HOMOGENEOUS REACTIONS OF MOLECULAR HYDROGEN IN SOLUTION

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MOLECULAR hydrogen (H_2) is a relatively unreactive substance. Its homogeneous reactions, both in the gas phase and in solution, are normally characterised by large activation barriers which reflect its high dissociation energy (*ca.* 103 kcal./mole) and the strong repulsion forces associated with its closed-shell electronic configuration.

The great majority of the known catalysts which lower the activation energies of hydrogenation reactions are solids. Common examples are the transition metals including Ni, Co, Pt, and Pd and certain metallic oxides such as CuO, Cr_2O_3, ZnO, and their mixtures. Despite their widespread application and the fact that their action has been widely studied, the detailed mechanism by which such catalysts function is still not fully understood. Theories have been advanced which relate the activities of hydrogenation catalysts to their lattice spacing [1, 2] and to their electronic properties [2, 3] but for the most part such theories still await critical confirmation. The limited progress which has been made in this field, particularly at the level of quantitative theory, reflects in large measure the complexity of these catalyst systems and the inherent difficulties associated with the study of heterogeneous reactions.

In view of this, recent demonstrations that some substances, notably the salts of certain metals, possess the property of activating molecular hydrogen homogeneously in solution and thus functioning effectively as homogeneous hydrogenation catalysts, have evoked considerable interest. Because the understanding of properties of molecules and ions in solution is generally in a more advanced state than that of solids, it might be expected that the study of such systems will lead to a more detailed knowledge of the nature of the catalytic process than has been provided thus far by the study of heterogeneous catalysts.

To date, more than fifteen systems have been discovered and studied in which H_2 is activated catalytically and undergoes homogeneous reaction in solution. The principal ones, together with the available kinetic data about each, are listed in Table 1. In discussing these systems, it is convenient to divide them into two categories, the first of which includes the reactions which proceed in organic solvents, and the second, reactions in aqueous solution.

[1] Beeck, *Rev. Mod. Physics*, 1945, **17**, 61.
[2] Trapnell, *Quart. Rev.*, 1954, **8**, 404.
[3] (a) Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 118; (b) Dowden, *Research*, 1948, **1**, 239; *J.*, 1950, 242.

TABLE 1. *Summary of homogeneous hydrogenation reactions*

Catalytic species	Solvent	Reaction studied	Temp. range	Kinetics for $- d[H_2]/dt$	$\Delta H\ddagger$ (kcal.)	$\Delta S\ddagger$ (e.u.)	Refs.
CuOAc	Quinoline	Reduction of Cu^{II} or quinone; para-H_2 conversion	25—117°	$k[H_2][Cu^I]^2$	13—16	(− 20)	5, 6, 7
CuOAc	Pyridine	$Cu^{II} \rightarrow Cu^I$	100	$k[H_2][Cu^I]$			9
AgOAc	Pyridine	$Ag^I \rightarrow Ag^0$	25—78	$k[H_2][Ag^I]$	12—14	(− 25)	9, 10
$Co_2(CO)_8$	Benzene, ether, etc.	Hydroformylation, hydrogenation, etc.	90—200				11, 12
Ethylene-platinous chloride	Toluene, acetone	$C_2H_4 + H_2 \rightarrow C_2H_6$	< 0				13
$Cu(OAc)_2$	Aqueous HOAc	$Cu^{II} \rightarrow Cu^I$ or $Cr_2O_7^= \rightarrow Cr^{+++}$	80—140	$k[H_2][Cu^{II}]$	24	− 7	15, 16
Cu^{++a}	Aqueous $HClO_4$	$Cr_2O_7^= \rightarrow Cr^{+++}$ etc.	80—140	$k[H_2][Cu^{++}]$	26	− 10	17
Ag^+	Aqueous $HClO_4$	$Cr_2O_7^= \rightarrow Cr^{+++}$	30—70	$k[H_2][Ag^+]^2$	15	− 22	21
Hg^{++}	Aqueous $HClO_4$	$Hg^{+++} \rightarrow Hg^{++}$	65—100	$k[H_2][Hg^{++}]$	18	− 12	23
Hg_2^{++}	Aqueous $HClO_4$	$Hg_2^{+++} \rightarrow Hg^0$	65—100	$k[H_2][Hg_2^{++}]$	20	− 10	23
MnO_4^-	Aqueous $HClO_4$	$MnO_4^- \rightarrow MnO_2$	30—70	$k[H_2][MnO_4^-]$	14	− 17	25
$Ag^+ + MnO_4^-$	Aqueous $HClO_4$	$MnO_4^- \rightarrow MnO_2$	30—60	$k[H_2][Ag^+][MnO_4^-]$	9	− 26	25
$Co(CN)_2$	Water	H_2 absorption	25	$k[H_2][Co^{II}]^2$	23	(− 7)	27, 28
OH^-	Water	para-H_2 conversion or D_2 exchange	80—110	$k[H_2][OH^-]$			34
NH_2^-	Ammonia	para-H_2 conversion or D_2 exchange	− 50	$k[H_2][NH_2^-]$			35

^{a} Kinetics given are for low $HClO_4$ concentration (0—0·025M).

Reactions in organic solvents

Cuprous Salts.—The first clear-cut demonstration that H_2 can be activated homogeneously in solution is due to Calvin.[4] In 1938 he showed that quinoline solutions of cupric acetate and cupric–salicylaldehyde complex could be reduced homogeneously by H_2 at temperatures of about 100°, the reaction proceeding in an autocatalytic manner as shown in Fig. 1.   The
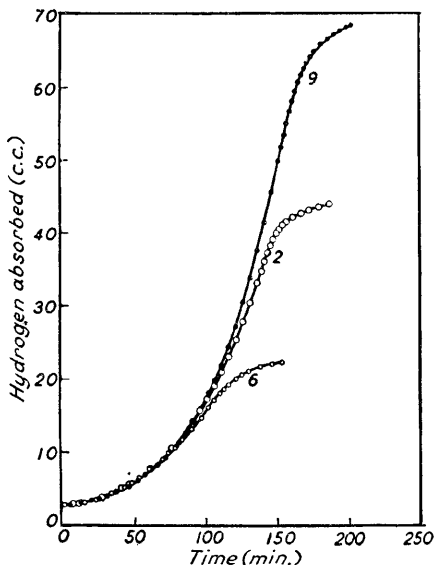

FIG. 1

Hydrogenation of cupric–salicylaldehyde complex in quinoline at 105° ; 396 *mm.* H_2.
No. 2, 2 *millimoles* Cu^{II} *salt ;   No.* 6, 1 *millimole ;   No.* 9, 3 *millimoles.*

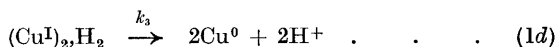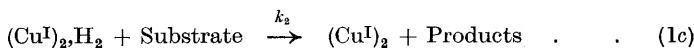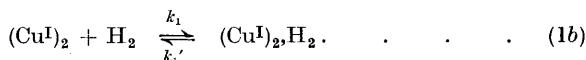(Reproduced, by permission, from Calvin, *Trans. Faraday Soc.*, 1938, **34**, 1181.)

breaks in the H_2 absorption curves correspond approximately to the stoicheiometric requirements for the complete reduction of Cu^{II} to Cu^{I}. The slower subsequent absorption of H_2 reflects the reduction of Cu^{I} to metallic Cu which was observed to separate out on prolonged standing.

