Mechanisms of Removal of Hydrogen from Palladium–Hydrogen by Oxidation.

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The controlled removal of hydrogen from palladium–hydrogen has been studied. In solutions of strong oxidising electrolytes, removal starts without appreciable induction periods. Ceric salts give readily controlled removal. Kinetic studies are reported on the system ceric ammonium sulphate–sulphuric acid–palladium–hydrogen.

Oxidation also proceeds when palladium–hydrogen is stored under water, exposed to oxygen. But when dry specimens are stored in the open air under normal conditions, palladium wire will retain hydrogen in concentrations as high as H/Pd = 0·6 for periods of up to one year. When similar specimens are enclosed with air or oxygen in glass tubing, the hydrogen is completely removed from the palladium by oxidation. This oxidation follows an induction period whose duration is affected by many variables. In particular, the induction period can be indefinitely prolonged when steps are taken to remove water vapour from the reaction vessel. It seems likely that the hydrogen is oxidised by oxygen by an ionic mechanism.

Under moist conditions, oxidation of metals by atmospheric oxygen could involve as one of the steps the oxidation of hydrogen atoms adsorbed on the surface of the metal. These hydrogen atoms are formed by discharge of hydrogen ions from solution. When the metal contains hydrogen in solid solution, as in palladium–hydrogen alloys, this adsorbed film of hydrogen can be maintained by diffusion from the interior. Mechanisms of removal of hydrogen from palladium–hydrogen by oxidation may thus be related to a number of key processes in the physical chemistry of corrosion, and of hydrogen in metals.

After palladium has been charged with hydrogen by electrolysis, the conditions for escape are as follows. With $H/Pd > 0{\cdot}6$, hydrogen rapidly escapes *in vacuo* from the alloy even at room temperatures. With $H/Pd \leqslant 0{\cdot}6$, hydrogen is held for indefinite periods at room temperature but escapes on heating to 200°. As discussed in this paper, removal can also be achieved by various processes of oxidation.

From alloys with $H/Pd \leqslant 0{\cdot}6$ removal at room temperature takes place when the alloy is made the anode of an electrolytic cell (Nähring, *Ann. Physik*, 1934, **21**, 303; Moore, *Trans. Electrochem. Soc.*, 1939, **75**, 237; Lewis, Roberts, and Ubbelohde, *Proc. Roy. Soc.*, 1953, **220**, 279. The present work deals with the removal of hydrogen by other oxidation processes. As shown below, ceric ammonium sulphate removes hydrogen from the alloy, with simultaneous quantitative reduction of the oxidising agent. This gives one method for controlled removal of portions of the hydrogen. Rate-measurements on this process are reported.

In the extensive literature on palladium–hydrogen, conflicting statements appear on the stability of the alloy when exposed to gaseous oxygen. Some authors (Michel, Bénard, and Chaudron, *Bull. Soc. chim.*, 1943, **12**, 336) claim immediate loss of hydrogen from palladium–hydrogen on exposure to air. Others (Sieverts, *Z. physikal. Chem.*, 1914, **88**, 103; Puoduzuikynas, *Z. Physik*, 1927, **46**, 253; Norberg, *Phys. Review*, 1952, **86**, 745) report the retention of hydrogen by palladium for long periods under normal atmospheric conditions.

In the present work slow oxidation by atmospheric oxygen always occurred when palladium–hydrogen was stored under water. Although dried palladium–hydrogen retained its hydrogen for indefinite periods in the open atmosphere, yet removal of the hydrogen to form water took place, after variable induction periods, when the palladium–hydrogen was enclosed in glass vessels. Though the duration of the induction period was influenced by many variables, water must apparently always be present before reaction with atmospheric oxygen can proceed at appreciable rates. Possible mechanisms for the removal of hydrogen from palladium by oxidation are discussed below. It seems likely that water is required because of easier oxidation of hydrogen when ionic mechanisms can play a part.

