Some Novel Electronic Effects in Hydrogenation Catalysis

THE SIGNIFICANCE OF ACIDITY AND REDOX POTENTIAL

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Recent work at the Johnson Matthey Research Centre has thrown fresh light upon the electronic effects in hydrogenation catalysis that underlie the whole nature of the catalytic act and in particular many of the effects that may manifest themselves as support metal interactions. The results show that currently accepted models of the catalytic act are incomplete, that ionic intermediates are sometimes important and that both the relative acidity of the reaction system and the redox potential of products and intermediates must be considered.

In the two most commonly accepted models for a hydrogenation reaction, one or both of the reactants are adsorbed on the surface, then reaction takes place and the product desorbs. These models are referred to as Eley-Rideal and Langmuir-Hinshelwood mechanisms, respectively. Such models frequently give an excellent representation of experimental results, but the parameter values so obtained cannot be confidently extrapolated in a quantitative manner from one reaction system to another.

In the Eley-Rideal and Langmuir-Hinshelwood models two types of parameter are important: adsorption coefficients representing the stabilities of the surface intermediates, and reaction rate constants representing the reactivity of the adsorbed intermediates. Naturally, one expects that these parameters are not uniquely determinable, but are in fact related, which is to say that the reactivity is in part influenced by the strength of adsorption. Thus, for example, in a recent international symposium on support-metal interactions (1) it was shown (2) that the ratio of adsorption coefficients for toluene and benzene derived from competitive hydrogenation via a Langmuir-Hinshelwood mechanism varied markedly with the apparent electronic state of the catalytic metal species when this was varied by changing the catalyst support or by using ammonia or hydrogen sulphide as catalyst modifiers. The changes in relative overall reactivity of these two reactants were, however, much smaller than expected since the increases in relative adsorptivity were offset by reduced relative reactivity.

Similar problems arise in the understanding of the all-important effects of alloying in bimetallic catalyst systems and the effects of metal dispersion on reactivity and selectivity.

In studying catalytic hydrogenation reactions we are accustomed to using the terms, "hydrogenation" and "reduction" synonymously. However, in electro-organic chemistry and other branches of chemistry "reduction", is given a more limited definition as meaning the addition of electrons to a substrate. In such a context hydrogenation involving the addition of a molecule of hydrogen becomes instead the addition of two electrons and two protons. Such additions can in principle be either sequential or in combination.

As a result of the considerations outlined above, we have studied a number of hydrogenation reactions in which the sequential addition of electrons and protons could be observed. In electro-organic chemistry, reactions of this type are customarily investigated by cyclic voltammetry in which the potential of the working electrode is controlled and changed

systematically. We chose instead to use a powdered carbon supported hydrogenation catalyst as our working electrode and to lower the reduction potential by the addition of hydrogen. These changes in the reduction potential of the reacting system are monitored by an inert gold sensor electrode operated in conjunction with a silver/silver chloride reference electrode. The experimental technique is very similar to that developed by Russian workers (3, 4) although the way we have used this technique differs in many other aspects, as will become apparent later.

Experimental Conditions

Hydrogenations were performed in an aqueous liquid phase system at ambient temperature and atmospheric pressure. The three necked 500 ml reaction flask was fitted with a standard glass electrode, a silver/silver chloride reference electrode and a gold wire sensor electrode to follow the potential of the catalyst. The hydrogen was sparged in at a rate of 100 ml/min and vented through a bubbler acting as a gas seal. The reaction flask contents were stirred by a magnetic stirrer at 600 rpm. Typically, 0.1 g 10 per cent palladium on carbon catalyst was used. Under these conditions the reactions studied are under gas mass transfer control where the rate is independent of the weight of catalyst used. Such conditions would normally apply in commercial applications of these catalysts. The reaction flask contents were buffered with appropriate combinations of sulphuric acid, acetic acid, sodium bicarbonate or sodium hydroxide. Standard phosphate (pH 7), citrate (pH 5.7) and borax (pH 9) buffers were also used.

