# The Oxidation of the Hypophosphite Ion by Water, Catalysed by Metal–Phosphorus and Metal–Boron Alloys

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The hydrolysis of the hypophosphite ion occurs according to equation (i) and is catalysed by nickel–phosphorus, cobalt–phosphorus, and nickel–boron alloys. The stoicheiometry and the kinetic behaviour have been examined by measuring the hydrogen evolved in the catalysed hydrolysis at 98·7 °C. Further information concerning the reaction mechanism has been obtained by carrying out the reaction in $D_2O$ or $D_2O–H_2O$ mixtures. The reaction can be followed by $^1H$ n.m.r. measurements of the concentrations of the species $H_2PO_2^-$ and $H_2PO_3^-$. The deuterium content of the gas evolved has also been studied. A reaction mechanism is proposed involving simultaneous reactions in which the hypophosphite molecule exchanges either one or both phosphorus-bound hydrogen atoms with the solvent.

$$H_2PO_2^- + H_2O \xrightarrow{\text{Cat.}} H_2PO_3^- + H_2 \qquad \text{(i)}$$

THE hydrolysis of the hypophosphite ion catalysed by metals or metal-alloys has been known for a long time and early studies[1-5] showed that the overall reaction is expressed by equation (1). Although some

$$H_2PO_2^- + H_2O \xrightarrow{\text{Cat.}} H_2PO_3^- + H_2 \qquad (1)$$

features of this reaction are now clear[6,7] the detailed mechanism has up to the present remained obscure. An understanding of this reaction is important for the ' electroless ' or autocatalytic deposition of metals using the hypophosphite ion as reducing agent[8-10,11] where reaction (1) occurs as a side-reaction. This work is

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[1] A. Wurtz, *Annalen*, 1844, **3**, 250.

[2] A. Sieverts and F. Loessner, *Z. anorg. Chem.*, 1912, **76**, 1.

[3] A. Sieverts and E. Peters, *Z. phys. Chem.*, 1916, **91**, 199.

[4] A. Bach, *Ber.*, 1909, **42**, 4463.

[5] H. Wieland and A. Wingler, *Annalen*, 1941, **434**, 198.

[6] W. Franke and J. Mönch, *Annalen*, 1941, **550**, 1.

[7] A. M. Lunyatskas and L. P. Valyantukyavichyute, *Trudy Academii Nauk Litovskii S.S.R.*, 1964, *B*1(36), 135.

[8] G. Gutzeit, *Plating*, 1959, **46**, 1158, 1378.

[9] K. A. Holbrook, Encyclopaedic Dictionary of Physics, Pergamon, Oxford, 1970, Suppl. Vol. 4, 277.

[10] K. M. Gorbunova and A. A. Nikiforova, Physicochemical Principles of Chemical Nickel-Plating, Israel Program for Scientific Translations, Jerusalem, 1963.

[11] A. A. Sutyagina, K. M. Gorbunova, and M. P. Glazunov, *Russ. J. Phys. Chem.*, 1963, **37**, 1096, 1196.

also relevant to studies of the anodic oxidation of the hypophosphite ion.[12,13]

## EXPERIMENTAL AND RESULTS

*Apparatus*.—Several different experimental arrangements were used. In the kinetic experiments a glass reaction vessel (volume *ca.* 100 ml) was heated by means of a vapour jacket. The reaction vessel carried a thermometer and was connected through a water-condenser to a gas-burette to enable the volume of hydrogen evolved to be measured. A weighed sample of catalyst was introduced through a stoppered opening in the reaction vessel.

For the n.m.r. studies a three-necked 25-ml reaction vessel was immersed in a water/oil thermostat and the reactant solution was stirred by means of a magnetic stirrer. Nitrogen was bubbled through the solution during a run and samples were periodically extracted by suction for n.m.r. examination.

For the examination of the deuterium content of the gas evolved when the solvolysis was carried out in $D_2O$, a small (5 ml) reaction vessel was used and heated by a vapour jacket. Gas samples were collected by attaching evacuated bulbs directly to the reaction vessel.