EXPERIMENTAL

Palladium (Johnson & Matthey) was in the form of wire of 0·27 mm. diameter, or strip 1·75 mm. wide × 0·075 mm. thick. Both wire and strip were 99·9% pure and contained as impurities: Ir, ≯0·05—0·1; Pt, Rh, ≯0·03—0·05; Cu, Ca, ≯0·02; Mg, ≯0·01; Fe, ≯0·005; Ag, ≯0·02%.

Electrolytic Charging and Direct Estimation of the Hydrogen Content.—The palladium was charged with hydrogen by electrolysis. For reasons previously discussed (Lewis, Roberts, and Ubbelohde, *loc. cit.*) the electrolyte used was a 2% solution of sodium fluoride and the current density was 1·3 amp./dm.^{2}.

Up to a dozen specimens of wire or strip 10 cm. long were mounted symmetrically in a Tufnol frame round a platinum anode and were charged simultaneously, to ensure similar conditions for the entry of hydrogen. The wire or strip was then washed with distilled water and dried with filter-paper. When a specimen was heated at 200° in an evacuated vessel of calibrated volume (Lewis *et al.*, *loc. cit.*) the pressure developed gave the Pd/H ratio in the alloy. Tests showed samples from one batch were reproducible to ±2%. This method is referred to below as " degassing analysis."

Atmospheric Oxidation of Palladium–Hydrogen in Aqueous Solution.—Charged specimens from one batch were placed under distilled water in conical flasks open to the air. By " degassing analysis " after various time intervals, it was found that hydrogen was slowly but completely removed at room temperature. The rate of removal was greatly increased if a stream of oxygen was bubbled through the water. Another four-fold increase in removal rate occurred when pure water was replaced by 2M-sodium hydroxide or 2M-sulphuric acid.

Irrespective of the pH, no loss of hydrogen could be detected if oxygen-free nitrogen was bubbled through the water instead of oxygen. All the experiments with oxidising solutions described below were therefore carried out under oxygen-free nitrogen.

Removal of Hydrogen from Palladium–Hydrogen by Oxidising Solutions.—Oxidising solutions tried were iodine in potassium iodide, potassium permanganate, and ceric ammonium sulphate in 1·0M-sulphuric acid, all 0·01M or 0·1M and standardised by established methods.

Iodine in potassium iodide. Reduction of iodine was estimated colorimetrically, by comparison with standard solutions of iodine in a simple comparator. More than 20 specimens of palladium, charged with hydrogen to concentrations up to 0·6 H/Pd, were immersed in 0·01M-solutions of iodine in potassium iodide. In all but four of these experiments no reduction of the iodine was observed. In one of four instances, reduction began after a time lag of 1 day, and in another case after a lag of 4 days. Reduction started immediately after immersion in the other two cases. No interpretation of these variable induction periods is offered at present.

Potassium permanganate. Only visual observations were made on permanganate solutions. On immersion of palladium–hydrogen in neutral or 2M-acid solutions of potassium permanganate at about 20°, flakes of manganese dioxide were rapidly formed on the surface of the palladium. These may have blocked access of fresh oxidising agent of the alloy, though further reduction was apparently not completely prevented. The precipitate gradually became dispersed through the solution. No attempts were made to follow rates of oxidation quantitatively.

Ceric ammonium sulphate. Reduction of this reagent was determined by titration. 15 Ml. of the solution of oxidising agent were placed in a number of 25-ml. stoppered flasks. Specimens were introduced either of the charged palladium–hydrogen, or of uncharged palladium (for blank experiments). At intervals, 1 ml. of solution was withdrawn and titrated against ferrous ammonium sulphate (tris-*o*-phenanthroline as indicator). Reactions were carried out in an ice-bath, or in baths kept by thermostat at 25° ± 0·1° and 50° ± 0·1°.

