilitate proton addition. Effective in this respect are mainly the negative charges from the sulfur atoms. The charges on the carboxylic groups are expected to have little effect, if any, being away from the center of events. This is why cysteamine, which is similar to cysteine but without the carboxylic groups exhibits a similar behavior.

There is of course some delocalization. The critical conditions must be created on the metal, but cysteine is not an innocent ligand. The spectra indicate (ref. 7)) that there is some metal-to-ligand back donation, presumably to the σ antibonding orbital of the RS^- fragment. In fact, with other sulfur ligands this delocalization may lead to a breaking down of the ligand itself. The electron then is not transferred to the solvent through hydride formation but it stops on the ligand. This happens, for example, in the case of mercaptoacetic acid (ref. 13), where it is the C-S bond that breaks (eq. 4) and in the case of cystine



$$\begin{array}{lllllllll} V(II) & + & \underset{\displaystyle SH}{\underset{|}{CH_2COO^-}} & \rightarrow & V(III) & + & HS^- & + & \dot{C}H_2COO^- \\ &&&&&& \downarrow && \downarrow \\ &&&&&& H_2S(g) && 1/2\begin{matrix}CH_2COO^- \\ | \\ CH_2COO^-\end{matrix} \end{array} \qquad (4)$$

(ref. 9) where it is the S-S bond that breaks by two (one- and two-electron) parallel paths (eqs. 5 and 6).

$$2V(II)+RSSR \xrightarrow{H_2O} 2V(III)+2RSH \qquad (5)$$

$$V(II)+RSSR \xrightarrow{H_2O} V(IV)+2RSH \qquad (6)$$

COMPARISON OF DIHYDROGEN FORMATION IN ACID AND NEUTRAL SOLUTIONS

Dihydrogen evolution from strongly acidic aqueous solutions of low-valent metal ions like V^{2+}, Cr^{2+}, and Eu^{2+} is usually slow, sometimes even difficult to detect - in spite of the fact that the concentration of hydrogen ion is many orders of magnitude higher compared to neutral solutions.

The reason is not thermodynamic. There is enough driving force in either case. The reason is rather kinetic. If the first, rate determining step in the mechanism, namely the formation of the hydride, is dissociative and independent of hydrogen ion concentration, it is really immaterial what the concentration of this ion really is. In addition, there is an important electrostatic factor: in acid the proton must be added to a positive ion overcoming repulsion. As has been already mentioned, in solutions around neutral there is negative charge accumulation to offset this repulsion.

Low-valent metal ions give dihydrogen at relatively slow rates even at HCl concentrations as high as 12M. However, the reaction is considerably accelerated (ref. 14) in the presence of binuclear complexes with metal-metal multiple bonds (**5**, Cycle 1, Fig. 1). These complexes form hydrides (**6**, Cycle 1), which then react with the reducing metal ion.

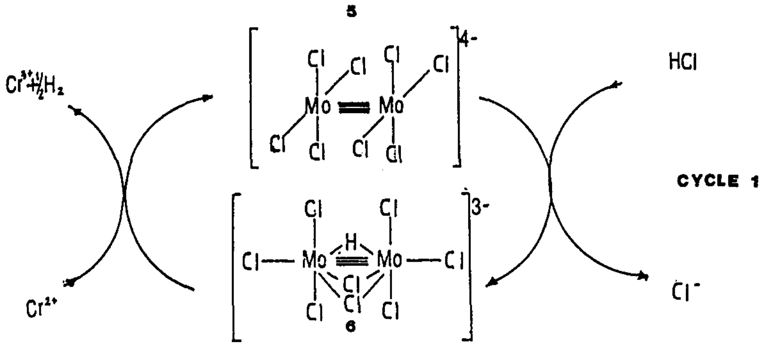


Fig. 1 The binuclear molybdenum complexes 5 and 6 accelerate the evolution of H_2 from Cr(II) in concentrated HCl solutions.