*Preparation of Solutions*.—Sodium hypophosphite (B.D.H.) was dried for *ca.* 5 h at 150 °C; the dried solid was found to contain *ca.* 0·7 mole % phosphite by the method of Jones and Swift.[14] For the kinetic experiments, solutions were prepared in distilled water, no buffers were added, and the pH was adjusted to 7·0 ± 0·1 with conc. HCl or NaOH. For the deuterium tracer experiments solutions were prepared either in distilled water or in 99·7% $D_2O$. In some experiments AnalaR sodium citrate was used as a buffer. Before making the final $D_2O$ solutions, all solutes were separately dissolved in $D_2O$ and the resulting solutions were evaporated to dryness under reduced pressure. The required amounts of the residues were dissolved in $D_2O$ to give the final solutions.

*Kinetic Studies: Catalyst Preparation*.—Catalysts were prepared by the deposition of a nickel–phosphorus film on a silica-gel support (60 to 120 mesh) from a plating solution containing sodium hypophosphite (0·1M), nickel chloride (0·1M), and sodium succinate (0·2M) at pH 6·0, and at *ca.* 80 °C. The silica gel was activated by immersion for 1 min in stannous chloride (0·01% aq., pH = 1·9) followed by a distilled water rinse and immersion for 1 min in palladous chloride (0·015% aq., pH = 3·0). The activated silica gel was immersed in the above plating solution for 4 min and during immersion it was kept in suspension by vigorous stirring of the solution. The resulting catalyst (Ni-6) contained on average *ca.* 5·3% by weight of phosphorus which was determined by the standard molybdenum-blue colorimetric estimation procedure. Nickel was determined by the standard dimethylglyoxime gravimetric procedure.[15]

*Procedure during a Run*.—The reaction vessel containing a sample (80 ml) of sodium hypophosphite solution was placed in a vapour-jacket thermostat and allowed to reach a steady temperature (98·7 °C). A weighed catalyst sample contained in a narrow glass tube and sandwiched between two glass-wool plugs was injected into the solution by means of a glass-rod plunger. The vessel was immediately stoppered and the volume of hydrogen evolved at constant pressure was measured.

*Kinetic Results*.—The total volumes of hydrogen ($V_\infty$) evolved at atmospheric pressure for sodium hypophosphite (0·025M) over a range of weights of catalyst are compared in Table 1 with the volumes of hydrogen ($V_{calc}$) calculated on the basis of equation (1).

TABLE 1

| Wt. of catalyst/g | $(V_\infty/V_{calc}) \times 100$ |
|---|---|
| 0·0350 | 97·0 |
| 0·0420 | 95·7 |
| 0·0504 | 96·8 |
| 0·0610 | 95·1 |
| 0·0700 | 96·7 |

A typical plot of the volume of hydrogen evolved (at s.t.p.) as a function of time for reaction on catalyst (Ni-6) is shown in Figure 1. The initial rates of hydrogen evolution were measured from such plots for several different amounts of catalyst and different concentrations of the hypophosphite ion. Figure 2 shows that the initial rate of hydrogen evolution is proportional to the amount of catalyst present. The dependence of the initial rate of hydrogen evolution upon hypophosphite concentration is more complex and is shown in Figure 3. Between 0·025 and 0·100M linear first-order plots were obtained but at lower hypophosphite concentrations these were curved (see Figure 4).