In operation we customarily first reduced the slurried catalyst and equilibrated the reaction system. The measured redox potential at equilibrium in general was in good agreement with the reversible hydrogen potential for that particular reaction pH. To this equilibrated system we then added a known amount of the substance to be hydrogenated and followed the change in redox potential with time. Typically, upon adding the reactant the potential

immediately rose and then began to fall at a decreasing rate. Eventually, however, the potential falls at an increasing rate and then very rapidly back to the original hydrogen equilibrium potential. The net result is a reduction wave whose half wave potential we can measure and the total time taken to complete a reduction can also be measured.

Results and Discussion
Quinone Hydrogenation

Our interest in the quinone hydrogenation system was two-fold. First, different quinones have known and well-defined half-wave reduction potentials that are reversible and rapidly established. Figure 1 shows the variation in redox potential with time when a mixture of various quinones was added to the palladium catalysed reaction system at pH 7. Several reduction waves are observed which correspond to the known half wave reduction potentials of
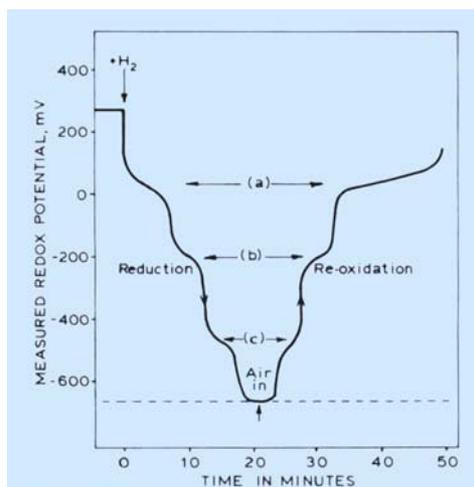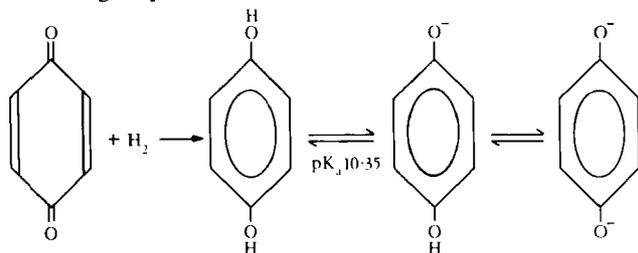

Fig. 1 As shown by the inflections in the potential/time curves the hydrogenation of a mixture of three quinones proceeds in sequential fashion. 1,4-benzoquinone (a) is hydrogenated completely before (b) 1,4-naphthaquinone which in turn is completely hydrogenated before (c) the anthraquinone 2,7 di-sulphonic acid. Subsequent oxidation dehydrogenates the products in the reverse sequence. 2 m moles of each quinone were used with 0.5 g 5% Pd/C catalyst at pH 7

the different quinones injected. The figure also shows the reversible nature of these reductions in that a mirror image is obtained if, at the completion of the hydrogenation, the oxidation potential is increased by adding air. It is important to note that the reduction of a particular quinone does not commence until all those with a higher potential have been completely hydrogenated. That is to say, the reduction is under complete control of the reduction potential of the system. Similar results have been reported recently in the commercially important hydrogenation of ethyl anthraquinone which is an intermediate in the manufacture of hydrogen peroxide (5). Here it was found, in a competitive hydrogenation experiment using both tetrahydro-2-ethyl-anthraquinone and 2-ethyl-anthraquinone, that the former was completely hydrogenated before the latter began to be hydrogenated in line with their relative redox potentials. Perhaps an even more dramatic illustration of redox potential control is shown in Figure 2. In this series of experiments we first hydrogenated a known amount of anthraquinone and to this reaction mixture then added varying amounts of benzoquinone. If less than an equivalent stoichiometric amount of benzoquinone was added, the only result seen was a rehydrogenation of the anthraquinone. If greater than a stoichiometric amount of benzoquinone was added, then reduction waves of both the excess benzoquinone and the stoichiometric quantity of anthraquinone produced by the dehydrogenation of anthrahydroquinone are seen.

