Catalytic Reduction of Hydrogen Ions in Solution in the Presence of Vitamin B_{12s} and Buffer Acids *

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The presence of buffer ions like borate. phosphate, carbonate, sulphite, ammonium, *etc.*, particularly those having acidic hydrogen atoms, enhances the evolution of hydrogen from solutions of vitamin B_{12s}. The rate of evolution is proportional to the concentrations of the buffer acid, B_{12s}, and H^+. In addition to the above ions, highly polarisable ions like cyanide and sulphide are very effective. Controlled potential electrolysis has been used as the analytical method and has led to a quantitative description of the rate of hydrogen evolution. The efficiency of the catalysts falls in the order $CN^- > HS^- > HSO_3^- \gg H_2PO_4^- > H_3BO_3 >$ pentane-2,4-dione > phenol $\gg NH_4^+ > HCO_3^- > H_2O$. A mechanism for the catalysis is proposed.

THE role of vitamin B_{12} and its derivatives as catalysts in many biochemical reactions is now established[1-4] and the possibility that it might catalyse simple reactions is obvious. Already, some catalytic reactions of vitamin B_{12} are known.[5-10] One such reaction is reduction of the proton to hydrogen involving a cyclic reduction-oxidation process with the species B_{12a} [cobalt(III)], B_{12r} [cobalt(II)], and B_{12s} [cobalt(I)].[11-14] In water B_{12s} decomposes to B_{12r} with the evolution of hydrogen, although the ratio of B_{12s} to hydrogen evolved does not follow a stoicheiometric relation, leading one to assume that the hydrogen, in all probability, arises in part from within the molecule.[11] This was confirmed by pH measurements on solutions during reduction of B_{12a} to B_{12s} and oxidation of the latter to B_{12r} [12] and also by the fact that this oxidation occurs even in aprotic solvents like *NN*-dimethylformamide.[15]

While investigating the effect of pH on the residual background current after reduction of B_{12a} to B_{12s} by controlled-potential electrolysis (c.p.e.),[12,16] it was found that the presence of buffer ions, *e.g.* phosphate, borate, phenolate, *etc.*, increased this constant current to a far greater extent than was to be expected from the effect of pH alone (as the pH of the solution decreases the overvoltage of hydrogen on mercury becomes more positive, resulting in a high residual current). This fact, together with the polarographic observation that a wave with half-wave potential of $-1{\cdot}6$ V changed with buffer composition, indicates that there must be a catalytic process in which the buffer ion plays a prominent role. Complete study of the reaction is not possible by polarographic methods as reaction occurs at a micro dropping-mercury electrode and the products are formed in microquantities. The c.p.e. method of preparation of B_{12r} or B_{12s} is virtually 100% efficient; it therefore provides a much better means of studying the reaction kinetics and also permits isolation and identification of the reaction products.

EXPERIMENTAL

Descriptions of the controlled-potential electrolysis (c.p.e.) apparatus, electrodes, *etc.*, and operational procedures are given elsewhere.[12] White Spot nitrogen (B.O.C.) contained *ca.* 10 p.p.m. dioxygen and was unsuitable for the present purpose; it was purified (oxygen concentration <1 p.p.m.) by passage over a reduced manganese(II) column which was made by heating manganese dioxide (B.D.H., MAR grade, 10—20 mesh) at 400—600 °C in a glass tube in a stream of hydrogen–nitrogen (1 : 9). The nitrogen was effectively cleaned by passage through two scrubbers containing potassium hydroxide and distilled water. Alternatively, the White Spot nitrogen was passed over a reduced BTS catalyst (BASF U.K. Ltd.) at 160—180 °C.[17] The chemicals used were of AnalaR grade except for pentane-2,4-dione (Koch–Light, puriss grade) which was distilled prior to use and mercaptoglycolic acid (Koch–Light, pure) which was used without further purification. AnalaR sodium sulphide crystals were washed with water to remove the polysulphide layer and dried on filter paper.