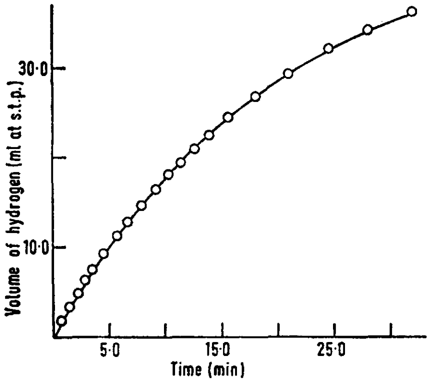

FIGURE 1 A typical plot of hydrogen evolved *versus* time for the nickel-catalysed hydrolysis of hypophosphite ion

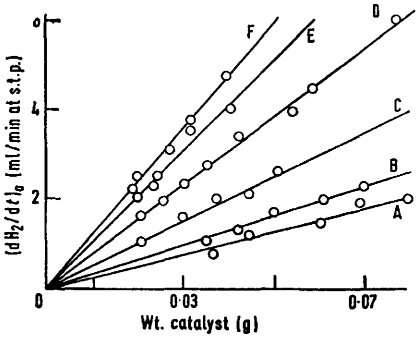

FIGURE 2 Initial rate of hydrogen evolution *versus* weight of catalyst. $[H_2PO_2^-]$ (M); A = 0·0125, B = 0·025, C = 0·05, D = 0·10, E = 0·15, F = 0·20

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[12] A. Hickling and D. Johnson, *J. Electroanalyt. Chem.*, 1967, **13**, 100.

[13] S. Trasatti and A. Alberti, *J. Electroanalyt. Chem.*, 1966, **12**, 236.

[14] R. T. Jones and E. H. Swift, *Analyt. Chem.*, 1953, **25**, 1272.

[15] R. Belcher and A. J. Nutten, 'Quantitative Inorganic Analysis,' Butterworths, London, 1960, p. 115.

No gas was evolved when solutions of sodium phosphite (0·1- to 0·5-M at pH = 7·0) were placed in contact with catalyst Ni-6. The reaction is therefore unaffected by the reaction product in solution.

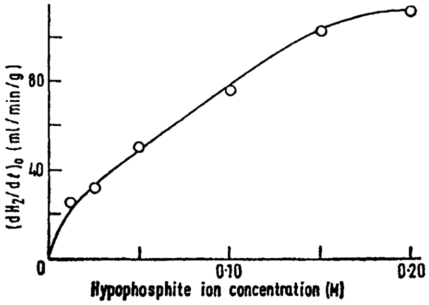

FIGURE 3 Initial rate of hydrogen evolution as a function of initial hypophosphite concentration

*Deuterium Tracer Studies: N.m.r.—Preparation of catalysts* (Ni-4) *and* (Co-4). Active nickel–phosphorus (Ni-4) and cobalt–phosphorus (Co-4) powder catalysts were prepared by seeding the following solutions with a small amount of previously prepared catalyst.

The solution for Ni-4: sodium hypophosphite (1·0M), nickel chloride hexahydrate (1·0M), lactic acid (0·3M) at pH = 7·0 and at 100 °C.

The solution for Co-4: sodium hypophosphite (1·0M), cobalt chloride hexahydrate (0·5M), sodium citrate (0·5M) at pH = 10·0 and at 100 °C.

These solutions, if heated long enough, decompose spontaneously precipitating metal–phosphorus powder. The seeding procedure accelerates this decomposition. Before use in $D_2O$ solutions, weighed catalyst samples were shaken in deuterium oxide and then evaporated to dryness under reduced pressure.

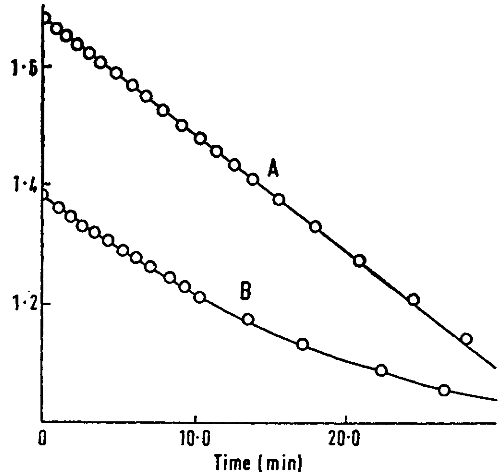

FIGURE 4 First-order log plots for two different initial hypophosphite concentrations: A, $[H_2PO_2^-] = 0{\cdot}025$M; B, $[H_2PO_2^-] = 0{\cdot}0125$M

*Procedure during a Run.*—The reaction vessel containing a solution of sodium hypophosphite in water or $D_2O$ was brought to a constant temperature (80·0 °C) while nitrogen was bubbled through the solution. An initial sample was withdrawn for n.m.r. examination, a weighed amount of catalyst was added, and samples were subsequently withdrawn at 2-min intervals for n.m.r. analysis.