As with potassium permanganate, all the palladium–hydrogen specimens began to reduce ceric solutions immediately after immersion. For rate measurements, ceric salts had the advantage over potassium permanganate in that the reduction product was colourless and soluble. Control experiments showed that some reduction of the ceric solution was caused by the hydrogen-free palladium at 50° in the 1·0M-acid solution used to prevent hydrolysis of the ceric sulphate. The rate curve for 50° was corrected to allow for this. Four experimental runs were carried out at each temperature, and the results averaged. Fig. 1 shows that the results agree with first-order kinetics with respect to the concentration of ceric ammonium sulphate during the first part of the reaction. With the possible exception of the reaction at 0°, examination for second-order kinetics by plotting C against t gave non-linear plots (not shown). The activation energy of the reaction as calculated from the slopes in Fig. 1 is as shown in the following table.

Temp.	0°	25°	50°
log k, sec.$^{-1}$	$-5{\cdot}54$	$-5{\cdot}34$	$-4{\cdot}89$
E (kcal./mole)	2·9	8	

By " degassing analysis " of the residual hydrogen, after removal of part by oxidation, it was verified that the amount of hydrogen lost was exactly equivalent to the amount of ceric ion reduced, for specimens containing H/Pd $\not> 0{\cdot}6$. Specimens of palladium–hydrogen degassed when further reduction of ceric ion was no longer detected contained no hydrogen within experimental error (H/Pd $< 0{\cdot}01$). As in other instances, specimens with H/Pd $> 0{\cdot}6$ lost some hydrogen spontaneously as bubbles of gas.

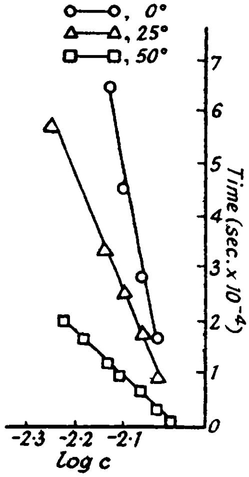


FIG. 1. *Logarithmic unimolecular plots of oxidation rates.*

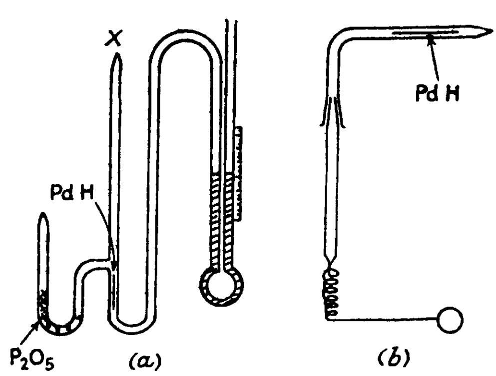


FIG. 2. *Reaction tubes for the oxidation of* Pd–H *by air.*

Preliminary experiments with 0·1M-solutions of ceric ammonium sulphate showed that removal was much faster than with 0·01M. Further studies of reaction rates were not attempted. Many other variables could obviously be explored in a complete study. The present investigations were intended as background to the observations on removal in the various circumstances described in this paper. It was considered especially important to examine whether any induction periods were shown in this system.

Stability of Palladium–Hydrogen in vacuo *and in Nitrogen.*—Experiments confirmed that the palladium wire and strip used in the present work retained hydrogen at concentrations of 0·6 H/Pd for indefinite periods at room temperatures *in vacuo* or in oxygen-free nitrogen.

Oxidation of Palladium–Hydrogen in Air.—An observation by Monckman (*Proc. Roy. Soc.*, 1888, **44**, 220) was confirmed. When palladium–hydrogen in wire form was heated in a Bunsen flame at one end, a tiny flame caused by combustion of hydrogen travelled along the wire from the point of heating. However, when the palladium–hydrogen was heated quickly to 200° after being enclosed in a Pyrex tube, the hydrogen was released as gas, similar to the effect *in vacuo*. At this temperature no detectable reaction with the air in the tube had occurred. On the temperature being then raised at one end of the palladium to red heat, by means of a Bunsen burner, an explosive reaction occurred between the hydrogen and the air.