Our second interest in the quinone system was in finding out what would happen at a high pH when hydroquinone, which is a weak acid (pK$_a$ 10.35), dissociates to give an anion and at even a higher pH a di-anion. Thus:
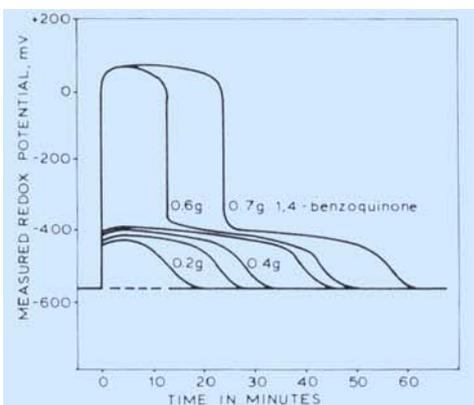

Fig. 2 If less than a stoichiometric amount of 1,4-benzoquinone is hydrogenated in the presence of a hydrogenated anthraquinone-2-sulphonic acid one only observes a single reduction wave corresponding to a rehydrogenation of the anthraquinone. If excess benzoquinone is added, however, two waves can be seen corresponding to the hydrogenation of the excess benzoquinone and rehydrogenation of the original amount of anthraquinone. (0.1 g 5% Pd/C catalyst at pH 5.7)
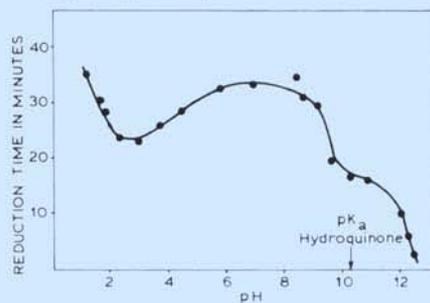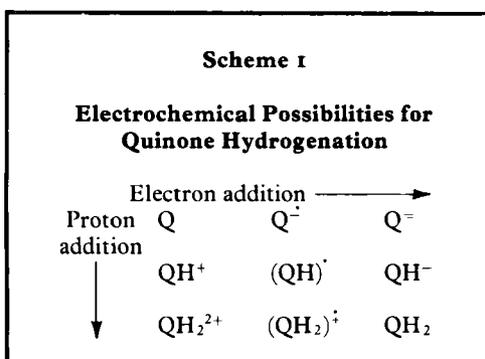

Fig. 3 The time taken to reduce 1,4-benzoquinone varies markedly with the pH of the reaction system. These changes are rationalised on the basis of proton and electron additions as given in Scheme 1, and summarised in 2

If, therefore, we "hydrogenate" quinone at a high pH we might form the di-anion by simple electron transfer without incurring the necessary kinetic penalty of having to add molecular hydrogen.

That this is indeed the case is

indicated by the results shown in Figure 3. Here we see the variation in reduction time at various pH values. It will be recalled that since we are under hydrogen mass transfer control, we should have expected that changing the pH would not have changed the reduction time. The marked changes observed and in particular the very high rates at the higher pH show that the reaction is apparently under electron transfer control. Adding acid upon the completion of reaction at the high pH gave no further reaction, showing that indeed reduction was completed much faster at the high pH under this electron transfer control. We are therefore proposing that the hydrogenation of quinone is better represented in the nomenclature of electro-organic chemistry, as shown in Scheme 1, in which the possible intermediates include radical anions and radical cations in addition to the normally assumed half hydrogenated neutral radical (QH)$^•$.

One aspect of such a scheme is that we might expect the reaction mechanism and inter-mediates involved to be pH dependent, a low pH favouring a possible cationic, and a high pH an anionic intermediate. Furthermore, in the presence of an active palladium hydrogenation catalyst we have the following equilibration (6)

$$H^+ + e^- \rightleftharpoons H_{AD}$$
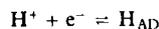
suggesting that the electronic potential is inversely related to the acidity or proton concentration.

Thus variations in the palladium catalysed hydrogenation rate shown for benzoquinone in Figure 3 are interpreted as shown in Scheme 2.

Nitrobenzene Hydrogenation

The quinone hydrogenation results discussed above represent a somewhat special case because these hydrogenations are reversible and can yield ionic products. Of more general interest are irreversible hydrogenations, of which nitrobenzene hydrogenation is an example having commercial significance. Since nitrobenzene is only slightly soluble in water, these experiments were performed in a 50 per cent CH$_3$OH/water solvent.

Very pronounced and well defined reduction waves were obtained upon injection of the nitrobenzene substrate, as shown in Figure 4. However, there was little variation in this case in hydrogenation time, as the pH was changed; but were marked changes in the potential shift of the half wave reduction potential. These results are best summarised in a potential/pH plot, as shown in Figure 5.