Calvin showed that the rate of reaction of H_2 depends only on the amount of Cu^{II} reduced, and concluded that the cuprous salt which is produced in the reaction is the catalytic species responsible for activating H_2.   Confirmation of this was provided by the demonstration that other substrates, such as p-benzoquinone, could also be hydrogenated homogeneously in the presence of dissolved cuprous acetate.   The rate of H_2 absorption depends only on the concentration of the cuprous salt, and is the same whether the substrate being reduced is a cupric salt or benzoquinone.   When para-H_2 was used to reduce cupric acetate, conversion was observed only after the reduction of Cu^{II} to Cu^{I} had proceeded to completion.[4]   This conversion

[4] Calvin, *Trans. Faraday Soc.*, 1938, **34**, 1181.

has recently been shown to occur through the same activated intermediate as the hydrogenation reactions.[5]

Originally the rate of activation of H_2 in this system was reported to be of first order in the concentration of dissolved H_2 and between first and second order in the total concentration of the cuprous salt, with an apparent activation energy of about 15 kcal./mole.[6] To account for these kinetics it was suggested that a dimer of the cuprous salt (probably in the form of a quinoline-containing complex) is the effective catalyst in this system, and that the reaction proceeds by the following mechanism:

$$2Cu^I \rightleftharpoons (Cu^I)_2 \qquad \qquad (1a)$$

$$(Cu^I)_2 + H_2 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} (Cu^I)_2,H_2 \qquad \qquad (1b)$$

$$(Cu^I)_2,H_2 + Substrate \overset{k_2}{\rightarrow} (Cu^I)_2 + Products \qquad (1c)$$

$$(Cu^I)_2,H_2 \overset{k_3}{\rightarrow} 2Cu^0 + 2H^+ \qquad \qquad (1d)$$

The observed kinetics require that $k_2 > k_1' > k_1 > k_3$.

However, in the light of recent work which suggests that when due account is taken of the inhibitory effects of impurities such as water and acetic acid, the rate of reaction appears to be exactly of second order in the total cuprous salt concentration, Calvin and Wilmarth [7] have questioned the evidence supporting the dimeric configuration of the catalyst species and have proposed, in place of reactions (1a) and (1b), a single termolecular rate-determining step, i.e.,

$$2Cu^I + H_2 \underset{k_1}{\overset{k_1}{\rightleftharpoons}} 2Cu^I,H \qquad \qquad (2)$$
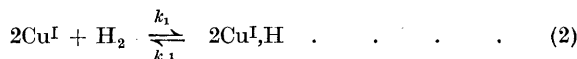
followed by reactions similar to (1c) and (1d). The earlier conclusion that the activated complex involves two Cu atoms still applies.

The catalytic activity varies with the nature of the cuprous salt.[7] In quinoline solution, the activities of the acetate, salicylaldehyde, and 4-hydroxysalicylaldehyde are similar, and somewhat higher than those of the stearate and benzoate. On the other hand, the cuprous nitrobenzoates and nitrosalicylaldehydes as well as the cuprous complexes of certain Schiff's bases are inactive. These results have been interpreted to indicate that the catalytic activity increases with the basicity of the anion of the cuprous salt. However, it seems difficult to extend this generalisation to all the salts and in the case of the substituted Schiff's bases, at least, steric effects also appear to be involved.[7] Wright and Weller [8] have shown that ethylene-diamine and ethylenediaminetetra-acetic acid inhibit the catalytic activity of cuprous acetate in the reduction of both p-benzoquinone and cupric acetate. However, it is not clear whether these reagents interfere with the

[5] Wilmarth and Barsh, J. Amer. Chem. Soc., 1953, **75**, 2237.

[6] (a) Calvin, ibid., 1939, **61**, 2230; (b) Weller and Mills, ibid., 1953, **75**, 769.

[7] Calvin and Wilmarth, ibid., 1956, **78**, 1301; Wilmarth and Barsh, ibid., p. 1305.

[8] Wright and Weller, ibid., 1954, **76**, 3345.

initial activation of H_2 by cuprous acetate or with a subsequent step in the reduction of the substrate.

The catalytic activity of a given cuprous salt is also affected by altering the solvent. Weller and Mills [6b] examined the hydrogenation of cupric acetate and of quinone, in the presence of cuprous acetate, in various solvents, chiefly organic bases. They found that pyridine, quinoline, and a number of their alkylated derivatives, as well as dodecylamine, support the catalytic activity of cuprous acetate. On the other hand, no catalytic activity was observed in a number of other solvents including dimethylaniline, dipentylamine, diethanolamine, 8-hydroxyquinoline, indole, formamide, and dibutyl phthalate. The results provide some indications that the catalytic activity increases with the base strength of the solvent and that it is also influenced by the solvent's chelating tendency and by steric considerations ; however, the data are insufficient to permit any quantitative correlations on these points.

It has recently been shown [9] that, in contrast to those in quinoline, the kinetics of activation of H_2 by cuprous acetate in pyridine and dodecylamine are of first order in the catalyst concentration. Coupled with molecular weight determinations which show cuprous acetate to be substantially unassociated in pyridine, these results suggest that the effective catalyst is a monomeric cuprous species. The reason for the apparent differences in kinetics and mechanism between quinoline and these solvents is not wholly clear. They have been attributed [9] to steric considerations involving differences in the sizes of the solvent molecules. However, related studies on some of the other systems to be described in this Review make it appear likely that differences in the basicity of the solvents are also involved.

Silver Salts.—The reduction of silver acetate by H_2 in pyridine solution, to metallic silver, has been reported to proceed at temperatures as low as $25°$.[9, 10] The rate is apparently homogeneously determined and is of first order in the concentration of dissolved H_2 and of silver acetate. The mechanism which has been advanced to explain these kinetics involves heterolytic dissociation of the H_2 molecule in the rate-determining step, *i.e.*,

$$AgOAc + H_2 \longrightarrow AgH + HOAc \text{ (rate-determining)} \quad . \quad (3a)$$
$$AgH + AgOAc \longrightarrow 2Ag + HOAc \text{ (fast)} . \quad . \quad . \quad . \quad (3b)$$

The formation of AgH as an intermediate seems plausible and energetically consistent with the observed activation energy of about 14 kcal./mole.