*N.m.r. Results.*—Proton n.m.r. spectra of aqueous solutions containing hypophosphite and sodium phosphite were examined using a Perkin-Elmer 40 Hz spectrometer. The spectra both consist of doublets due to the phosphorus-bonded hydrogen atoms but with different coupling constants which enable the hypophosphite and phosphite species to be distinguished. The coupling constants were found to vary with pH, limiting values were found to be for $H_2PO_2^-$, $J_{PH} = 520$ Hz and for $HPO_3^{2-}$ $J_{PH} = 568$ Hz in good agreement with the values reported by Haas and Gillman.[16] The peak-heights were used for quantitative determination of the hypophosphite and phosphite ions and linear calibration graphs were obtained (Figure 5).

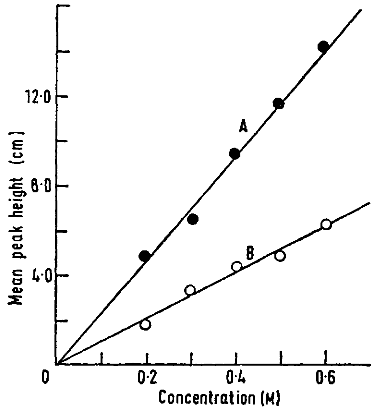

FIGURE 5 Peak height *versus* concentration plots for hypophosphite and phosphite ions: A = hypophosphite ion; B = phosphite ion

Hydrolysis experiments were carried out using catalysts Co-4 or Ni-4 with $D_2O$ or $H_2O$ and an initial concentration of 0·5M-sodium hypophosphite. N.m.r. analysis was used to determine the amounts of hypophosphite and phosphite present at 2-min intervals. The phosphite formed is plotted against the hypophosphite consumed in Figure 6. For the nickel catalyst in $H_2O$ the slope (line

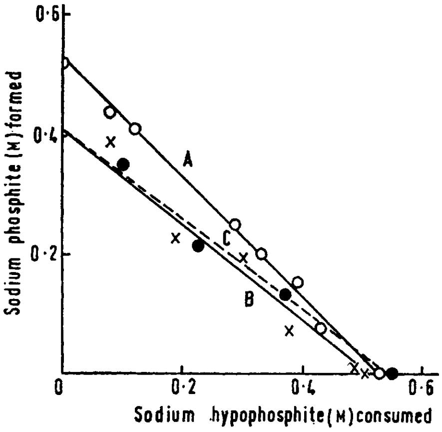

FIGURE 6 The relation between hypophosphite lost and phosphite formed. A(○), Ni-4 in $H_2O$; B(×), Ni-4 in $D_2O$; C(●), Co-4 in $D_2O$

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[16] T. E. Haas and H. D. Gillman, *Inorg. Chem.*, 1968, **7**, 2051.

A) is close to the theoretical value of unity. For Ni-4 in $D_2O$ (line B) the slope is 0·80 ± 0·15 and for Co-4 in $D_2O$ (line C) the slope is 0·75 ± 0·12.

The possibility of homogeneous exchange between hydrogen from either hypophosphite or phosphite ions and deuterium in the solvent was investigated by carrying out a control run in the absence of catalyst. The solution for the control run contained 0·5M-phosphite initially as well as 0·5M-hypophosphite. No exchange was apparent from the appearance of n.m.r. spectra of samples taken during the run. The experiment was repeated at a pH of 5·5 (the final pH for a standard run in the presence of the catalyst) and again no exchange was apparent.