Procedure.—Reduction of B_{12a} to B_{12s} was carried out at a controlled potential, usually at $-1{\cdot}4$ V against a saturated calomel electrode (s.c.e.), and the electrolysis was continued for a fairly long period after the initial reduction of B_{12a} to B_{12s}. In the absence of buffer ions there was little or no residual current at a pH above *ca.* 7·0. Addition of buffer ion increased the continuous background current. The deviation from the initial background current of the blank solution was therefore an indication of the occurrence of a catalytic process.

The general procedure was to prepare a concentrated oxygen-free solution of the buffer in the supporting electrolyte (potassium chloride) at the required pH. Small volumes of this solution were injected into the electrolysis

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* A preliminary report of some of these results was published in ref. 13.

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cell (containing the previously electrolysed supporting electrolyte) using standard syringe techniques. The resulting solution was electrolysed and the blank residual current determined. An oxygen-free B_{12a} solution of known concentration was then added to the completely electrolysed blank containing a high concentration (0·1—0·2M) of buffer.* Further electrolysis of the solution allowed determination of the new residual current. Whenever there was a reasonable increase in residual current, a more rigorous experiment was carried out by first electrolysing the B_{12a} solution to B_{12s} and subsequently monitoring the current after adding different amounts of the buffer solution. During the electrolysis the pH of the solution changed slightly. Unless the buffer capacity was good in the experimental pH range, the pH of the solution was adjusted to ±0·1 unit of the required value by adding oxygen-free acid or alkali solution from a microsyringe. The reactions were studied under thermostatted conditions at 25 ± 0·5 °C.

In order to compare the results of different experiments, it is necessary to correct for the volume change during the additions. Under identical conditions the current is inversely proportional to the volume.[18] The corrected reading, $(dQ/dt)_{corr.}$, is therefore given by equation (1).

$$(dQ/dt)_{corr.} = (dQ/dt)_{expt.}\ (\text{volume of solution})/(\text{reference volume}) \quad (1)$$

Similarly, the results were also corrected for changes in the concentration of the anion and B_{12a}.

RESULTS

Effect of Tetraborate Ion on the Reduction of B_{12a} *to* B_{12s} *at* −1·4 V.—(a) *Effect of ion concentration.* At a fixed pH (9·2 ± 0·02, disodium tetraborate is self buffered), disodium tetraborate increased the final background current. A plot of final coulometer reading change per unit of time, *i.e.* dQ/dt (the residual current), against the concentration of tetraborate ion (Figure 1) was linear within the limits of experimental error in the concentration range examined. The constant background current is due to a catalytic process, the rate of which is proportional to the concentration of tetraborate.

(b) *Effect of* B_{12a} *concentration.* At pH 9·2 the catalytic current was independent of B_{12a} (or B_{12s}) concentration $>4 \times 10^{-5}$M; at lower concentrations an increase in the catalytic current with $[B_{12a}]$ was observed. At low pH (8·2) a small decrease was, however, observed with increasing $[B_{12a}]$ (Figure 2). The dependence of dQ/dt on $[B_{12a}]$ at low concentrations of B_{12a} and its representation by a linear plot of $(dQ/dt)^{-1}$ against $[B_{12a}]^{-1}$ shows that it obeys the typical adsorption equation (2) of Langmuir,

$$1/I = (1/k'[B_{12a}]) + (k''/k')$$

or

$$I = k'[B_{12a}]/(1 + k''[B_{12a}]) \quad (2)$$

where k' and k'' are constants. Presumably, at high $[B_{12a}]$ the mercury cathode is effectively covered with B_{12a} molecules, thus forming a layer which prevents unchanged B_{12a} from reaching the electrode surface.