No loss of hydrogen could be detected when charged specimens were stored in the open air at room temperature. For more detailed tests, charged specimens were enclosed in an atmosphere of air in simple containers of Pyrex glass tubing of 3—5 mm. bore (Fig. 2*a*). In special experiments, a Pyrex spiral gauge with mirror was sealed on (Fig. 2*b*) to permit continuous recording of changes in pressure by means of a light-beam falling on a rotating drum carrying light-sensitive paper. More generally, in view of the large number of experiments carried out, it proved convenient to use a simple manometer (Fig. 2*a*). The indicator liquid in the manometer was mercury or Apiezon oil, or other liquids as indicated below. Tubes were kept in the laboratory at about 18°. Visual readings of the manometer pressure were taken at intervals. Corrections for slight fluctuations of room temperature and pressure, which might obscure the induction period, were made from observations with an apparatus of similar volume which had no alloy introduced into it.

These simple containers had side arms into which phosphoric oxide could be introduced. This avoided contamination of the walls of the container near to the specimen by phosphoric acid. Alternatively, the containers could be opened momentarily at *X* to introduce drops of water or hydrogen peroxide near to the palladium–hydrogen before resealing.

General Observations on the Induction Period preceding Rapid Oxidation of the Palladium–Hydrogen.—When specimens of palladium wire charged to concentrations of *ca.* $H/Pd \leqslant 0{\cdot}6$ were degassed after being in the open air for periods up to 1 year, they still contained as much hydrogen as specimens charged under the same conditions and degassed immediately after charging. Occasionally, some loss of hydrogen was observed from specimens in the form of strip, although most of these had also retained their initial content of hydrogen.

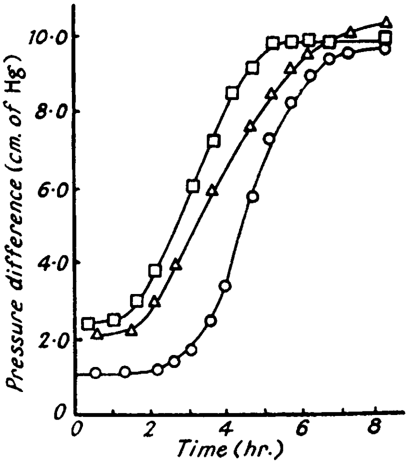


FIG. 3. *Illustrations of induction periods in the oxidation of* Pd/H *by air*

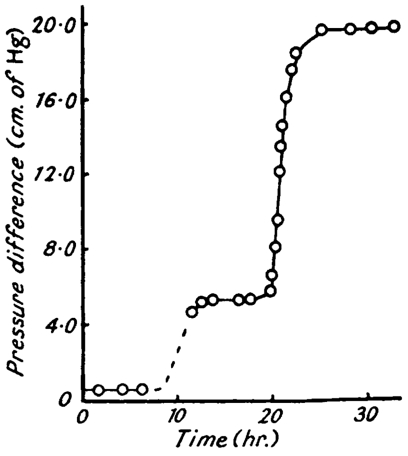


FIG. 4. *Oxidation of two specimens of* Pd/H *side by side.*

However, when specimens were enclosed as described above, pressure–time curves showed that after a variable but much shorter period the hydrogen from the palladium combined with oxygen in the air. During the period of detectable pressure changes a fine mist of water droplets was formed on the glass walls immediately around the specimen. Potassium iodide–starch being used as reagent, no hydrogen peroxide could be found in these deposited droplets. No back-pressure changes were ever observed, due to an accumulation of hydrogen peroxide followed by its catalytic decomposition with re-formation of oxygen. A few of the many curves obtained are reproduced in Fig. 3 to illustrate the general course of the reaction. By degassing the palladium after all pressure changes had ceased, any residual hydrogen was almost always found to be less than the limits of detectability ($H/Pd \ngtr 0{\cdot}01$). The volume of hydrogen gas at S.T.P. originally contained in each specimen was $\sim$3 ml.