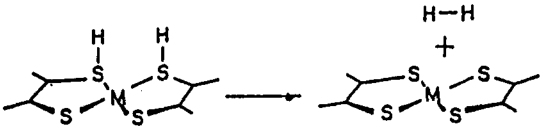
In this case, the formation of the hydride is associative, but still slow compared to acid-base proton transfer. The proton is added to the multiple bond and the rate is first order in $[H^+]$. Nevertheless, the requirement for accumulation on the metal core of negative charge still holds. The experiments were done with high HCl concentrations, not just high hydrogen ion concentrations, but also high chloride concentrations and it is interesting that the rate constant in 6M HCl, 6M PTSH (the non-complexing paratoluolosulphonic acid) is $2.5\times10^{-4}s^{-1}$, i.e. considerably smaller than the value in 12M HCl (1.9×10^{-4} s^{-1}). The difference has been attributed to axial coordination of Cl^- - more in 12M HCl - which causes a weakening of the metal-metal bond and a simultaneous increase of the effective negative charge on the multiple bond and of the proton nucleophilicity.

OTHER HYDROGEN PRODUCING SYSTEMS

The steps suceeding hydride formation are best studied in systems where this formation is not rate determining, e.g. starting from a relatively stable hydride. Unfortunately, there are no kinetic studies, at least with thioligands, on the transformation of the hydride to dihydrogen.

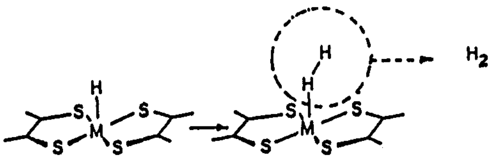
Theoretically, Alvarez and Hoffmann (ref. 15) considered the following two mechanisms:

(1) A concerted elimination of H_2 from an 1,1'-S atom diprotonated complex:



which for d^8 complexes was found to be thermally forbidden, but allowed photochemically, and also allowed for less than eight d electrons.

(2) A proton attack on a hydrido complex, followed by H_2 elimination:



The photochemical formation of H_2 which is quoted in ref. 15 as experimental evidence was shown later to be complicated by solvent photolysis and photo chemical destruction of the dithiolene (ref. 16). However, there are other, more stable dithiolenes such as the square planar 7, M=Ni, R_1=Ph, R_2=(2-Cl)Ph, z=-1, n=2{(bis(2-chlorodithiobenzyl)nickel)}, which can indeed act as photosensitizer and also as catalyst in the photochemical H_2 formation (ref. 17). With complexes of the general formula 7 dihydrogen is also formed electrochemically (ref. 18, M=Co,Rh, $R_1=R_2$=CN, n=2, z=-1).

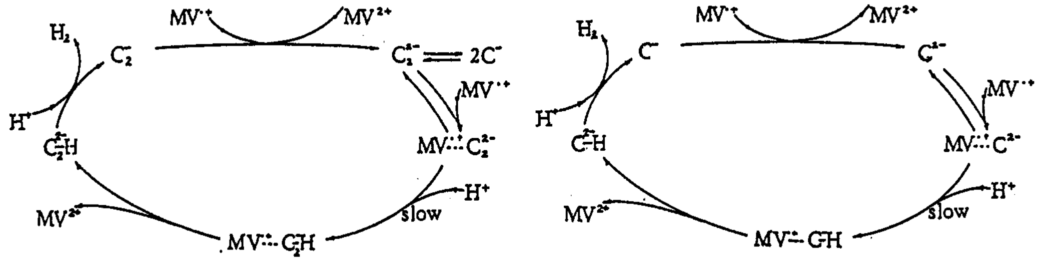
In electron transfer from the methylviologene free radical ion (N,N'-dimethyl-4,4'-dipyridine) to water with the monoanion of bis(2-chlorodithiobenzyl)nickel as the catalyst (ref. 19) the rate is second order in the concentration of the

$$2MV^{\cdot +} + 2H^{+} \rightarrow 2MV^{2+} + H_2 \qquad (7)$$

catalyst (m=2) and depends linearly on the concentration of $MV^{\cdot +}$ and the water

$$\text{Rate} = k[\text{cat}]^{m}[MV^{\cdot +}][H_2O] \qquad (8)$$

content of the acetone-water mixed solvent. This behavior can be explained by postulating proton addition as the rate determining step, as in Cycle 2, (Fig. 2) involving a partial ring opening by M-S bond scission, similar to that postulated for V(II)-cysteine.