The reactivity varies with the nature of the silver salt.[10] Thus the fluoride reacts about five times as rapidly as the sulphate and acetate, while solutions of silver trifluoroacetate, chloride, perchlorate, and nitrate are inactive. These marked variations in reactivity have been ascribed to differences in basicity of the anions, and the correlation thus obtained seems to provide support for the postulated rate-determining step (3a). The hydrogenation of silver acetate has also been observed in dodecylamine solution.[9]

[9] Wright, Weller, and Mills, *J. Phys. Chem.*, 1955, **59**, 1060.
[10] Wilmarth and Kapauan, *J. Amer. Chem. Soc.*, 1956, **78**, 1308.

Dicobalt Octacarbonyl.—Early work on the " Oxo " or hydroformylation reaction in which an olefin reacts with H_2 and CO in the presence of a cobalt metal catalyst, *i.e.*,

$$CHR{:}CH_2 + H_2 + CO \longrightarrow CH_2R{\cdot}CH_2{\cdot}CHO \qquad . \qquad . \qquad (4)$$

led Adkins and Krsek [11] to suggest that this reaction is homogeneously catalysed. Several other workers [12] have since confirmed this conclusion, which is supported by a variety of evidence including the insensitiveness of the reaction to the presence of carbon monoxide and of sulphur compounds which normally poison metallic cobalt catalysts.

The conditions usually employed in the " Oxo " synthesis involve temperatures between 90° and 200° and partial pressures of 50—200 atm. each of carbon monoxide and hydrogen, in the presence of metallic cobalt. In addition to hydroformylation, a number of other reactions involving H_2, such as hydrogenation of olefins and reduction of alcohols, have been observed to take place under these conditions.[12] These reactions are all homogeneously catalysed and proceed in a variety of organic solvents including ether, benzene, ethanol, methyl*cyclo*hexane, etc. Apparently the solvent does not play as important a rôle or exert as specific an influence in these systems as in the case of the cuprous and silver salt-catalysed reactions described earlier.

It is probable that under the conditions of these reactions, metallic cobalt reacts with carbon monoxide, forming a number of carbonyls including dicobalt octacarbonyl, *i.e.*,

$$2Co + 8CO \; \rightleftharpoons \; Co_2(CO)_8 \; . \qquad . \qquad . \qquad . \qquad (5)$$
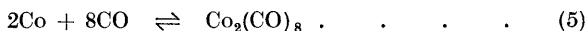
Evidence has been obtained to indicate that $Co_2(CO)_8$ [or the related cobalt hydrocarbonyl, $HCo(CO)_4$] is the effective catalyst in these reactions and that it functions homogeneously.[11, 12] In particular, it has been demonstrated that molecular H_2 is split readily by the reaction

$$Co_2(CO)_8 + H_2 \; \rightleftharpoons \; 2HCo(CO)_4 \qquad . \qquad . \qquad . \qquad (6)$$
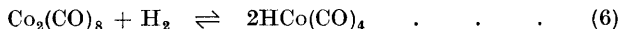
Thus it is likely that $Co_2(CO)_8$ is responsible for the catalytic activation of H_2 and that the final products arise from the reaction of $HCo(CO)_4$ with the substrate. More work must be done before the detailed kinetics and mechanisms of these reactions are understood.

It seems not unlikely that the catalytic activity of $Co_2(CO)_8$ (*i.e.*, the ease with which it splits H_2 homogeneously) is related to the presence of an unoccupied low-lying, delocalised electronic orbital, into which electrons from the H_2 molecule can be transferred readily.
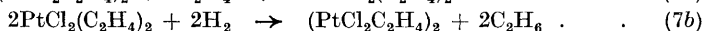
Ethyleneplatinous Chloride.—The hydrogenation of ethyleneplatinous chloride in toluene or acetone solution has recently been investigated by Flynn and Hulburt.[13] It was shown that at temperatures below − 10°, in the presence of an excess of ethylene, ethane is formed without the

[11] Adkins and Krsek, *J. Amer. Chem. Soc.*, 1948, **70**, 383 ; 1949, **71**, 3051.

[12] Wender, Levine, and Orchin, *ibid.*, 1950, **72**, 4375 ; Wender, Orchin, and Storch, *ibid.*, p. 4842 ; Orchin, *Adv. Catalysis*, 1953, **5**, 385 ; Wender, Sternberg, and Orchin, *J. Amer. Chem. Soc.*, 1953, **75**, 3041.

[13] Flynn and Hulburt, *ibid.*, 1954, **76**, 3393, 3396.

accompanying deposition of metallic platinum. The following mechanism has been proposed for this reaction :

$$(PtCl_2C_2H_4)_2 + 2C_2H_4 \;\rightleftharpoons\; 2PtCl_2(C_2H_4)_2 \qquad . \qquad . \qquad (7a)$$

$$2PtCl_2(C_2H_4)_2 + 2H_2 \;\rightarrow\; (PtCl_2C_2H_4)_2 + 2C_2H_6 . \qquad . \qquad (7b)$$

Although the evidence for a homogeneous reaction of H_2 in this system appears fairly convincing, the detailed kinetics and the nature of the catalyst species remain to be established.

Reactions in Aqueous Solution

Cupric Salts.—In 1909, Ipatieff and Werchowsky [14] observed that aqueous solutions of cupric acetate were reduced by hydrogen under relatively mild conditions to cuprous oxide. This reaction has since been demonstrated [15] to occur homogeneously in solution, the kinetics being of first order in the concentrations of cupric acetate and of hydrogen as shown
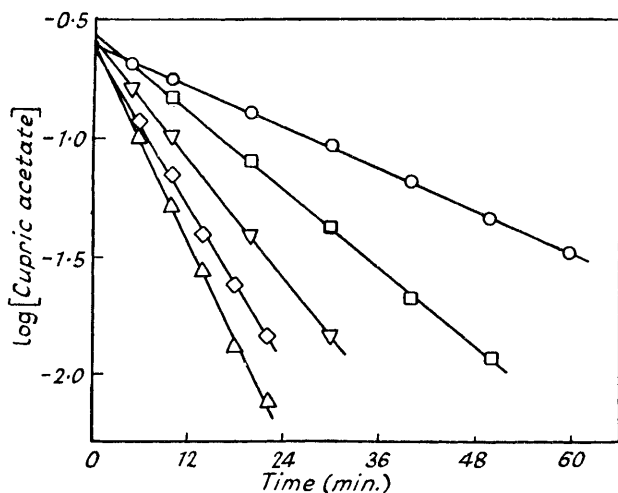
FIG. 2

First-order rate plots for the reduction of cupric acetate in aqueous solution at various H_2 partial pressures ; 130°.