Effect of Water on the Induction Period.—The duration of the induction period and the rate of the subsequent reaction were very variable. The effect of water was examined in some detail. Definite lengthening of the induction period was observed when the reaction tube and specimen were very carefully dried. Very great lengthening of the induction period (in almost all cases to indefinite periods) was observed when phosphoric oxide was introduced into the reaction vessel and held either in a side arm or behind a glass wool plug.

Although water seemed necessary for reaction to start, the presence of water did not result in all cases in a complete suppression of the induction period. For example, Fig. 4 shows how two specimens, side by side in the same container, reacted independently. During the distinct interval between the ends of the two induction periods, the second specimen was intimately surrounded by the water vapour produced by the first specimen.

Apparently, many other variables also affect the induction period. Effects recorded below were less sharply conclusive and reproducible than the effect of intensive drying, but definite trends were exhibited when comparison was made over a large number of experiments under comparable conditions.

(1) Tubing bore. Increasing the bore of the tubing lengthened the induction period and decreased the rate of reaction.

(2) Manometer liquid. The induction period was lengthened, compared with mercury, when dibutyl phthalate or Apiezon oil was used as manometer liquid.

(3) Surface area and extent of cold-working of the palladium. The induction period was longer with palladium wire than with strip.

(4) Effect of ageing palladium–hydrogen. When specimens of wire with H/Pd ~0·6 had been left in the open air for about 6 months before being introduced into a reaction vessel, the induction period was indefinitely long even in the presence of water vapour. Hydrogen was, however, readily and immediately removed from these specimens by solutions of ceric ammonium sulphate.

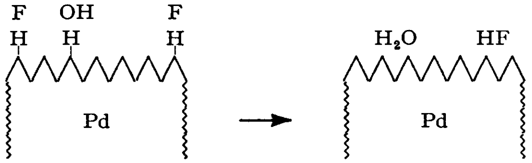
(5) Initial concentration of hydrogen in the palladium. Induction periods were shorter the higher the initial concentrations of hydrogen, up to H/Pd = 0·6.

(6) Effect of trimethylamine. This substance was tested because it is a typical anti-oxidant in oxidation chains involving peroxide radicals. When the specimens after charging were quickly dipped in trimethylamine and wiped dry before introduction into the reaction vessel, the induction period was lengthened and the rate of the subsequent reaction reduced.

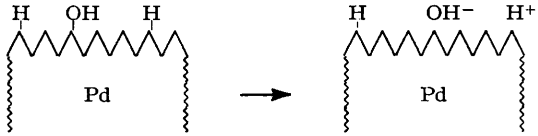
(7) Effect of hydrogen peroxide. When charged specimens were quickly dipped in 100-vol. hydrogen peroxide made just alkaline and then wiped with filter-paper before introduction into a reaction vessel, the induction period was reduced and in some cases removed. Attempts were also made to introduce minute traces of hydrogen peroxide in acid, neutral, or alkaline solution, either close to, or on to the surface of a specimen already within a reaction tube. Such traces did not appear to bring the induction period preceding oxidation to an abrupt end. These observations were, however, complicated because of pressure changes resulting from decomposition of peroxide, especially when in actual contact with the metal surface. Possible effects of antioxidants added to commercial hydrogen peroxide to stabilise it are unlikely to complicate the experiments, since sufficient pure peroxide should have distilled on to the specimens, from drops placed nearby, to give a fair test.

DISCUSSION

(1) *Electrochemical Removal of Hydrogen from Palladium–Hydrogen.*—The experiments now reported link oxidations by acid ceric sulphate with anodic oxidation previously described by a number of authors (*locc. cit.*). In anodic removal of hydrogen, the mechanism of reaction may involve adsorption of discharged atoms of F or discharged radicals OH on the surface, followed by the desorption of HF or H_2O :

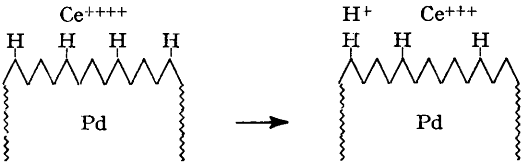


Without further evidence, it is not possible to distinguish between this process and one in which OH or F are desorbed as ions after electron transfer from proximate hydrogen :



As soon as a vacant site is formed in the surface of the alloy, it can become occupied by a fresh hydrogen atom diffusing from the interior.