(c) *Effect of* pH (*Figure* 3). The tetraborate system is particularly useful in understanding the role of the buffer in the catalytic process in relation to pH, as blanks at low pH values were relatively small and it is possible to fix the pH at a desired value for a fairly long time during electrolysis. The pH of the tetraborate solution was varied by adding oxygen-free hydrochloric acid or potassium hydroxide, keeping $[B_4O_7^{2-}]$ and $[B_{12a}]$ constant at a high concentration of potassium chloride, *i.e.* at fixed ionic strength. It was difficult to study the effect of pH at values <6 as self decomposition of B_{12s} was enhanced. The rate was very high at low pH and approached the value of the blank at high pH. In fact at pH >12, the addition of tetraborate had no effect on the catalytic current. The possibility of formation of polyborate ions at high pH is not excluded; however, the extent of formation of such species is not likely

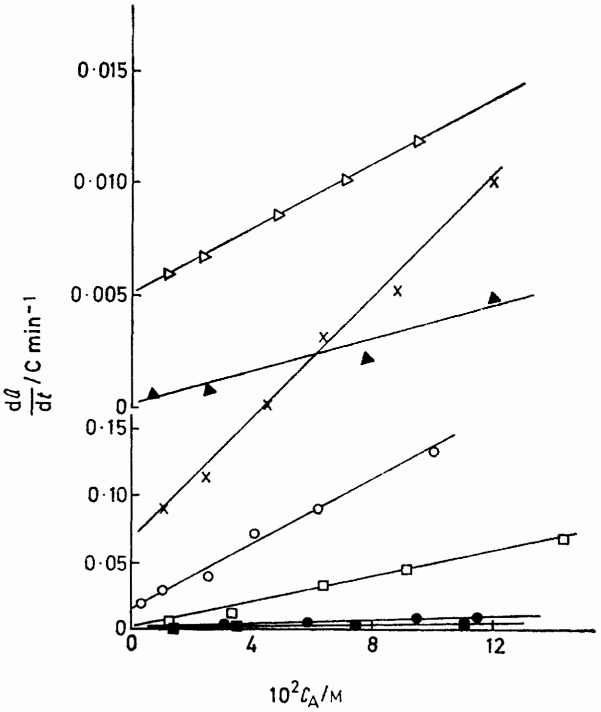

FIGURE 1 Dependence of the catalytic current on the total concentration (c_A) of buffer for $1·6 \times 10^{-4}$M-B_{12a} in 0·1M-KCl: (○), borate (pH 9·2); (□), phenol (9·5); (■), phenol (12·0); (●), phosphate (8·9); (△), hydrogencarbonate (9·2); (▲), hydrogensulphite (10·4); and (×), ammonium

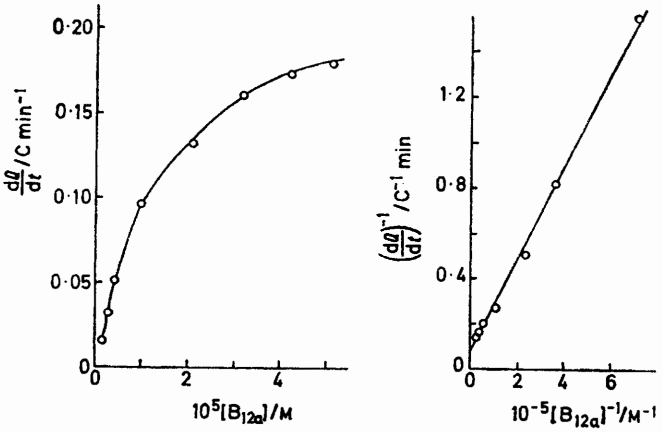

FIGURE 2 Effect of B_{12a} concentration on catalytic current (dQ/dt) in 0·05M-tetraborate buffer (pH 9·18 ± 0·01), and 0·1M-KCl

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* 1M = 1 mol dm^{-3}.

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to be very large compared with mononuclear species in solutions containing 0·05M-tetraborate at pH 6—10 as used here (Figure 3). A similar pH dependence of the rate of catalytic evolution of hydrogen was observed for phosphate buffers.