Partial pressures (atm.) of hydrogen : ○ 6·8, □ 13·6, ▽ 20·4, ◇ 27·2, △ 34·0.

(From Dakers and Halpern, *Canad. J. Chem.*, 1954, **32**, 969.)

in Fig. 2. Hydrogen is apparently activated by interaction with a molecule of cupric acetate. This behaviour is in marked contrast to that reported earlier for the reduction of cupric salts in quinoline solution (Fig. 1), where only the cuprous species exhibits catalytic activity. In aqueous solution cupric acetate was also shown [16] to catalyse the homogeneous hydrogenation of other dissolved substrates such as $Cr_2O_7^{=}$.

[14] Ipatieff and Werchowsky, *Ber.*, 1909, **42**, 2078.

[15] Halpern and Dakers, *J. Chem. Phys.*, 1954, **22**, 1272 ; Dakers and Halpern, *Canad. J. Chem.*, 1954, **32**, 969.

[16] Peters and Halpern, *ibid.*, 1955, **33**, 356.

It was subsequently found that this catalytic activity is not confined to cupric acetate but is exhibited by a variety of other cupric salts and complexes.   Typical of the results obtained are the rate plots in Fig. 3
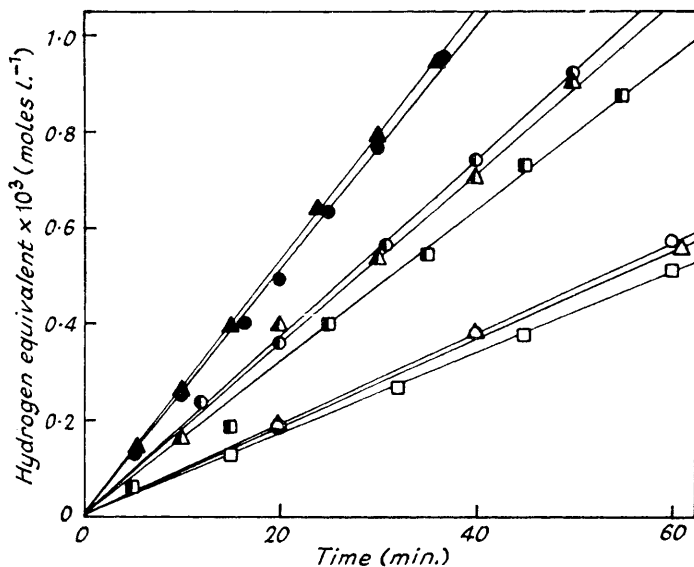

FIG. 3

Effect of cupric perchlorate on the rate of reaction of hydrogen with various reducible substrates ;   110° ;   20 atm. H_2.

Oxidant				$Cu(ClO_4)_2$ (moles/l.)		
				0·10	0·20	0·30
$Cr_2O_7^=$.	.	.	.	○	◑	●
IO_3^- .	.	.	.	△	▲	▲
Ce^{4+} .	.	.	.	□	◨	◼

(From Peters and Halpern, *J. Phys. Chem.*, 1955, **59**, 793.)

showing the reduction of various substrates by H_2 in the presence of different amounts of cupric perchlorate.[17]   The rate at which H_2 reacts is seen to be essentially independent of the nature or concentration of the substrate. Providing that the hydrogen-ion concentration did not exceed about 0·1M, the kinetics for the various cupric salts were all of the form

$$- d[H_2] / dt = k[H_2][Cu^{II}]   .   .   .   .   (8)$$

The apparent catalytic activity, reflected in the magnitude of k, varied considerably from one cupric salt to another,[18] as shown in Table 2.

The perchlorate system was subjected to a detailed kinetic study.[17, 19] In this medium no complexing of Cu^{++} is believed to occur and hence the simple Cu^{++} ion constitutes the catalytic species.   At low $HClO_4$ concentrations (< 0.1M-H^+) the kinetics are essentially expressed by equation (8),

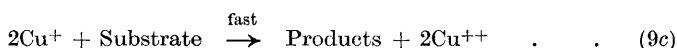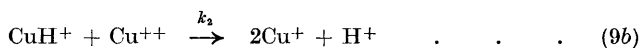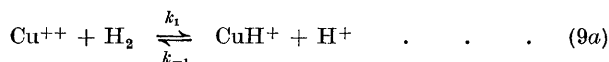[17] Peters and Halpern, *J. Phys. Chem.*, 1955, **59**, 793.
[18] *Idem, Canad. J. Chem.*, 1956, **34**, 554.
[19] Halpern, Macgregor, and Peters, *J. Phys. Chem.*, 1956, **60**, in the press.

TABLE 2. *Effect of complexing agents on the catalytic activity of Cu^{++} in aqueous solution*

Medium	Probable cupric species	Relative catalytic activity	Medium	Probable cupric species	Relative catalytic activity
Butyrate . .	$Cu(O \cdot COPr^i)_2$	150	Chloride . . .	$CuCl_4^=$	2·5
Propionate .	$Cu(O \cdot COEt)_2$	150	Perchlorate . .	Cu^{++}	1
Acetate . .	$Cu(OAc)_2$	120	Glycine . . .	$CuGl_2$	< 0·5
Sulphate . .	$CuSO_4$	6·5	Ethylenediamine	$Cu(EDA)_2^{++}$	0·1

and are consistent with the assumption of a simple bimolecular rate-determining step involving one H_2 molecule and one Cu^{++} ion.[17] However, with increasing hydrogen-ion concentration a marked decrease in rate was noted, as well as a tendency for the kinetic dependence on the Cu^{++} concentration to shift from first toward second order. The following mechanism has been proposed [19] to account for these results :

$$Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+ \qquad . \qquad . \qquad . \quad (9a)$$

$$CuH^+ + Cu^{++} \overset{k_2}{\longrightarrow} 2Cu^+ + H^+ \qquad . \qquad . \qquad . \quad (9b)$$

$$2Cu^+ + Substrate \overset{fast}{\longrightarrow} Products + 2Cu^{++} \qquad . \qquad . \quad (9c)$$

Application of the steady-state treatment to this mechanism leads to the following rate expression :

$$- \frac{d[H_2]}{dt} = \frac{k_1[H_2][Cu^{++}]^2}{[Cu^{++}] + (k_{-1}/k_2)[H^+]} \qquad . \qquad . \qquad . \quad (10)$$

This equation becomes equivalent to (8) at low hydrogen-ion concentrations but correctly predicts a decrease in rate, as well as a shift from first- to second-order dependence on $[Cu^{++}]$, as the hydrogen-ion concentration increases. At 110° the value of k_{-1}/k_2 was found [19] to be 0·25.