The first point of interest in Figure 5 is that the observed half wave potentials are much less
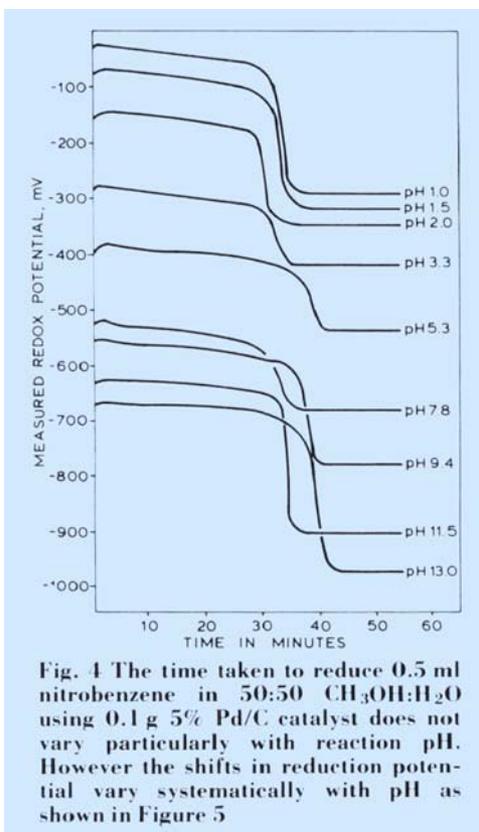
Fig. 4 The time taken to reduce 0.5 ml nitrobenzene in 50:50 CH₃OH:H₂O using 0.1 g 5% Pd/C catalyst does not vary particularly with reaction pH. However the shifts in reduction potential vary systematically with pH as shown in Figure 5

intermediate pH range 3 to 7 the slope is −59 mV and this in turn corresponds to an intermediate to which equal numbers of protons and electrons have been added. Again, in the formalism of Scheme 1, this corresponds to a neutral free radical or to a species commonly assumed to represent the half hydrogenated state. At yet higher pHs above pH 7, the slope again changes to only −29 mV which corresponds to the addition of **two electrons** for every proton and the anion of Scheme 1.

We thus see that in the case of nitrobenzene hydrogenation, even though the rate of reaction did not markedly change with pH as in the case of the benzoquinone, we would seem to have
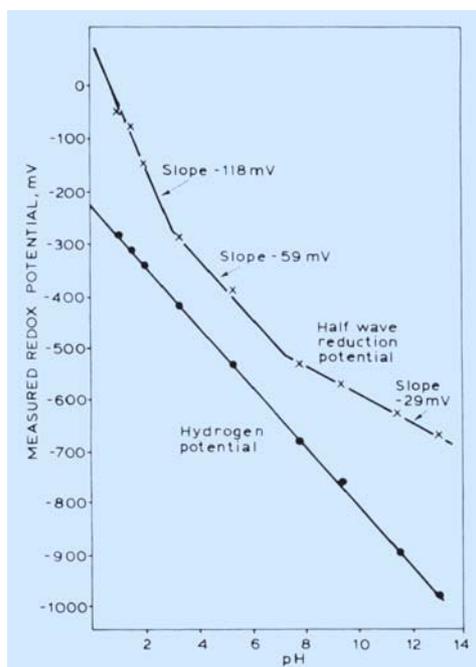

Fig. 5 In nitrobenzene hydrogenation the shift in redox potential relative to the hydrogen potential is greatest at both low and high pHs. These shifts are in all cases much less than the 826 mV to be expected for a reversible hydrogenation, indicating that they are due to reaction intermediates. The high slope below pH 2 implicates a cationic radical species; between pH 2–7 a neutral radical species is suggested whereas the low slope above pH 7 suggests an anionic species

than the reversible hydrogenation potential. This can be calculated thermodynamically from the known change in thermodynamic free energy as being +826 mV relative to the reversible potential for 1 atmosphere hydrogen using the Nernst expression:

$$\triangle G = -nF \triangle E$$

the inference being that these well defined half wave potentials represent hydrogenation intermediates formed reversibly on the surface of the catalyst. Of particular interest, however, are the relative changes in these half wave potentials as the pH changes as given by the slopes of the curves shown in Figure 5. At a low pH, below about three, this slope approximates to −118 mV, which is what we should expect from a species formed by the addition of **two protons** for each electron. In the Scheme 1 presented earlier, such an intermediate corresponds to a radical cation. In the

clear evidence of the existence of both anionic and cationic charged reaction intermediates. This could affect reaction selectivity, stereochemistry or poison sensitivity of the catalyst.