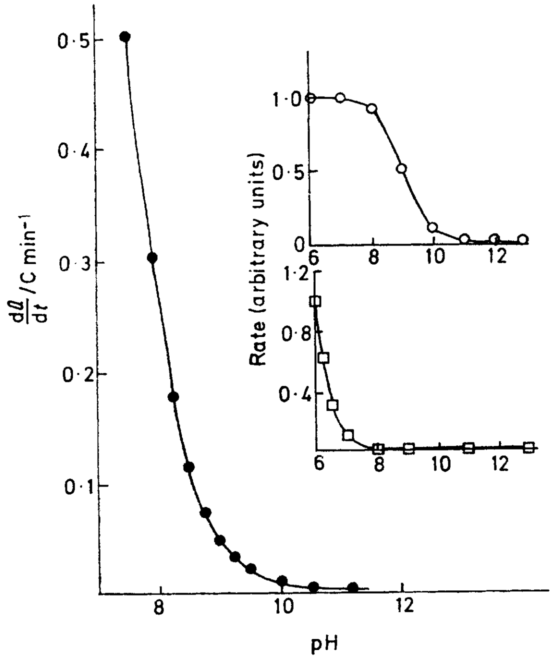


FIGURE 3 Effect of pH on the catalytic current for the reaction of B_{12s} with tetraborate [0·5M-KCl, 0·05M-$Na_2B_4O_7$,$10H_2O$ (pH 9·2), 1·62 × 10^{-4}M-B_{12a}]: (●), experimental (corrected for blank); (○), theoretical using the expression Rate ∝ $1/(1 + K_a[H^+]^{-1})$; (□), theoretical using the expression Rate ∝ $[H^+]/(1 + K_a[H^+]^{-1})$ (scale arbitrary, pK_a 9·2)

(d) *Amount of hydrogen evolved.* In order to determine whether there is a stoicheiometric relation between the amount of electricity consumed in the reduction of B_{12a} and the amount of hydrogen evolved, the volume of gas from the c.p.e. cell containing the degassed solution was collected over water in a graduated burette thermostatted at the temperature (20 °C) of the cell and its volume was measured from time to time as the electrolysis continued. The amount of hydrogen released in the presence of tetraborate was much greater than in the blank (Table 1). At pH 7·8 ± 0·1, after correction for the blank and pressure, the rate of evolution of hydrogen was 0·026 cm^3 min^{-1}; this amount of hydrogen will consume 0·22 C min^{-1} of charge for the reaction $H^+ \longrightarrow \frac{1}{2}H_2$. The observed corrected coulometric reading was 0·29 C min^{-1}; this somewhat high value may be due to loss of some gas from the coulometric vessel, but it is clear that hydrogen evolution is the main path of electrolysis.

TABLE 1

Hydrogen evolution during the reduction of B_{12a} to B_{12s} in the presence (*a*) and absence of tetraborate (*b*)

	Volume of H_2 collected	Duration of expt.	Rate of H_2 evolution	Coulometer reading
	cm^3	min	cm^3 min^{-1}	C min^{-1}
(*i*) 1·22 × 10^{-4}M-B_{12a} (20 cm^3) in 0·1M-KCl containing 0·05M-$Na_2B_4O_7$,$10H_2O$ and hydrochloric acid, pH 7·8 ± 0·1, 20 °C, 740 mmHg				
a	5·70	180	0·0317	0·3282
b	0·45	180	0·0025	0·0356
(*ii*) 1·00 × 10^{-4}M-B_{12a} (20·6 cm^3) in 0·1M-KCl containing 0·05M-$Na_2B_4O_7$,$10H_2O$, pH 9·20 ± 0·02, 20 °C, 740 mmHg				
a	0·33	180		0·0128
b	0·05	120		0·0013