These considerations demonstrate how a change in the apparent order of the reaction with respect to the catalyst concentration may occur, without a real change in the mechanism of the H_2 activation process. This is of interest in view of the fact that a number of other catalyst systems (including cuprous acetate which has already been described) have been reported in which a shift from first to second order in the catalyst concentration is observed on changing the solvent.

The suggestion that CuH^+ is the activated intermediate in the Cu^{++}-catalysed reactions has been further supported [20] on the grounds that (*a*) a similar intermediate has been postulated to explain the activation of H_2 by cuprous salts in quinoline (*i.e.*, equation 2), (*b*) energetically the formation of CuH^+ seems more plausible than that of the other intermediates such as Cu^+ and Cu^0, which might be considered to result from the reaction of an H_2 molecule with a Cu^{++} ion, and (*c*) the promoting influence of various

[20] Halpern, *Adv. Catalysis*, 1956, **9**, in the press.

anions on the catalytic activity of Cu^{++}, which increases in the same order as their basicity (Table 2), is readily explained by assigning to them the rôle of stabilising the H^+ ion which is released in the initial step.

A schematic potential-energy diagram, depicting the activation process according to the above mechanism, and showing the formation of CuH^+ as an intermediate,[20] is presented in Fig. 4 (a). The activated complex corresponds to the crossing point of the two curves and probably has a configuration resembling $[Cu^{++}\cdots H^-\cdots H^+]$. The mechanism entails, essentially, the displacement of a hydride ion from H_2 to the catalyst, both electrons involved in the Cu^+–H bond being contributed by the H_2 molecule. In this light, the rôle of Cu^{++} may be considered to be essentially that of
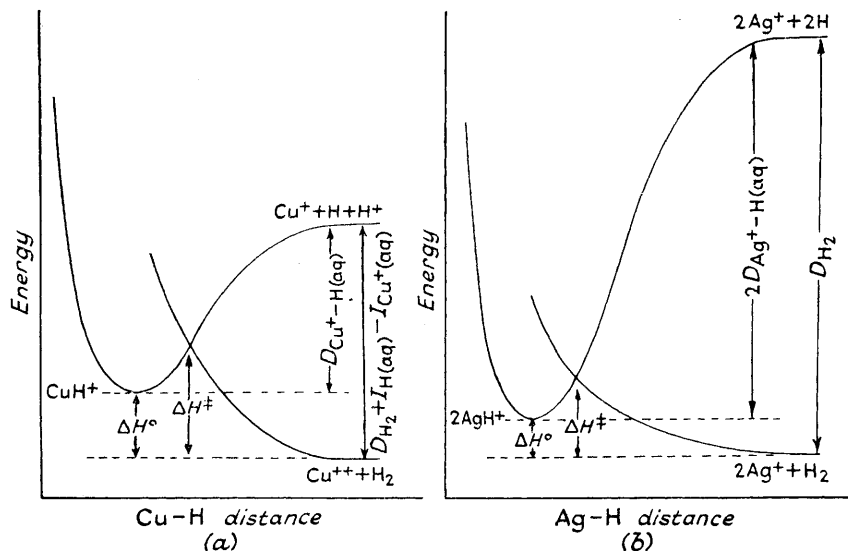

FIG. 4

Schematic potential-energy diagrams for the activation of H_2 in aqueous solution by
(a) Cu^{++} *and* (b) Ag^+.

an electron acceptor, suggesting that its catalytic activity may be related to the presence of a low-lying (*i.e.*, $3d$ or hybrid) unoccupied orbital into which the H_2 electrons can enter. The lowering of the catalytic activity of Cu^{++} on chelation with glycine and ethylenediamine (Table 2) probably reflects the fact that, in the chelate complexes, these orbitals are used in forming covalent bonds with the ligands. This phenomenon parallels the well-known poisoning of heterogeneous metallic catalysts by electron-donating substances such as sulphur compounds.

Silver Salts.—Salts of silver have also been observed [21] to activate H_2 homogeneously in aqueous solution and to catalyse the hydrogenation of substrates such as $Cr_2O_7^{--}$ at temperatures as low as 30°. The kinetics are of first order in the concentration of dissolved H_2 and of second order

[21] Webster and Halpern, *J. Phys. Chem.*, 1956, **60**, 280.

in Ag^+ as shown in Fig. 5.   In this respect the behaviour of Ag^+ in aqueous solution differs from that of cuprous or silver salts in pyridine [9, 10] but
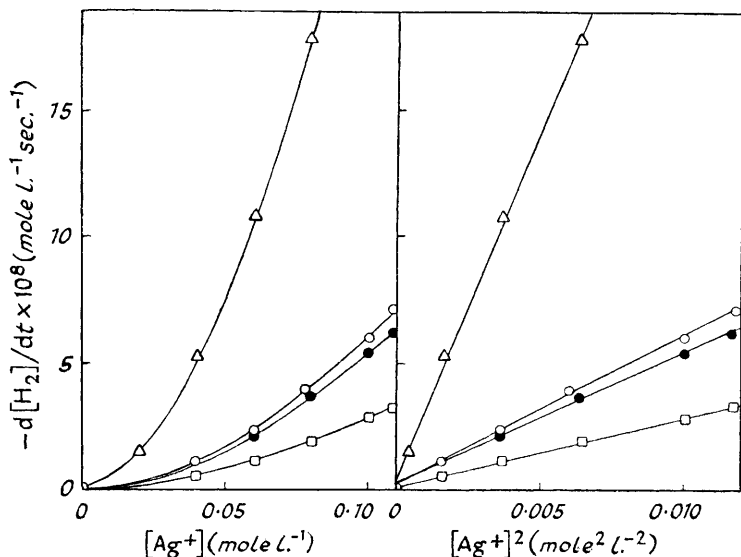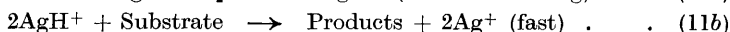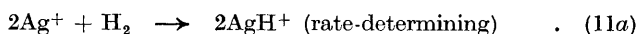

FIG. 5

Effect of silver salts on the rate of the reaction between H_2 *and* $Cr_2O_7^=$ *in aqueous solution.*

Temperatures :   □ 40° (ClO_4^-),   ○ 50° (ClO_4^-),   △ 70° (ClO_4^-),   ● 50° (NO_3^-).