Hydrogenation of 2-butyne-1,4-diol

The palladium catalysed hydrogenation of butyne-diol is of interest because it proceeds in two quite clearly defined sequential stages. The butyne-diol is first selectively hydrogenated to butenediol and this hydrogenation is virtually complete before the butene-diol is then hydrogenated to the butane-diol. This selectivity

Fig. 7 The redox potential shifts for both steps of the butyne-diol hydrogenation are again much less than would be expected for a reversible reaction. The shift for the first reaction step (●) is constant over the whole range of pH suggesting an allylic radical intermediate. For the second step of the reaction (×) the higher slope below pH 7 suggests a cationic intermediate changing to a neutral alkyl radical above pH 7
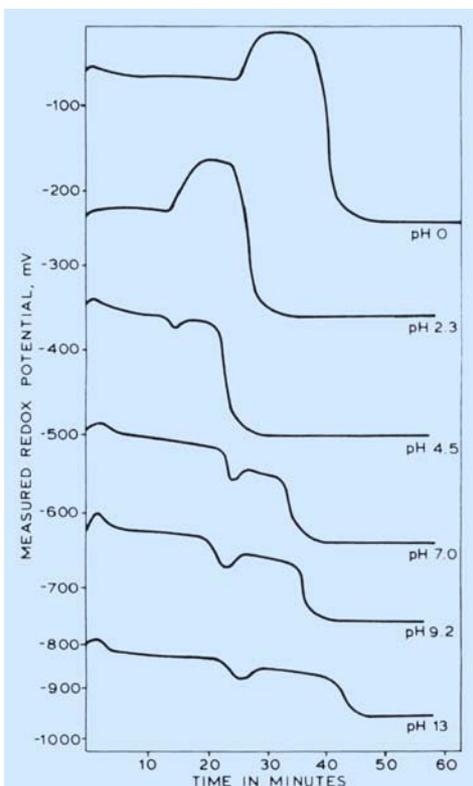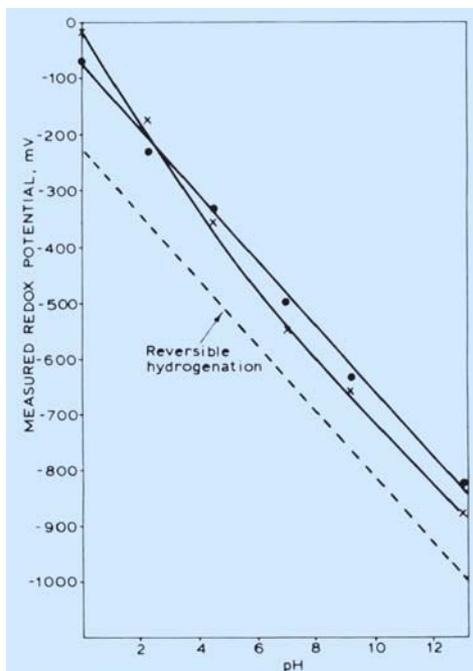
Fig. 6 The two step sequential nature of the palladium catalysed hydrogenation of butyne-diol to butene-diol and then to butane-diol is clearly apparent from the measured potential changes. At a low pH the potential shift is greater for the second step, butene-diol hydrogenation, in contrast to the quinone results shown in Figure 1. The hydrogenation times for each step in the reaction also change markedly, see Figure 8

is generally ascribed to the much stronger absorption of the butyne-diol relative to the butene-diol with the consequence that the butene-diol intermediate hydrogenation product is desorbed and virtually excluded from the catalyst surface. We were curious to see whether a case might be made for this selectivity being due to redox potential control, much in the way as we saw earlier is the case in the selective hydrogenation of the different quinones. The reversible redox potential for the first step of this reaction (est. 625 mV) is considerably higher than for the second (430 mV).