Effect of Other Buffers and Anions.—The study using tetraborate shows that a weak acid species, H_3BO_3, of the buffer together with B_{12s} are responsible for the catalysis. In order to discover the specific requirements of the system, a number of other buffers were studied. In these experiments the concentration of B_{12a} was maintained at a value much above that required for maximum reaction rate. Linear relations between the concentration of buffer and (dQ/dt), corrected for blank, similar to that for borate were found for pentane-2,4-dione, phenol, potassium dihydrogenphosphate, sodium hydrogensulphite, potassium hydrogencarbonate, and ammonium chloride (Figure 1). In Figure 4 typical coulometric curves, *i.e.* Q against t plots, for the reduction of B_{12a} to B_{12s} in the presence and absence of potassium hydrogencarbonate are shown. All buffers were less active at high pH, though phenol showed considerable catalytic activity above pH 12·0. A study of the ammonium chloride system was not possible at high pH as ammonia was spontaneously evolved. In view of the facts that mercapto-groups are the major reducing groups of protein molecules and that catalytic oxidation of thiols is known, the effects of mercaptoglycolic acid and sodium sulphide were studied. In the case of mercaptoglycolic acid an unusually high blank was observed; nevertheless, from the results it is obvious that the acid is a good reagent in this respect. Sodium sulphide was even better. Because of experimental difficulties arising from rapid changes in pH of potassium cyanide solution, it was not possible to study in detail the effect of cyanide which also aids catalysis; here also the final background current was high and B_{12s} was the final product. The

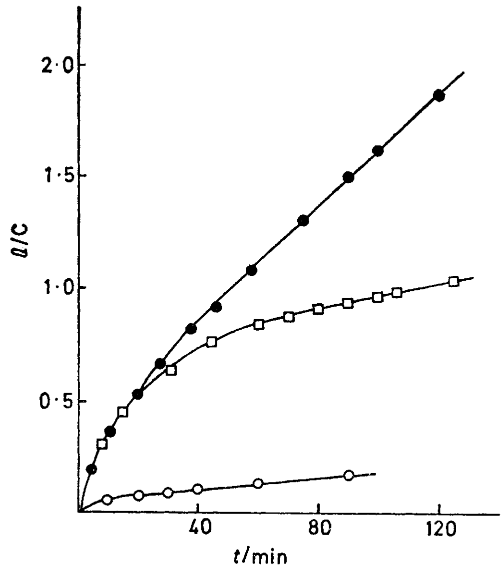


FIGURE 4 Typical coulometric curves for the reduction B_{12a} to B_{12s} in the presence (●) and absence of 0·1M-potassium hydrogencarbonate (pH 9·2 ± 0·1): (□), using 3 × 10^{-3}M-B_{12a} (1 cm^3) in 0·1M-KCl at −1·4 V against a s.c.e.; (○), blank solution

rate of hydrogen evolution was high at the high experimental pH, although a decrease in rate was observed with increasing pH.

DISCUSSION

Before proceeding to analyse the results and to formulate equations to fit them, it is necessary to find an order in the efficiency of the ions mentioned. Cations were found to have no significant effect on the catalytic current. The buffers and salts used in this study can be conveniently classified according to their quantitative behaviour in the electrolysis cell as follows. (*i*) Those for which the final background current in the presence of B_{12s}, and the total amount of charge consumed by B_{12a}, is the same both in the presence and in the absence of the anions. These salts are therefore regarded as catalytically inert; in this class are NO_3^-, Cl^-, SO_4^{2-}, OH^-, *etc.* (*ii*) Those for which the final background current is the same as the blank, but the total amount of charge used up to reduce B_{12a} to B_{12s} is much higher than expected for two-electron reduction and the background current increases as the concentration of the anion increases; ethylenediaminetetra-acetic acid (H_4edta) and acetic acid fall in this category. (*iii*) Those for which the final constant background current is higher than that of the blank. These buffers are therefore catalytically active and this class includes: borate, phosphate, pentane-2,4-dionate, ammonium, phenol, hydrogencarbonate, cyanide, hydrogensulphite, sulphide, and mercaptoglycolate. In these cases the final product is B_{12s}. (*iv*) This group of buffers leads to a final background current equal to that of the blank but the reaction product is not B_{12s}; for nitrite it is B_{12r} and with bromate B_{12a} is formed as the final product. Evidently these oxidising anions prevent the formation of B_{12s} and B_{12r}.

