spectrometric measurements, to T. Sugata for his collaboration in a part, and to K. Tanaka for his discussion.

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The Formation of Palladium Hydride by Reaction of Formic Acid at Palladium Electrodes

The hydrogen in palladium hydride electrodes can be used for the catalytic hydrogenation of ethylene (*1*) or acetylene (*2*). We have now examined the reverse type of catalytic process at a palladium electrode where hydrogen is a product of the reaction and not one of the reactants. Formic acid was chosen for study since the usual mode of decomposition on metal catalysts (*3*) is

$$HCOOH \rightarrow CO_2 + H_2 \qquad (1)$$

Treatment with aqueous formic acid (*4*) has been used to convert a palladium electrode into palladium hydride but rate data are lacking. The behavior of formic acid at metal electrodes is of interest in connection with some research on fuel cells as it may appear either as a by-product or an intermediate in the oxidation of methanol or of formaldehyde (*5*).

The experimental technique was similar to that previously described (*1, 6*). The amount of hydrogen in a fine palladium wire (0.0122-cm diam.) was determined by measurement of the ratio R/R_0, R being the electrical resistance and R_0 the resistance of the wire free from hydrogen. In some cases, electrode potentials of the wire were also determined and expressed with respect to a Pt/H_2 electrode in the same solution as the palladium wire. Experiments were carried out at 25° or 50°C and the specimens were immersed in aqueous solutions of formic acid which were stirred by a stream of argon. Some experiments were carried out with formic acid supplied by Hopkin and Williams, Ltd., others with AnalaR grade material from British Drug Houses, Ltd., but both gave similar results.

RESULTS AND DISCUSSION

Some characteristic results for R/R_0 are shown in Fig. 1(a) and the derived values of H/Pd are given in Fig. 1(b). No evolution of gas at the electrode was observed.

The initial rates of absorption of hydrogen were determined from the slopes of the curves for H/Pd at zero time. Nine results in separate experiments with 5 M formic acid at 50° gave rates within the limits of 7.3×10^{16} to 13.9×10^{16} molecules/sec cm^2 of apparent surface; the average value was 10.0×10^{16}. Initial rates with 1 M solutions were smaller by a factor of 2.0 to 2.5 and the apparent activation energy for both strengths of solution was about 5 to 6 kcal/mole. An initial rate at 50°C close to that for 5 M formic acid was found using 2.5 M sodium formate and so formate ions may react as readily as undissociated formic acid molecules.

Now rates of absorption of hydrogen of 10^{17} molecules/sec cm^2 are comparable with those obtained for wires immersed in aqueous solutions saturated with hydrogen gas under a pressure of about 10 atm and with similar conditions of stirring (*6*) and