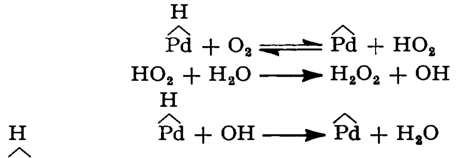
It seems likely that oxidation of palladium–hydrogen by ceric sulphate is analogous in mechanism to anodic oxidation. Either there is direct sorption of ceric ions on the surface, followed by electron transfer and desorption :



or the ceric ions produce free (OH) radicals in solution, in the oxidation–reduction equilibrium (cf. Ubbelohde, *J.*, 1935, 1605) $Ce^{4+} + OH^- \rightleftharpoons Ce^{3+} + OH$ and the adsorption of OH is followed by oxidation of hydrogen atoms on the surface precisely as in anodic discharge. The oxidation–reduction potential of ceric sulphate ($E^0 = 1{\cdot}61$ v) seems sufficient to promote such a process. The rapid increase in oxidation rate with increase in concentration of Ce^{4+} gives some support to this second possibility. It is noteworthy that in 0·01M-ceric sulphate, the rate of oxidation corresponds with a current density of 0·05 amp./dm.^{2} (if it is assumed that Faraday's law applies accurately to anodic oxidation). In 0·1M-solutions the oxidation rate corresponded approximately with 1 amp./dm.^{2}.

So far as present evidence goes, the rate of oxidation is of zero order with respect to the H/Pd ratio at low concentrations of ceric sulphate. This can be explained on either of the above mechanisms, if the controlling reaction rate refers to the chemical action of OH or Ce^{4+} at a surface always effectively covered with hydrogen atoms bonded to surface palladium atoms. This would be the case if the rate of emergence of fresh hydrogen atoms on to vacant palladium atoms in the surface is rapid compared with the other reaction rates.

(2) *Oxidation of Palladium–Hydrogen by Atmospheric Oxygen in Aqueous Solution.*—Oxidation of hydrogen in palladium–hydrogen by atmospheric oxygen may be related to the oxidation of other metals in aqueous solution. A free-radical mechanism or an ionic mechanism offers possible explanations. The processes are thought to occur at the metal surfaces, which need not, however, be uniformly covered with hydrogen. The free-radical mechanism might involve as likely steps



$$\overset{H}{\widehat{Pd}} + O_2 \rightleftharpoons \widehat{Pd} + HO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i)}$$

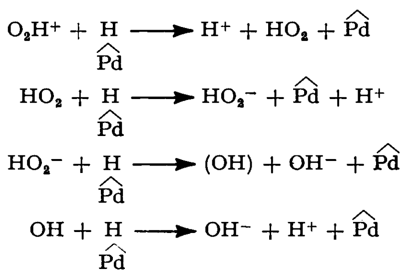
$$HO_2 + H_2O \longrightarrow H_2O_2 + OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(ii)}$$

$$H \qquad \overset{H}{\widehat{Pd}} + OH \longrightarrow \widehat{Pd} + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iii)}$$

(The symbol $\widehat{Pd}$ refers to hydrogen atoms chemisorbed on palladium atoms in the surface.)

It has not yet proved possible to detect the accumulation of hydrogen peroxide, but any hydrogen peroxide is probably decomposed too rapidly catalytically by the palladium. This would agree with the observation that transitional metals are not found to exhibit the Russell effect (cf. Churchill, *Trans. Electrochem. Soc.*, 1939, **76**, 341).