(From Webster and Halpern, *J. Phys. Chem.*, 1956, **60**, 280.)

resembles that of cuprous salts in quinoline.[5, 6, 7]   The most probable mechanism parallels that which has been proposed for the latter system, *i.e.*,

$$2Ag^+ + H_2 \longrightarrow 2AgH^+ \text{ (rate-determining)} \qquad . \quad (11a)$$
$$2AgH^+ + \text{Substrate} \longrightarrow \text{Products} + 2Ag^+ \text{ (fast)} \quad . \qquad . \quad (11b)$$

The normal termolecular kinetics (Table 1), coupled with energetic considerations, lend support to this mechanism.   The activation path by which AgH^+ is formed is shown [20] schematically in Fig. 4 (*b*).   The H_2 molecule is depicted as splitting homolytically through an activated complex whose configuration probably resembles $[Ag^+\cdots H\cdots H\cdots Ag^+]$.   A slight deviation from the second-order dependence on the Ag^+ concentration, in the direction of lower order,[21] suggests that there may also be a small contribution to the observed activation of H_2 through an alternative path, *i.e.*,

$$Ag^+ + H_2 \longrightarrow AgH + H^+. \qquad . \qquad . \qquad . \quad (12)$$

This resembles the path which had been proposed earlier (equation 3*a*) for the first-order activation of H_2 by silver salts in pyridine, where it is probably favoured because of the greater basicity of the solvent.   There is an important parallel here with the Cu^{++}-catalysed reactions in aqueous solution

where the apparent kinetic dependence on the Cu^{++} concentration also shifts from first to second order as the acidity (*i.e.*, hydrogen-ion concentration) of the solution is increased.

Mercuric and Mercurous Salts.—The reduction of mercuric salts by H_2 has been observed [22], [23] to proceed homogeneously in aqueous solution at temperatures as low as 60°. In perchlorate medium the reaction proceeds in two stages (*A* and *B* in Fig. 6), the first corresponding to the reduction of Hg^{++} to Hg_2^{++} and the second to the reduction of Hg_2^{++} to metal.
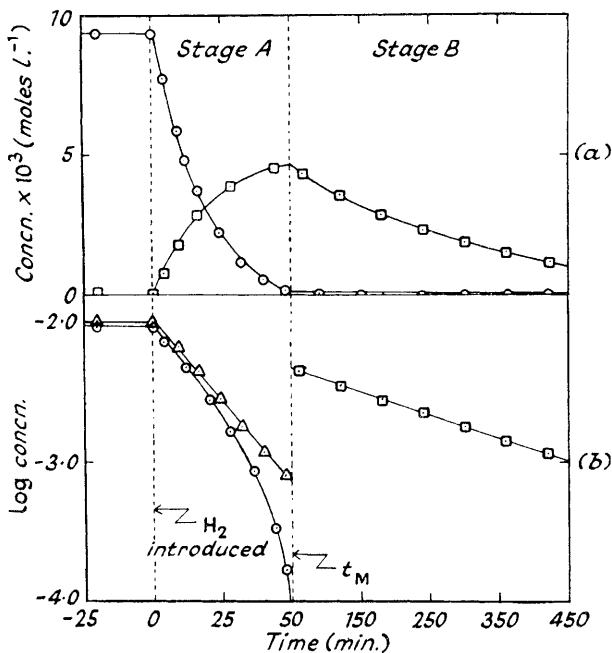

Fig. 6

Reduction of mercuric perchlorate by H_2 *in* $0.05M$-$HClO_4$ *solution at* $74.8°$; 4.0 *atm.* H_2.

In (*a*): $\bigcirc = [Hg^{++}]$, $\square = [Hg_2^{++}]$.
In (*b*): $\bigcirc = \log [Hg^{++}]$, $\square = \log [Hg_2^{++}]$, $\triangle = \log \{[Hg^{++}] + [k_2/(2k_1 - k_2)][Hg^{++}]°\}$.

(From Korinek and Halpern, *J Phys. Chem.*, 1956, **60**, 285.)

The transition between the two stages, corresponding to the first appearance of metallic Hg, and the constant ratio of $[Hg_2^{++}]$ to $[Hg^{++}]$ during the second stage, are governed by the thermodynamics of the process,

$$Hg \text{ (l.)} + Hg^{++} \rightleftharpoons Hg_2^{++} \qquad . \qquad . \qquad . \quad (13)$$
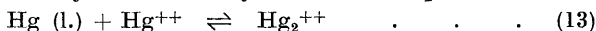
whose equilibrium constant, K, is about 70 at 60°.

It has been demonstrated [23] that both Hg^{++} and Hg_2^{++} contribute to the activation of H_2, the kinetics at any point being given by
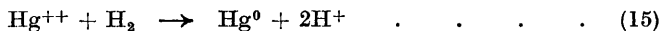
$$- d[H_2] / dt = k_1[H_2][Hg^{++}] + k_2[H_2][Hg_2^{++}] \qquad . \qquad . \quad (14)$$

[22] Halpern, Korinek, and Peters, *Research*, 1954, **7**, 61s.
[23] Korinek and Halpern, *J. Phys. Chem.*, 1956, **60**, 285,

The linear plots shown in Fig. 6 (b) are based on functions obtained through integration of this expression.

The kinetics (Table 1) support the assumption of two independent and additive rate-determining steps in which H_2 molecules are activated by homogeneous reaction with Hg^{++} and Hg_2^{++}, respectively. It seems reasonable, by analogy with the suggestions made earlier for Cu^{++} and Ag^+, that the active intermediate which is formed in this step is HgH^+. However, on energetic grounds the formation of Hg atoms by a two-electron transfer from H_2, i.e.,

$$Hg^{++} + H_2 \longrightarrow Hg^0 + 2H^+ \qquad . \qquad . \qquad . \qquad . \qquad (15)$$
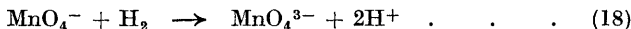$$Hg_2^{++} + H_2 \longrightarrow 2Hg^0 \text{ (or } Hg_2) + 2H^+ \qquad . \qquad . \qquad (16)$$

also appears very favourable and probably constitutes the simplest rate-determining process consistent with the observed kinetics.[20, 23]

It is of interest that, in contrast to Cu^{++}, the presence of various complexing anions markedly reduces the reactivity of Hg^{++} toward H_2, probably reflecting the much greater stability of the mercuric complexes. The rates of reaction with H_2 of mercuric salts have been observed [24] to decrease in the following order : perchlorate, nitrate > acetate > chloride > bromide.
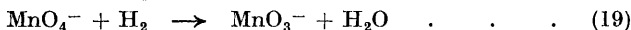
Permanganate Reduction.—The reduction of MnO_4^- by H_2 in acid solution, i.e.,

$$MnO_4^- + \tfrac{3}{2}H_2 + H^+ \longrightarrow MnO_2 + 2H_2O \qquad . \qquad . \qquad (17)$$

has recently been shown to be a homogeneous reaction.[25] The kinetics are of first order each in the concentrations of MnO_4^- and H_2, suggesting that one H_2 molecule and one MnO_4^- ion participate in the rate-determining step. On energetic grounds,[20] the formation of Mn^{VI} (with the simultaneous formation of a H atom) appears inconsistent with the observed activation energy of 14 kcal./mole, and it is more probable that Mn^V is formed in the first instance according to

$$MnO_4^- + H_2 \longrightarrow MnO_4^{3-} + 2H^+ \qquad . \qquad . \qquad . \qquad (18)$$
or
$$MnO_4^- + H_2 \longrightarrow MnO_3^- + H_2O \qquad . \qquad . \qquad . \qquad (19)$$

Under the conditions which were used, Mn^V is known to disproportionate readily to give the observed product, MnO_2.