*Deuterium Tracer Studies: Gas Analysis.*—In addition to the catalysts Ni-4, Co-4, and Ni-6, the preparations of which are described above, some results in this section refer to the use of catalyst Ni-10[17] and Ni-7 which was prepared by the decomposition of nickel oxalate under vacuum at 300 °C.[18]

*Procedure during a Run.*—A sample (2 ml) of solution was placed in the reaction vessel and allowed to heat to constant temperature. A weighed catalyst sample was washed in $D_2O$ as described above and then added to the solution in the reaction vessel. An evacuated sample vessel was connected to the reaction vessel to collect the gas as it was evolved. Samples of the gas evolved were taken at various times during the reaction or alternatively the whole of the gas evolved was collected in one large sample vessel. The mass spectrometric determination of the %D content of the evolved gases has been described previously.[17]

*Gas-analysis Results.*—The hydrolysis of the hypophosphite ion (0·11M) in $D_2O$ was studied using five different catalysts and a range of conditions of temperature and pH. The analytical results in Table 2 show that the %D in the gas evolved varies from 38·2 to 42·6%.

TABLE 2

| Catalyst | Initial pH | $t$/°C | Molar ratios | | | %D |
|---|---|---|---|---|---|---|
| | | | $H_2$ : | HD : | $D_2$ | |
| Ni-4 | 9·0 | 98·5 | 1·91 | 2·04 | 1·00 | 41·0 |
| Ni-4 | 9·0 | 56·4 | 2·10 | 2·02 | 1·00 | 39·3 |
| Ni-4 | 9·3 | 23·0 | 2·45 | 2·92 | 1·00 | 38·6 |
| Ni-6 | 8·5 | 56·4 | 2·35 | 2·42 | 1·00 | 38·2 |
| Ni-7 | 8·5 | 23·0 | 2·24 | 2·10 | 1·00 | 38·6 |
| Ni-10 | 7·0 | 22·0 | 2·03 | 2·39 | 1·00 | 40·6 |
| Co-4 | 9·0 | 23·0 | 1·72 | 2·15 | 1·00 | 42·6 |

Several runs were carried out with different initial concentrations of sodium hypophosphite in the range 0·05- to 0·5-M using catalyst Ni-10 at 22·0 °C and pH 7·0. Little variation in the %D content of the gas evolved was found; the values ranged from 39·7 to 41·5%.

Although the percentage deuterium in the total gas evolved for complete reaction is approximately constant, a systematic change in %D with extent of reaction was observed. This is illustrated by the results in Table 3 for Ni-6 catalyst at 45 °C, 0·5M-hypophosphite and pD = 7·0.

Figure 7 contains some plots of %D *versus* reaction time for the hydrolysis using different catalysts and temperatures. In all cases the low initial deuterium content rises to a limiting value as the reaction proceeds.

TABLE 3

Gas composition as a function of reaction time

| Sampling time/min | Molar ratios | | | %D |
|---|---|---|---|---|
| | $H_2$ : | HD : | $D_2$ | |
| 0—6 | 7·64 | 3·46 | 1·00 | 22·60 |
| 6—20 | 2·74 | 2·21 | 1·00 | 35·37 |
| 20—31 | 2·00 | 1·91 | 1·00 | 39·82 |
| 31—43 | 1·63 | 1·69 | 1·00 | 42·71 |
| 43—54 | 1·56 | 1·70 | 1·00 | 43·43 |
| 54—76 | 1·36 | 1·55 | 1·00 | 45·39 |
| 76—125 | 1·34 | 1·58 | 1·00 | 45·66 |
| 125—196 | 1·38 | 1·74 | 1·00 | 45·38 |
| 196—276 | 1·51 | 1·79 | 1·00 | 44·07 |
| 276—310 | 1·60 | 1·92 | 1·00 | 43·36 |