The effect of pH on the rate of reaction for the class (*iii*) anions (discussion is restricted to this class) can be considered as (*a*) a simple dependence on the weak acid concentration, *i.e.* Rate $\propto c_A/(1 + K_a[H^+]^{-1})$ where c_A is the total concentration of the buffer and K_a is the dissociation constant of the weak acid, or (*b*) a dependence on $[H^+]$ and the weak acid concentration, Rate $\propto c_A[H^+]/(1 + K_a[H^+]^{-1})$. For different pH values the rate of reaction in these expressions can be computed as a function of pH. Comparison of the experimental and theoretical curves shows that expression (*b*) represents the situation closely, at least at low pH (6·5—10·0) (Figure 3).

The preferential choice of expression (*b*) from such a visual comparison has its obvious limitations. One convenient way of confirming dependence (*b*) is to plot Rate$(1 + K_a[H^+]^{-1})$ against $[H^+]$. Expression (*a*) should give a horizontal straight line and (*b*) a straight line passing through the origin with a linear dependence on the hydrogen-ion concentration. Such plots for two pH ranges, 11·0—7·5 and 9·5—6·5, are given in Figure 5. The curve rises from pH 9·5 and attains what appears to be a steady state at pH <7·0, *i.e.* there is a linear dependence on hydrogen-ion concentration. At pH values above 9·5 the curve shows a sharp rise. In the pH range 9·5—7·0 the deviations from linearity are too large to be explained as experimental errors. Evidently some chemical processes are involved which have not yet been taken into consideration. As the hydrogen-ion concentration increases the value of Rate$(1 + K_a[H^+]^{-1})$ exhibits a less than first-order dependence on $[H^+]$, suggesting some protonation process with pK_a *ca.* 8. This could be associated with B_{12a}, B_{12r}, or their complexes with boric acid; however, as yet there is no clear evidence for complex formation with boric acid. Although the nature of the actual process is far from certain and there are a number of interesting possibilities, it is not unreasonable to conclude from the hydrogen-ion dependence in Figure 5 that expression (*b*) is applicable at low pH; the small positive intercept at higher pH suggests that some combination of (*a*) and (*b*) applies. At very high pH (>10) the corrin ring of B_{12} is attacked by OH^- in a very different way, leading to the sharp rise in the curve; the experimental error in this region is also too large to derive meaningful conclusions. The possibility that more than two protons from the solution participate in the reaction at any given time is excluded as one molecule of B_{12s} reacts with one proton only. As in the borate system, it is assumed that the only reaction is that of reduction of H^+ to hydrogen; the cases of cyanide and phenol, in which a catalytic current is observed even at high pH, are also excluded.

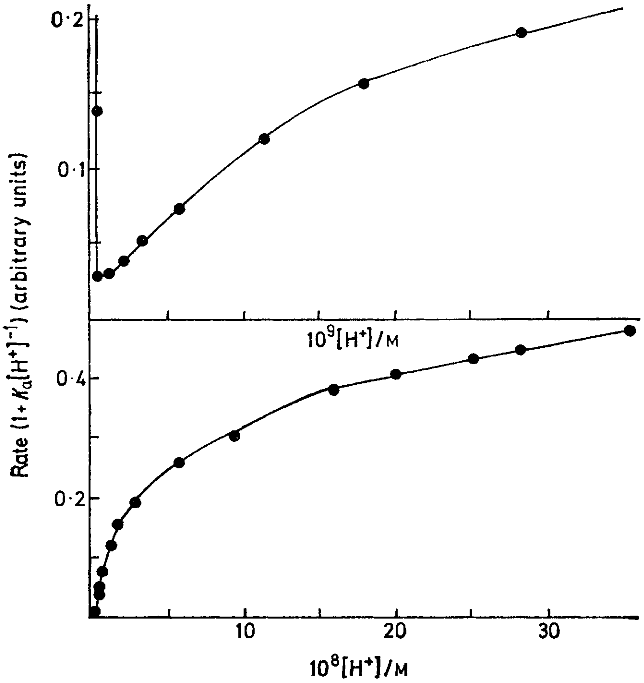


FIGURE 5 Plots of Rate$(1 + K_a[H^+]^{-1})$ in arbitrary units against hydrogen-ion concentration; upper curve pH 11·0—7·5, lower curve pH 9·5—6·5