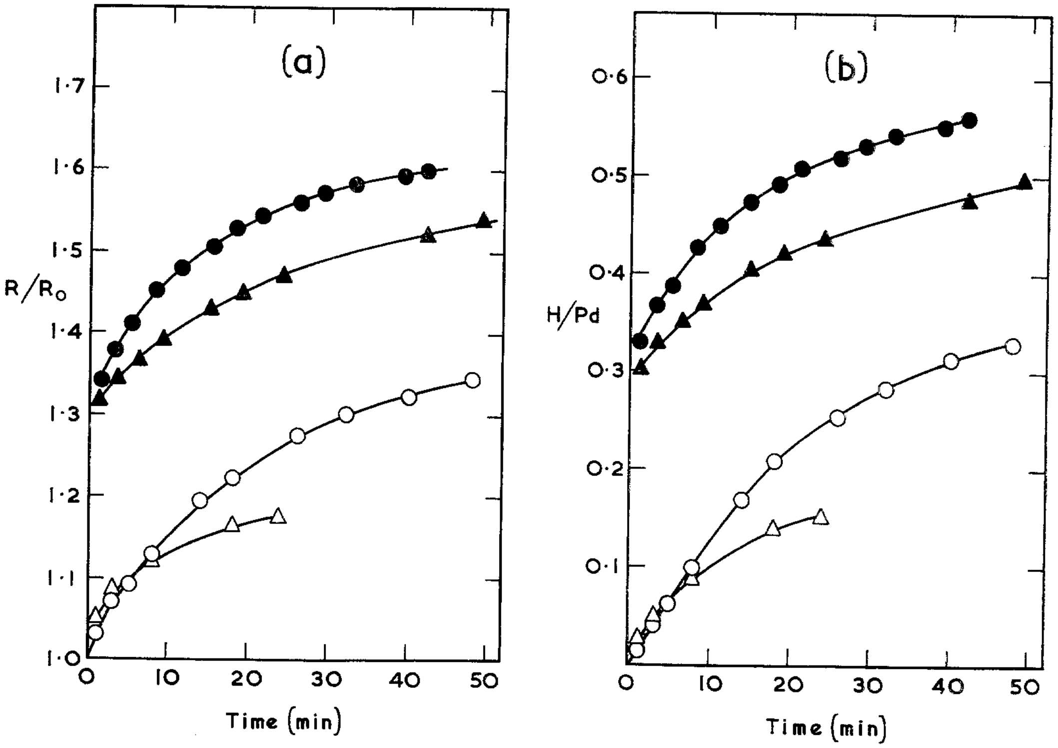

FIG. 1. The open symbols represent typical examples of the change of R/R_0 with time [Fig. 1(a)] and of the corresponding derived values of H/Pd [Fig. 1(b)] for specimens immersed in 5 M HCOOH at 50°C. The filled symbols represent experiments with the same specimens (after outgassing, flaming, and repalladizing) under identical conditions of stirring but partially charged with hydrogen initially.

so formic acid is a reasonably effective hydriding agent for the *initial* process.

The subsequent behavior of the systems was less reproducible than the initial rates of reaction. The rate of absorption of hydrogen always decreased and if the experiment was continued for a sufficient time the hydride started to revert to metal, as shown in Fig. 2(a). The maximum values of R/R_0 were generally 1.4 to 1.6 but occasionally only 1.1 to 1.2. Obviously the decomposition of formic acid by reaction (1) was gradually slowing down and once the supply of hydrogen from this source ceased the subsequent decreases of R/R_0 indicated that desorption of hydrogen from the palladium hydride occurred automatically in the argon-saturated solution. Values of R/R_0 have not been converted to H/Pd because desorption commenced from points within a hysteresis loop in the "desorption" relationships between H/Pd and R/R_0 (*7*).

The measurement of electrode potentials, some of which are shown in Fig. 2(b), support the conclusions derived from the changes of R/R_0 with time. In the early stages, the potential E was about +40 mV, which is equivalent to a pressure of hydrogen of some 60 mm. This pressure corresponds to the coexistence of the α- and β-phase hydrides of palladium at 50°C (*6*). In the latter stages, when evolution of hydrogen was occurring, the potential rose corresponding to a decrease in the equivalent partial pressure of hydrogen at the electrode.

The decline in the rate of decomposition was not attributable to a decrease in catalytic activity with increasing hydrogen content of the palladium. Specimens partially hydrided by treatment with hydrogen gas until R/R_0 was about 1.3 gave the same initial rates of absorption of hydrogen as found with specimens initially free of hy-