If the hydrolysis of the hypophosphite ion is carried out in mixtures of water and deuterium oxide, it is found that preferential evolution of hydrogen occurs. This 'isotope-separation effect' is illustrated by the data (for Ni-10 catalyst) in Figure 8 where the dashed line indicates the results expected if no isotope separation occurred. In this case the proportion of deuterium expected in the gas would be *ca.* 40% of that in the solvent (*cf.* Table 2). An isotope separation factor $S$ can be defined[19] by equation (2) in which $[H/D]_{gas}$ refers to that arising from the solvent, *i.e.* 40% of the total gas evolved. If $b$ is the % deuterium in the total gas evolved, then that in the gas from the solvent is 2·5$b$ since the hypophosphite ion yields only hydrogen from the P–H bonds. If $a$ is the % $D_2O$ in the solvent, then equation (2) becomes (3) leading to (4),

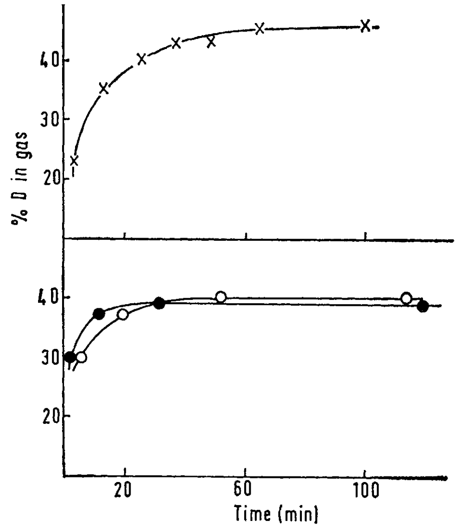

FIGURE 7 Percentage deuterium in the gas evolved as a function of time for the reaction in deuterium oxide. × Ni-6, $[H_2PO_2^-]$ = 0·5M, 45 °C; ● Ni-6, $[H_2PO_2^-]$ = 0·1M, 57 °C; ○ Ni-4, $[H_2PO_2^-]$ = 0·1M, 57 °C

$$S = \frac{[H/D]_{gas}}{[H/D]_{solution}} \tag{2}$$

$$S = \left[\frac{100 - 2{\cdot}5b}{2{\cdot}5b}\right] \Big/ \left[\frac{100 - a}{a}\right] \tag{3}$$

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[17] K. A. Holbrook and P. J. Twist, *J. Chem. Soc.* (*A*), 1971, 890.

[18] N. V. Sidgwick, 'The Chemical Elements and Their Compounds,' Clarendon, Oxford, 1950, 2, 1435.

[19] J. O'M. Bockris, 'Modern Aspects of Electrochemistry,' Butterworths, London, 1954, pp. 198—213.

and if $(40 - b)/b$ is plotted against $(100 - a)/a$, a straight line of slope equal to the isotope separation factor $S$ should result. Such a plot of the data of Figure 8 is shown in Figure 9 from which an isotope-separation factor of 8·9 for the nickel–boron catalyst (Ni-10) can be derived.

$$\frac{[40 - b)}{b} = S\left[\frac{100 - a}{a}\right] \qquad (4)$$

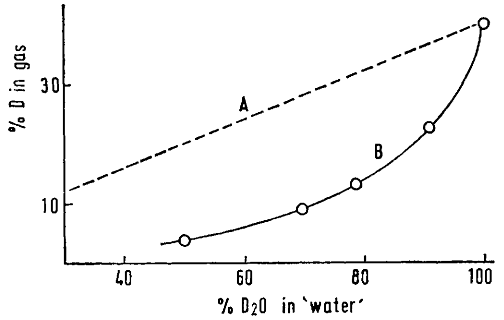


FIGURE 8 Percentage deuterium in gas *versus* % $D_2O$ in the 'water' for the reaction in mixtures of $H_2O$ and $D_2O$: A, no isotope separation; B, observed separation

## DISCUSSION

The principal results obtained from measurements of hydrogen evolution show that the stoicheiometry of reaction (1) is obeyed, 95—97% of the theoretical yield of hydrogen being found (Table 1) and that the reaction is unaffected by phosphite ions. The order of the reaction in hypophosphite ion is variable (Figure 3) although at low hypophosphite concentrations (0·025—0·100M) the reaction is first order.