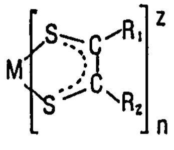


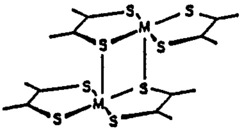
CYCLE 2 CYCLE 3

Fig. 2 The anions of the dimer of bis(2-chlorodithiobenzyl)nickel and of the monomeric tris(4-methoxydithiobenzyl)tungsten catalyze the formation of H_2 in acetone-water solutions of $MV^{\cdot +}$. In the absence of catalysts $MV^{\cdot +}$ does not give H_2. It rather decomposes by a completely different and much slower path.

The monoanion of 7 is a free radical, so the hypothesis that it dimerizes seems very plausible. Moreover, considering the dithiolene ligands as dianionic (ref. 20), the monoanion of 7 is formally a d^7 nickel complex and such complexes are known to form M-S dimers, 8 (ref. 21). For M=Ni the Ni-S distance in 8 is ca. 3.5 Å.

7





8

The formation of the ion pair $MV^{\cdot +}...C_2^{2-}$ is postulated in order to explain the dependence of the rate on $[MV^{\cdot +}]$. Both $MV^{\cdot +}$ and MV^{2+} are known (ref. 22) to form with anionic dithiolenes solid state structures with alternating planar chains.

More supporting evidence that the dissociative process is indeed a common one is obtained with the prismatic tungsten complex 7, M=W, R_1=Ph, R_2=(4-CH_3O)Ph, z=-1, n=3 {tris(4-methoxydithiobenzyl)tungsten}, which also catalyses the formation of dihydrogen from the methylviologene free radical in acetone-water mixtures. Here the reaction is first order in the catalyst (m=1 in eq. 8), and the rate depends on the water content of the solvent rather than the concentration of the protons. The observations are again readily explained with a cycle (Cycle 3, Fig. 2), which is similar to Cycle 2 but without dimerization. The monomer itself has enough electron storing capacity to be an effective catalyst. Here again rate determining is the opening of the ring.

All hydrogen producing complexes discussed in this paper are anionic. However, it is not the overall negative charge (ref. 23) or neutrality (ref. 24) that is important in our case. It is rather the effective charge on the metal center. Schrauzer and Rabinowitz (ref. 25) calculated the charge distribution of 7, z=0,-1,-2, $R_1=R_2$=H and found that the negative charge on the nickel increase progressively from -0.07 to -0.29 to -0.59, as the overall negative charge changes from zero to minus two. In the same series the charge on sulfur changes from +0.105 to -0.03 to -0.17. Thus, local conditions become increasingly more favorable as we go from the neutral complex to the mono- and di-anion, while the probability for electrophilic attack on sulfur that may lead to ring destruction also increases. It is noted, however, that at least with this particular complex, the electrostatic factor favors proton oxidative addition on the metal.

CONCLUDING REMARKS

An alternative title for this paper would be "A Novel Mechanism for Proton Transfer: Dissociative Proton Oxidative Addition". The dissociative character of most of the proton addition mechanisms described is their most interesting and unexpected aspect. It is also interesting that compared to ordinary acid-base proton transfer, proton oxidative addition, either dissociative or associative, is relatively slow, requiring considerable reorganization.

Other highlights are that this proton addition leads to stoichiometric or catalytic electron transfer to the solvent (water) and formation of dihydrogen, in competition to electron transfer to the ligands.

Proton addition is favored by accumulation of negative charge on the metal, but under these conditions there is also negative charge accumulation on the sulfur atoms, which favors electrophilic attack and dissociation. In fact sulfur seems to be quite special, presumably because the M-S bond relatively weak and becomes even weaker by electrophilic attack.