At the end of the reduction of B_{12a} to B_{12s} there is a constant current, $I = \mathrm{d}Q/\mathrm{d}t$. Since the reaction is accompanied by constant evolution of hydrogen from the solution, the current can be used to measure the reaction rate. It has also been shown that $I \propto$ Rate $\propto c_{\mathrm{B}}$ and [HA], where c_{B} is the total concentration of $\mathrm{B_{12a}}$ and [HA] that of the undissociated acid. In the case

$$c_{\mathrm{A}} = [\mathrm{HA}] + [\mathrm{A^-}] = [\mathrm{HA}] + (K_{\mathrm{a}}[\mathrm{HA}]/[\mathrm{H^+}])$$
$$\text{or } [\mathrm{HA}] = c_{\mathrm{A}}/(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1}) \qquad (3)$$

of borate the rate of reaction varies directly as $[\mathrm{H^+}]$ at constant [HA] and c_{B}. Thus expression (4) is

$$\text{Rate} \propto c_{\mathrm{A}}c_{\mathrm{B}}[\mathrm{H^+}]/(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1}) \qquad (4)$$

obtained. In the concentration range where the rate is independent of $\mathrm{B_{12a}}$ concentration, equation (4) can be written as (5). Thus $I = \mathrm{d}Q/\mathrm{d}t \propto c_{\mathrm{A}}[\mathrm{H^+}]/(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1}) = k_{\mathrm{c}}c_{\mathrm{A}}[\mathrm{H^+}]/(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1})$ or $k_{\mathrm{c}} = I(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1})/c_{\mathrm{A}}[\mathrm{H^+}]$, where k_{c} is the catalytic constant.

$$\text{Rate} \propto c_{\mathrm{A}}[\mathrm{H^+}]/(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1}) \qquad (5)$$

From the gradient of a plot of I against c_{A} and the pH of the solution k_{c} was calculated at the experimental hydrogen-ion concentration of the solution (Table 2).

Mechanism.—One general scheme for the activation of hydrogen by metal chelate complexes has been studied by Calvin,[19] Halpern,[20] and Parris and Williams.[21] The mechanism involves the heterolytic step (6). The

$$\mathrm{H_2 + M \cdots B \longrightarrow MH^- \cdots H^+B} \qquad (6)$$

nature of the most effective base, B, in the reaction is not understood. Evolution of hydrogen from the $\mathrm{B_{12s}}$ system is the reverse of (6). Here the nature of HB has been examined in the hope of discovering the regulating factor activating $\mathrm{H_2}$. The following conclusions may be drawn.

TABLE 2

Catalytic constants, k_{c}, for different buffer acids

Buffer acid	Solution pH	Gradient [a] C min^{-1} mol^{-1}	pK_{a} buffer acid	$10^{-9}k_{\mathrm{c}}$ [b]
$\mathrm{H_2PO_4^-}$	8·88—8·98	0·065	7·10	3·80
$\mathrm{H_3BO_3}$	9·22—9·18	1·197	9·20	3·59
$\mathrm{HCO_3^-}$	9·14—9·30	0·076	10·40	0·14
Phenol	9·57—9·48	0·458	9·90	2·15
Pentane-2,4-dionate	8·85—8·79	2·081	9·00	2·29
$\mathrm{NH_4^+}$	8·23—8·11	1·346	9·40	0·21
$\mathrm{HSO_3^-}$	10·32—10·50	0·048	7·20	2 000

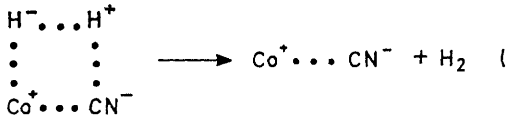
[a] Of plot of $\mathrm{d}Q/\mathrm{d}t$ against concentration of buffer. [b] $k_{\mathrm{c}} = (\text{Gradient})(1 + K_{\mathrm{a}}[\mathrm{H^+}]^{-1})/[\mathrm{H^+}]$.