It is of interest that Mn^V can be formed either by a two-electron transfer from H_2 to MnO_4^- (equation 18) or by the transfer of an oxygen atom from MnO_4^- to H_2 (equation 19). By using ^{18}O-labelled $KMnO_4$, it has been demonstrated [26] that a mechanism of the latter type applies in the permanganate oxidation of benzaldehyde. However, it is not necessarily preferred e. The rather low value of the activation entropy of the reaction – 17 e.u., Table 1) finds readier explanation on the basis of the alternative mechanism, since the activated complex would probably be more ionic and, hence, more highly hydrated than the reactants in this case.

In the presence of Ag^+, a kinetic contribution to the reduction of MnO_4^-,

[24] Korinek and Halpern, *Canad. J. Chem.*, 1956, **34**, 1372.
[25] Webster and Halpern, *Trans. Faraday Soc.*, in the press.
[26] Wiberg and Stewart, *J. Amer. Chem. Soc.*, 1955, **77**, 1786.

of the form $k[H_2][Ag^+][MnO_4^-]$, was observed. This has been attributed [25] to the activation of H_2 through an alternative mechanism involving the formation of Mn^{VI} and AgH^+ as intermediates, *i.e.*,

$$MnO_4^- + Ag^+ + H_2 \longrightarrow MnO_4^= + AgH^+ + H^+ . \qquad . \quad (20)$$
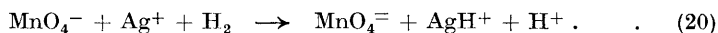
followed by fast reactions to give the observed product, MnO_2. This path is favoured by a very low activation energy (9 kcal./mole, Table 1).

Miscellaneous Hydrogenation Reactions.—It has been observed [27] that aqueous solutions of cobaltous cyanide readily absorb H_2 at room temperature, the total amount taken up corresponding approximately to one hydrogen atom per cobalt atom. The reduction of certain dissolved substrates such as cinnamic acid can also be effected in this system, apparently through a homogeneous reaction with H_2. The rate of H_2 uptake has been reported to be of first order in H_2 and of second order in Co^{II}, and to attain a maximum value when the mole ratio of CN^- to Co^{II} in the solution is approximately 4·5. Winfield [28] has concluded that the catalytic species is a dicobalt complex with the possible configuration $[(CN)_4Co$—$C\equiv N \longrightarrow Co(CN)_4]^{-5}$. The analogy with dicobalt octacarbonyl is striking.

The ability to activate H_2 homogeneously has also been attributed to solutions of certain complex salts of rhodium and palladium.[29] However, the nature of the catalysts in these systems remains to be established.

Kaneko and Wadsworth [30] recently reported that the hydrogenation of aqueous solutions of $Co(NH_3)_2SO_4$, to yield metallic Co, can be effected at temperatures of 150—245°, in the presence of colloidal graphite or of a dissolved quinol. In the latter case the reaction is presumably homogeneous, and although some metallic cobalt is present in the system, its catalytic activity does not appear to be significant. The proposed mechanism, which still awaits confirmation, implies that H_2 reacts homogeneously with the quinone, to form a quinol intermediate which, in turn, reduces the cobaltous salt. In contrast to the carbonyl and cyanide complexes discussed earlier, the ammine complexes of cobalt do not appear to activate H_2 homogeneously.

At temperatures of up to 150°, no tendency to activate H_2 homogeneously in aqueous acetate or perchlorate solution could be detected [31] for the following metal ions : Ca^{++}, Mg^{++}, Zn^{++}, Mn^{++}, Co^{++}, Ni^{++}, Cd^{++}, Pb^{++}, Al^{+++}, Fe^{+++}, UO_2^{++}, and VO_3^-.

Base-catalysed Exchange Reactions.—In 1936, Wirtz and Bonhoeffer [32] observed that potassium hydroxide catalysed the homogeneous exchange of H_2 with the deuterium in heavy water at temperatures of about 100°. The validity of this result was subsequently questioned by Abe [33] who attributed the catalysis to traces of impurities such as colloidal iron oxides. However,

[27] Iguchi, *J. Chem. Soc. Japan*, 1942, **63**, 1752, 634.
[28] Winfield, *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 217.
[29] Iguchi, *J. Chem. Soc. Japan*, 1939, **60**, 1287 ; Sibata and Matumoto, *ibid.*, 1939, **60**, 1173.
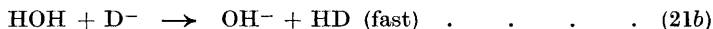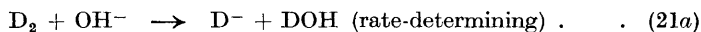[30] Kaneko and Wadsworth, *J. Phys. Chem.*, 1956, **60**, 457.
[31] Peters and Halpern, unpublished results.
[32] Wirtz and Bonhoeffer, *Z. phys. Chem.*, 1936, **177**, A, 1.
[33] Abe, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 1941, **38**, 287.

a recent careful re-investigation of this system by Wilmarth and his co-workers [34] appears to have confirmed the essential validity of the earlier work ; catalysis of the homogeneous conversion of para-H_2 by aqueous alkali solutions was also demonstrated.