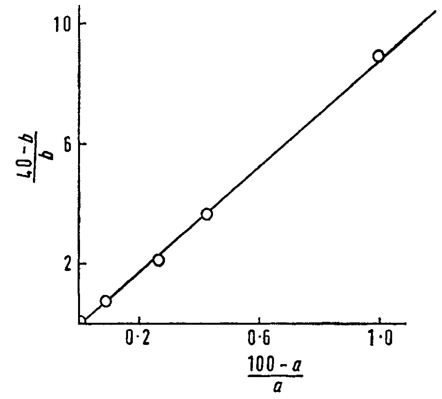
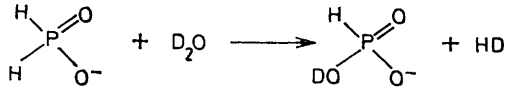


FIGURE 9 The isotope separation effect: $a$ = % $D_2O$ in 'water;' $b$ = %D in gas evolved



(5)

(6)

The use of n.m.r. to measure hypophosphite- and phosphite-ion concentrations has proved to be valuable for the hydrolysis carried out in $D_2O$. Two possible overall reactions can occur in this solvent, leading to the replacement of either one [equation (5)] or both [equation (6)] P–H bonds by P–D bonds. Since the fully deuteriated phosphite species produced in (6) is not detected by proton n.m.r. spectroscopy, the measured reaction corresponds only to (5). From the observed slope of line B in Figure 6 it can therefore be concluded that under these conditions 80% of the reaction occurs by the overall path (5) and presumably the remaining 20% by path (6). Since path (5) produces HD whereas (6) leads to $H_2$, the total percentage deuterium in the gas for complete reaction should be 40% which agrees well with the gas-analysis results presented in Table 2. Similar results have previously been reported by Franke and Mönch[6] and by Sutyagina *et al.*[11] Previous detailed mechanisms for the metal-catalysed solvolysis of the hypophosphite ion have been put forward by Gutzeit[8] and by Lukes.[20] The Gutzeit mechanism involves the simultaneous loss of two hydrogen atoms from the hypophosphite ion to the catalyst in step (7) followed by steps (8) and (9) where M represents a

$$2M + H_2PO_2^- \longrightarrow 2MH + PO_2^- \qquad (7)$$

$$PO_2^- + D_2O \xrightarrow{Cat.} DPO_2(OD)^- \qquad (8)$$

$$2MH \xrightarrow{Cat.} 2M + H_2 \qquad (9)$$

surface site and $D_2O$ is assumed to be the solvent for the sake of clarity. The Lukes mechanism written in these terms for alkaline or neutral conditions involves a rate-determining transfer of a hydride ion (10) followed by step (11). Both of these mechanisms are consistent

$$M + H_2PO_2^- + D_2O \longrightarrow MH^- + HPO_2(OD)^- + D^+ \qquad (10)$$

$$MH^- + D_2O \longrightarrow HD + M + OD^- \qquad (11)$$

with first-order kinetics in hypophosphite ion and since it has been concluded that overall processes (5) and (6) occur simultaneously, an obvious correlation appears to be that the Gutzeit mechanism applies to process (6) and the Lukes mechanism simultaneously accounts for process (5).