(*a*) The reverse process cannot be catalysed by simple anions like $\mathrm{CO_3^{2-}}$, $\mathrm{NO_3^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{ClO_4^-}$, *etc.*, which do not possess acidic hydrogen.

(*b*) The more acidic hydrogen atoms possessed by a given species, the more effective is, in general, the species, *e.g.* $\mathrm{H_2PO_4^-} > \mathrm{HPO_4^{2-}}$, $\mathrm{H_3O^+} > \mathrm{H_2O}$, and $\mathrm{NH_4^+} > \mathrm{NH_3}$. However, it has been found that $\mathrm{B(OH)_3}$ is more effective than $\mathrm{B(OH)_4^-}$; in this case it would appear that the anionic charge lowers the effect of the species possessing the most number of acidic hydrogen atoms.

(*c*) In general, it seems that the higher the positive charge on the acidic hydrogen atom the better the catalysis. This is in agreement with the orders $\mathrm{H_3O^+} >$ $\mathrm{NH_4^+}$ and $\mathrm{H_2PO_4^-} >$ pentane-2,4-dione $>$ phenol $>$ $\mathrm{HCO_3^-} > \mathrm{H_2O}$ (Table 2); in these two series the order is that of decreasing acid strength. Acidity, in general, does not reflect the charge density on hydrogen and no general relation with pK_{a} amongst anionic, neutral, and cationic species is expected. This is also supported by the observation of Beck[22] that catalysis of hydrogenation by $\mathrm{Ag^+}$ in the presence of bases, B, is greatest for the base fluoride which on combination with a proton leaves the hydrogen atom with the greatest positive charge.

Some selectivity, apart from that which can be accounted for on the above basis, has also been observed. Thus, RSH and $\mathrm{HSO_3^-}$ have been found to be very good catalysts. It is to be noted that a free $\mathrm{HS^-}$ group as in NaHS is more effective than bound in mercaptoglycolic acid. HCN is also very effective. It is possible that highly polarisable ligands such as $\mathrm{HSO_3^-}$, RSH, and HCN can interact more strongly with Co $\cdots$ H (as in $\mathrm{B_{12s}}$) in a four-centre attack[21] [equation (7)]. The



(7)

anomalous behaviour at high pH of the two anions containing no acidic hydrogen atom, *i.e.* cyanide and phenolate, arises from a completely different reason. These anions are reducible and a possible explanation of the occurrence of the high catalytic current is that these groups are further reduced in the presence of $\mathrm{B_{12s}}$ to substances which in turn catalyse the process. This was not verified as no examination of the products was made. The overall mechanism of the catalytic evolution of hydrogen from solution in the presence of $\mathrm{B_{12a}}$ and a weak acid can be depicted as in equations (8)—(11).

$$\mathrm{Co^{III}} \xrightarrow{2e^-} \mathrm{Co^{I}};\ \mathrm{HA} \rightleftharpoons \mathrm{H^+ + A^-} \qquad (8)$$
$$\mathrm{Co^{I} + H^+} \rightleftharpoons \mathrm{Co^{I} \cdots H^+} \rightleftharpoons \mathrm{Co^{III} \cdots H^-} \qquad (9)$$
$$\mathrm{Co^{III} \cdots H^- + HA^+} \longrightarrow \mathrm{Co^{III} + A^- + H_2} \qquad (10)$$
$$\mathrm{Co^{I} + H^+ + HA} \longrightarrow \mathrm{Co^{III} + A^- + H_2} \qquad (11)$$

This involves intermediate formation of cobalt hydride, a species which is known to be present in equilibrium concentration in reduced $\mathrm{B_{12a}}$ solutions.[23]

I thank Dr. R. J. P. Williams for many valuable suggestions, the Government of West Bengal, India, for support, and the Inorganic Chemistry Laboratory, Oxford, for providing the facilities.

[3/341 *Received*, 14*th February*, 1973]

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