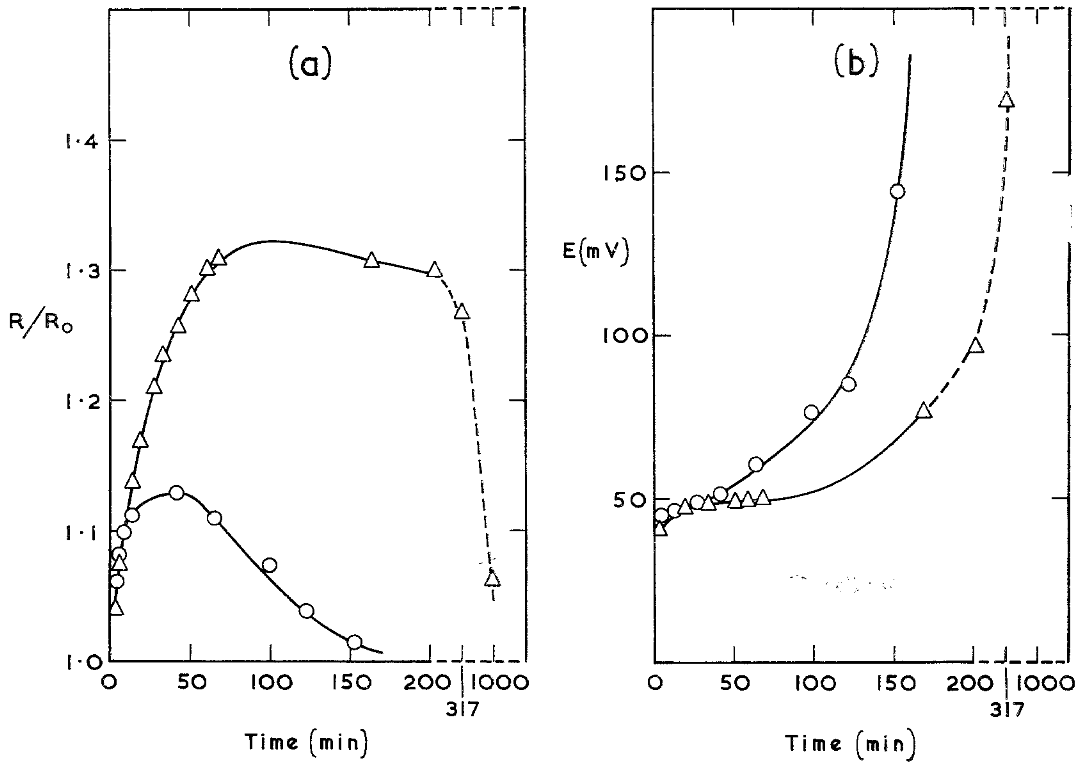

FIG. 2. Examples of the changes in time in 5 M HCOOH at 50°C of R/R_0 [Fig. 2(a)] and of the corresponding changes in E [Fig. 2(b)] which illustrate the change over from a decreasing rate of absorption of hydrogen to a spontaneous evolution of hydrogen from the specimens.

drogen; this is shown by the results in Fig. 1.

Experiments were carried out to see if one or more of the possible decomposition products of formic acid was acting as a poison. No marked effects on the rates of change of R/R_0 (and so of H/Pd) or of E were observed if vigorous bubble streams of either carbon monoxide or carbon dioxide were substituted for argon either before or during an experiment. On the other hand, the addition of a quantity of formaldehyde to a solution of 5 M formic acid, sufficient to give a ratio of HCHO to HCOOH of about 1 in 20, resulted in an abrupt halt in the rate of increase of R/R_0. The specimen, however, remained sufficiently active catalytically with respect to hydrogen for it to lose hydrogen on further standing in the argon-saturated solution, or to absorb hydrogen when the solution was saturated with hydrogen gas. When freshly palladized specimens were immersed in an argon-saturated solution of formaldehyde and formic acid, there was no indication of an increase in R/R_0. Thus, a possible source of the poisoning may be the decomposition of formic acid by the reaction

$$2HCOOH \rightarrow HCHO + CO_2 + H_2O \qquad (2)$$

We confirmed that in the normal experiments without added formaldehyde the poisoning was selective. Thus, although the decomposition of formic acid ceased, the palladium absorbed hydrogen readily if hydrogen gas was bubbled through the solution. Also specimens charged with hydrogen by immersion in formic acid (until $R/R_0 \sim 1.4$) retained an ability to reduce ethylene but at a rate some three times slower than the rate for specimens charged directly by hydrogen gas (*1*).

There is other evidence to support the idea that formaldehyde may interfere in reactions of formic acid on surfaces. It has been suggested (*3*) that the formation of polymeric species from traces of formaldehyde may poison the catalyzed decomposition of gas-phase formic acid. Furthermore, formaldehyde has been found (*8*) to be more resistant to electrochemical oxidation than either methanol or formic acid and an aldehydic species has been suggested (*5*) as the electrode poison responsible for the decreasing rates of electrolytic oxidation of formic acid with time at constant voltage (*5, 9*). A consequence of the poisoning we observe is that immersion in formic acid seems an unreliable method of charging palladium with hydrogen.

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Infrared Spectrum of Methyl Oleate Adsorbed on Silica

Although very much work has been carried out concerning the infrared spectrum of silica, little has been published on the spectrum of molecules adsorbed on silica. Sheppard and Yates (*1*) studied the spectra of methane, ethylene, acetylene, and hydrogen adsorbed on porous silica glass. The perturbing effect of the surface forces on adsorbed molecules caused small shifts towards lower wavenumbers in the frequency of the bands in the IR spectra. Sidorov (*2*), studying the spectrum of acetone and benzaldehyde on the same adsorbent, discovered that the wavenumber of the first overtone of the fundamental frequency of the carbonyl group decreased; the wavenumber of the carbon–hydrogen stretching vibration increased. Galkin, Kiselev, and Lygin (*3, 4*) studied the spectrum of benzene adsorbed on silica.

We have studied the spectrum of methyl oleate adsorbed from a solution in heptane on a pressed disc of Aerosil. The spectrum of the adsorbed molecules was recorded after removal of the solvent. With Aerosil dried at 750°C the following phenomena were observed:

The sharp band at 3738 cm^{-1}, ascribed to isolated surface hydroxyl groups, decreased with increasing surface concentration and a new band at 3420 cm^{-1} was formed. In addition to these changes in the silica spectrum, various changes in the spectrum of the adsorbed molecule were observed. Details are collected in Table 1. Although the frequency of the band at 3003 cm^{-1} remained the same, a change in intensity was observed.

Using Aerosil dried at 120°C the same phenomena were observed, except that the shift of the $>CH_2$ and $—CH_3$ vibrations was hardly noticeable.

These results suggest that a hydrogen bond is formed between the carbonyl group