Acknowledgements

The work was done in collaboration with my colleagues Dr. E. Vrachnou-Astra, Dr. J. Konstantatos, and Prof. C. Mertis. I thank them for giving me the opportunity to review it. It is also a pleasure to acknowledge the contributions of Dr. E. Hontzopoulos, Dr. G. Kalatzis, Dr. M. Kravaritou, Dr. A. Shehadeh, and Ms C. Mitsopoulou.

REFERENCES

1. J. Llopis and A. Sanchez Robles, Anales de Quim., 51B, 661 (1955).
2. A.A. Vlček, Coll.Czech.Chem.Comm., 22, 948 (1957).
3. D. Bingham and M.G. Burnett, J.Chem.Soc. (A), 1970, 2165.
4. K.D. Kopple, G.F. Svatos, and H. Taube, Nature, 189, 393 (1961).
5. L.A. Nikonova, S.A. Isaeva, N.I. Perskowa, and A.E. Shilov, J.Mol.Catal., 1, 367 (1975).
6. G.N. Schrauzer and M.L. Palmer, J.Am.Chem.Soc., 103, 2659 (1981).
7. (a) G. Kalatzis, J. Konstantatos, E. Vrachnou-Astra, and D. Katakis, J.Am.Chem.Soc., 105, 2897 (1983). (b) J. Konstantatos, G. Kalatzis, E. Vrachnou-Astra, and D. Katakis, J.Chem.Soc., Dalton, Trans., 1985,2461.
8. Originally (ref. 7b), it was suggested that it is the metal-nitrogen rather than the metal-sulfur bond that breaks.
9. Unpublished results.
10. P.A. Giguère, J.Chem.Educ., 56, 571 (1979).
11. J.L. Beauchamp, A.E. Stevens, and R.R. Corderman, Pure & Appl. Chem. 51, 967 (1979).
12. T. Ziegler, Organometallics, 4, 675 (1985).
13. J. Konstantatos, G. Kalatzis, E. Vrachnou-Astra, and D. Katakis, Inorg. Chem., 22, 1924 (1983).
14. C. Mertis, M. Kravaritou, A. Shehadeh, and D. Katakis, Polyhedron, in press.
15. S. Alvarez and R. Hoffmann, An.Quim.B. 82, 52 (1986).
16. (a) R. Henning, W. Schlamann, and H. Kisch, Angew.Chem.Int.Ed.Engl., 19, 645 (1980). (b) Battaglia, R. Henning, B. Dinh-Ngoc, W. Schlamann, and H. Kisch, J.Mol.Catal., 1983, 239. (c) J. Bücheler, N. Zeng and H. Kisch, Angew. Chem. Inter. Ed. Engl., 21, 783 (1982). (d) A. Fernandez and H. Kisch. Chem. Ber., 117, 3102 (1984). (e) N. Zeng, J. Bücheler, and H. Kisch, J.Am.Chem.Soc., 107, 1459 (1985).
17. E. Hontzopoulos, E. Vrachnou-Astra, J. Konstantatos and D. Katakis, J. Photochem. 30, 117 (1985).
18. A. Vlček and A.A. Vlček, Inorg.Chim.Acta, 41, 123 (1980).
19. E. Hontzopoulos, J. Konstantatos, E. Vrachnou-Astra, and D. Katakis, J.Mol.Catal., 31, 327 (1985).
20. S. Alvarez, R. Vicente, and R. Hoffmann, J.Am.Chem.Soc., 107, 6253 (1985).
21. (a) C.J. Fritchie, Acta Cryst., 20, 107, 1966. (b) A. Kobayashi and Y. Sasaki, Bull.Chem.Soc.Japan, 50, 2650 (1977).
22. H. Kisch, A. Fernandez, Y. Wakatsuki, and H. Yamazaki, Z. Naturforsch. 40b, 292 (1985).
23. R.A. Grey, G.P. Pez, and A. Walle, J.Am.Chem.Soc., 103, 7536 (1981).
24. J. Halpern, Pure & Appl. Chem., 59, 173 (1987).
25. G.N. Schrauzer and H.N. Rabinowitz, J.Amer.Chem.Soc., 90, 4297 (1968).