There are however, some difficulties in accepting this idea of two independent concurrent mechanisms. In particular it is difficult to explain the variation of %D in the gas evolved with reaction time which would require the Gutzeit mechanism to predominate in the early stages of the reaction. A possible mechanism which can account for most of the observed features of the reaction is described by steps (12)—(16). This mechanism is similar in some respects to that which we have proposed previously[17] for the hydrolysis of the borohydride ion under similar conditions. In this mechanism, hydride-ion transfer to the surface occurs by the three steps (12)—(14), the first two of which are written as reversible processes. Steps (15) and (16) have previously been proposed to account for the electrochemical evolution of hydrogen on nickel

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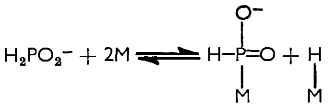
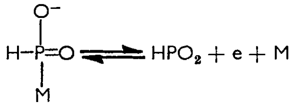
[20] R. M. Lukes, *Plating*, 1964, **51**, 969.

cathodes in aqueous alkaline solution.[21] The overall reaction (5) is given by the sum of steps (12) to (16).



$$H_2PO_2^- + 2M \rightleftharpoons H{-}\overset{\overset{O^-}{|}}{\underset{\underset{M}{|}}{P}}{=}O + \underset{\underset{M}{|}}{H} \qquad (12)$$



$$H{-}\overset{\overset{O^-}{|}}{\underset{\underset{M}{|}}{P}}{=}O \rightleftharpoons HPO_2 + e + M \qquad (13)$$

$$HPO_2 + D_2O \longrightarrow HPO_2(OD)^- + D^+ \qquad (14)$$

$$M + e + D_2O \longrightarrow MD + OD^- \qquad (15)$$

$$MD + MH \rightleftharpoons 2M + HD \qquad (16)$$

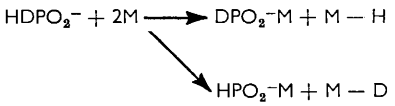
Adsorbed deuterium atoms produced in step (15) may lead to HD by step (16). If the surface were saturated with hydrogen and deuterium atoms, one would expect to find approximately equilibrium proportions of $H_2$, $D_2$, and HD produced by steps analogous to (16), and consequently about 50% deuterium in the gas evolved.

The fact that less deuterium is found is explained by the occurrence of overall reaction (6). Proton n.m.r. experiments have shown that *ca.* 80% of the total phosphite formed is $HPO_2(OD^-)$. If it is assumed that the remaining 20% is $DPO_2(OD^-)$, as seems reasonable, then the occurrence of reaction (6) to the extent 20% of the total reaction would result in 40% deuterium in the gas evolved.

A mechanism which could account for this would involve steps (12)—(15) followed by the participation of adsorbed deuterium atoms in the reverse step (—12) rather than (16), *i.e.*

$$M - D + HPO_2^-M \longrightarrow HDPO_2^- + 2M \qquad (-12)$$

This removal of deuterium from the gas could account for the low percentage deuterium found in the gas in the initial stages of the reaction (Table 3). As the reaction proceeds and the species $HDPO_2^-$ builds up, it could lead to the production of adsorbed H atoms and D atoms again by the reactions



$$HDPO_2^- + 2M \longrightarrow DPO_2^-M + M - H$$

$$HDPO_2^- + 2M \longrightarrow HPO_2^-M + M - D$$

Eventually the system appears to come to an equilibrium position with 20% $D_2PO_3^-$ in solution and *ca.* 40% deuterium in the gas evolved.

It is not so obvious why the % deuterium reaches a limiting value before the completion of the reaction (unlike the borohydride system [17]) although this appears to indicate the establishment of a constant proportion of P–D bonds in the hypophosphite produced by step (—12). The occurrence of an isotope separation effect in mixtures of water and $D_2O$ is evidence for the electrochemical step (15) and reflects the difference in rate for this step when $H_2O$ and $D_2O$ are involved. The magnitide of the effect observed is similar to that found in the hydrolysis of the borohydride ion [17] and in the electrochemical evolution of hydrogen on metal cathodes.[19]

[1/1985 *Received, 27th October*, 1971]

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[21] S. Srinavasan, H. Wroblowa, and J. O'M. Bockris, *Adv. Catalysis*, 1967, **71**, 394—396.