Acceleration of oxidation by atmospheric oxygen when the solution is made either acid or alkaline favours an ionic mechanism, which may require regions of different potential in order that they may proceed smoothly (cf. Evans, " Introduction to Metallic Corrosion," Edward Arnold, London, 1948, p. 27) :



$$OH_3^+ + O_2 \rightleftharpoons O_2H^+ + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iv)}$$

$$O_2H^+ + \underset{\widehat{Pd}}{H} \longrightarrow H^+ + HO_2 + \widehat{Pd} \quad . \; . \; . \; . \; . \; . \; . \quad \text{(v)}$$

$$HO_2 + \underset{\widehat{Pd}}{H} \longrightarrow HO_2^- + \widehat{Pd} + H^+ \quad . \; . \; . \; . \; . \; . \; . \quad \text{(vi)}$$

$$HO_2^- + \underset{\widehat{Pd}}{H} \longrightarrow (OH) + OH^- + \widehat{Pd} \quad . \; . \; . \; . \; . \; . \; . \quad \text{(vii)}$$

$$OH + \underset{\widehat{Pd}}{H} \longrightarrow OH^- + H^+ + \widehat{Pd} \quad . \; . \; . \; . \; . \; . \; . \quad \text{(viii)}$$

In alkaline solutions the first steps are probably somewhat different :

$$O_2 + \underset{\widehat{Pd}}{H} \longrightarrow O_2H + \widehat{Pd} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(ix)}$$

$$O_2H + OH^- \longrightarrow HO_2^- + OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(x)}$$

$$OH + \underset{\widehat{Pd}}{H} \longrightarrow OH^- + \widehat{Pd} + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(xi)}$$

with the subsequent removal of H_2O_2 as at (vii) and (viii) above.

(3) *Oxidation of Palladium–Hydrogen by Atmospheric Oxygen in the Air.*—Whilst the above steps are still tentative, they throw some light on the possibilities in the gas phase. The long induction periods observed in many cases might be due to the existence of a poisoning layer of adsorbed atoms at the surface of palladium–hydrogen. Poisons from the drying agent used have been suggested in similar cases (Hinshelwood and Williamson, " The Reaction between Hydrogen and Oxygen," Clarendon Press, Oxford, 1934, p. 3; Schwab, " Catalysis," Macmillan and Co., London, 1937, p. 37). Oxygen is known to inhibit sorption of hydrogen by activated palladium (Ubbelohde, *Trans. Faraday Soc.*, 1932, **28**, 275). Presumably chemisorbed oxygen forms an adsorbed layer difficult to remove. On the principle of microscopic reversibility, if chemisorbed oxygen slows down the process $2\widehat{Pd} + H_2\,\text{(gas)} \longrightarrow PdH\,\text{(solid)}$ it must also slow down the reverse process. Some evidence is reported above suggesting such chemical poisoning by traces of volatile impurities in the open atmosphere, or by trimethylamine. However, the definite influence of water in shortening the induction period supports the view that water must accumulate in cracks and crevices of the metal before oxidation can proceed smoothly by an ionic mechanism. On this view the induction period would correspond with the time required to build up a system in which an ionic mechanism can proceed. Ionic oxidation itself does not seem to involve induction periods. Since water does not always immediately suppress the induction period, traces of hydrogen peroxide may be slowly formed by autoxidation in the water collected in minute crevices in the metal. So far as any hydrogen peroxide can accumulate, it could act as an electrolyte. In accordance with equations (iv) and (x) it has been verified that electrolytes furnishing hydrogen ions accelerate oxidation.

Finally, attention may be drawn to the practical consequences of this investigation. Treatment by ceric sulphate can be a very convenient method for partial withdrawal of hydrogen from palladium–hydrogen. Again, charged specimens are best kept in a dry inert atmosphere if required not to lose their hydrogen. When the metal is in a finely divided state, in the form of powder or sponge, palladium–hydrogen may be pyrophoric on exposure to air, and access to oxygen must be completely prevented at all times (Ubbelohde, unpublished observations).

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