The kinetics of both the exchange and the conversion reaction are of first order in OH^- and in dissolved H_2 or D_2. It has been suggested [34] that the reaction may occur either through the intermediate formation of a hydride ion, i.e.,

$$D_2 + OH^- \longrightarrow D^- + DOH \text{ (rate-determining) .} \qquad . \quad (21a)$$
$$HOH + D^- \longrightarrow OH^- + HD \text{ (fast) .} \qquad . \qquad . \qquad . \quad (21b)$$

or through a concerted attack on D_2 of an OH^- ion and an H_2O molecule, which may be depicted [32] as

$$HO^- |H^+ + D^-| |D^+ + {}^-OH| \rightleftarrows HO^- + HD + DOH \quad . \quad (22)$$
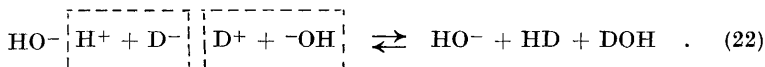
The formation of D^- (or H^-) as an intermediate appears to be energetically consistent with the observed activation energy [34] of about 23 kcal./mole. The two mechanisms depicted above become equivalent if step (21b) is very fast and the lifetime of the intermediate D^- correspondingly short. That this is in fact the case is indicated by the failure to detect any reduction of a dissolved substrate such as $CrO_4{}^{2-}$ under these conditions.[31]

An analogous $NH_2{}^-$-catalysed para-H_2 conversion and D_2–NH_3 exchange in liquid ammonia at $-50°$ has also been observed.[35] The kinetics parallel those of the OH^--catalysed reaction in water, although the activation energy is presumably much lower (estimated at 10 kcal./mole). An analogous mechanism has been proposed for this system.

Conclusions

Among the important conclusions arising from these studies on homogeneous hydrogenation reactions in solution is that, contrary to views once commonly held, hydrogenation catalytic activity does not necessarily depend on either an electronic band structure or a geometrical arrangement of atoms characteristic of the solid state. Thus, conclusive evidence has been obtained in recent years that a number of simple substances, for the most part metal ions or metal-containing compounds, can activate H_2 homogeneously in solution. At present it appears difficult to advance a single " mechanism " for the activation process which will apply without serious qualification to all the reaction systems that have been studied. Thus there are indications that H_2 can be activated by a variety of processes including homolytic or heterolytic fission of the H–H bond, or electron transfer from the H_2 molecule to the catalyst, and that superficially similar catalysts, or even a given catalyst under different conditions or in different solvents, can activate H_2 by different mechanisms.

[34] Claeys, Dayton, and Wilmarth, J. Chem. Phys., 1950, 18, 759 ; Wilmarth, Dayton, and Flournoy, J. Amer. Chem. Soc., 1953, 75, 4549.
[35] Wilmarth and Dayton, ibid., p. 4553.

There seems to be some basis for dividing the systems studied into two categories. In the first group which includes Cu^I salts in quinoline, Ag^I and Hg^I salts and cobaltous cyanide in aqueous solution, and $Co_2(CO)_8$ in organic solvents, the activation process requires the presence of two metal atoms. In these systems the mechanism may most reasonably be depicted as involving the homolytic dissociation of H_2, i.e.,

$$2M \text{ (or } M_2) + H_2 \rightarrow 2MH \qquad . \qquad . \qquad . \qquad (23)$$

The second category includes Cu^{II}, Hg^{II}, and MnO_4^- salts in aqueous solution as well as Cu^I and Ag^I salts in pyridine. In these systems, only one metal atom or ion seems to participate in the activation process, which probably involves either the transfer of the hydrogen electrons to the catalyst, i.e.,

$$M + H_2 \rightarrow M^= + 2H^+ . \qquad . \qquad . \qquad . \qquad (24)$$
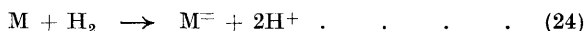
or the heterolytic dissociation of H_2, i.e.,

$$M + H_2 \rightarrow MH^- + H^+ . \qquad . \qquad . \qquad . \qquad (25)$$
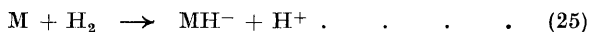
In these cases, a suitable base, usually the anion of the metal salt or a solvent molecule, is required to stabilise the hydrogen ions which are released in the activation process. This probably explains the important rôle of the solvent and of complexing anions in these systems.

In connection with the above classification of catalysts, particular interest attaches to the studies on Cu^{++} in aqueous solution which illustrate how an apparent transition from one type of mechanism to the other can occur, for a given catalyst, with a change in the properties of the solvent.

It is of interest that a heterolytic dissociation mechanism similar to that represented by equation (25) has been proposed to explain the heterogeneous catalytic activation of H_2 by oxide semiconductors such as zinc oxide [36] and the biological activation of H_2 by the enzyme hydrogenase.[37] The latter may be considered as a special and very interesting case of a homogeneous hydrogenation catalyst. Its chemical structure and the detailed mechanism by which it functions still remain to be elucidated.

If any property emerges which appears to be common to all the species which have been observed to activate H_2 homogeneously, and which may well prove to be a prerequisite for both homogeneous and heterogeneous hydrogenation catalysts, it is that the catalyst must have a high electron affinity. This generally implies the presence of low-lying, unoccupied electronic orbitals or bands. The process of activation of H_2 appears to involve, in each case, some measure of displacement (not necessarily complete transfer) of electrons from the H_2 molecule to the catalyst.[38] The explanation for this probably lies in the fact that the formation of an activated complex, involving an electronically saturated molecule such as H_2, generally involves the promotion of electrons into anti-bonding orbitals. Hence, a lowering of the activation energy is to be expected if the activated complex is coupled with a suitable electron acceptor. An interpretation of catalytic

[36] Parravano and Boudart, *Adv. Catalysis*, 1955, **7**, 47.

[37] Krasna and Rittenberg, *J. Amer. Chem. Soc.*, 1954, **76**, 3015.

[38] Halpern and Peters, *J. Chem. Phys.*, 1955, **23**, 605.

activity along these lines has been proposed by Eyring and Smith.[39]   The specific suggestion that heterogeneous catalysis may involve the transfer of electrons from the adsorbed reactant to electronic bands or levels in the catalyst has also been advanced previously [3b] and supported by a variety of experimental evidence.[40]   However, the detailed mechanism by which this may be achieved seems to vary widely from system to system.

An apparent exception to the classification of homogeneous catalysts and the generalised interpretation of catalytic activity outlined above, is the base-catalysed exchange reaction of H_2 in water or ammonia, which does not involve any metal ion or metal-containing compound.   However, it seems likely that the activation of H_2 in this system occurs by a special mechanism involving only proton shifts, without the formation of any active reducing intermediate.   According to this view, OH^- and NH_2^- are not hydrogenation catalysts but only bring about an exchange reaction of H_2 with the solvent in which the H_2 (or HD) molecule is regenerated.

[39] Eyring and Smith, *J. Phys. Chem.*, 1952, **56,** 972.

[40] Couper and Eley, *Discuss. Faraday Soc.*, 1950, **8,** 172 ; Dowden and Reynolds, *ibid.*, p. 184 ; Schwab, *ibid.*, p. 166 ; Kemball, *Proc. Roy. Soc.*, 1952, **214,** *A*, 413.