Our results are shown in Figures 6, 7 and 8. In all cases two sequential reduction waves are clearly in evidence and we can determine both
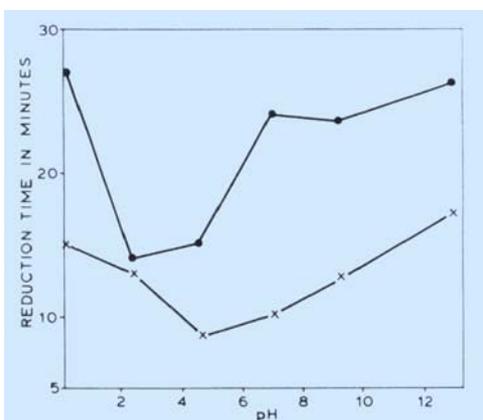
Fig. 8 The reduction times for both steps of the butyne-diol hydrogenation are less at an intermediate pH although the optimum pH is less for the first step (●) than for the second (×). The first step in the reduction is, in all cases, slower than the second

the reduction half wave potentials (Figure 7) and the reduction times (Figure 8) for each sequential stage. In all cases, however, the reductions are irreversible and the half wave potentials considerably less than those corresponding to the reversible reaction.

Somewhat surprisingly, we note that the reduction half wave potential is higher at a low pH for the second stage of reaction than for the first. We are not able, therefore, to invoke a simple explanation of relative redox potentials to explain the reaction selectivity as we did for the quinone hydrogenation. The difference between the two systems lies in the reversibility of the quinone hydrogenation in contrast to the irreversibility of the butyne and butene-diol hydrogenation.

As we discussed earlier in the case of nitrobenzene hydrogenation, we can obtain some information on the nature of the surface intermediates from a consideration of the slope of the curves of redox potential versus pH. When we do this (Figure 7) we find that the half wave reduction potentials for butyne-diol parallel the hydrogen curve over the whole pH range, indicating that the active intermediate is an orthodox half hydrogenated neutral radical species. For the triple bond hydrogenation we might speculate that this could be some form of allyl radical. Neutral alkyl radicals are also indicated for butene-diol hydrogenation at a high pH. Under acidic conditions (pH < 7), however, the slope increases and again a radical cation is suggested as becoming the surface intermediate. We shall return to this point later. At a high pH the half wave potential for formation of the allylic surface radical is higher than

Selective Lead Poisoning of a Palladium Catalyst					
0.4 g 5% Pd/C paste		Normal acetic acid (pH 2.3)		0.2 g 2-butyne-1,4-diol	
Lead added		Reduction time minutes		Half wave potential mV R.H.E.	
Concentration $\times 10^5$ moles	Pb : Pd mole ratio	$C_4^= \to C_4^=$	$C_4^- \to C_4^\circ$	$C_4^= \to C_4^=$	$C_4^= \to C_4^\circ$
0	0	14	11	+145	+195
1.0	0.06	17	16	+140	+165
2.0	0.12	20	24	+125	+110
2.7	0.16	25	70	+90	+30
3.0	0.18	34	>180	+60	+20

that for the alkyl surface radical, that is to say the former is more stable in line with what we might expect from a consideration of the relative free radical stabilities.

The reduction times for the different reduction stages are correlated in Figure 8. Although for a given pH the alkene hydrogenation is in all cases more rapid than that for the alkyne, the relative difference changes with pH. In particular we note that the rates in both cases go through a maximum (that is reduction times are a minimum) as the pH is varied, but that the optimum pH for alkyne hydrogenation is lower than that for alkene hydrogenation. Such maxima in the rate are implicit in our Scheme I, given the relative promoting effects of proton and electron concentration and the inverse relationship between them.

Effect of Lead Poisoning on Palladium Catalyst Selectivity

In catalysts of the Lindlar type, lead acetate is used to selectively poison a palladium catalyst. Such a poisoned catalyst may still be effective for hydrogenating triple bonds and yet is ineffective for hydrogenating double bonds. We were therefore interested in studying the effect of lead addition to our palladium catalysed butyne-diol hydrogenation system. The lead was added as a very dilute solution of lead nitrate to the reduced catalyst slurry. We found no apparent effect of these modest lead additions either at a low or a high pH. In the pH range 2 to 5, however, marked effects were observed, as shown in the Table. Although the addition of lead decreased the half wave reduction potentials and increased the time taken for reduction for both the first and second stages of the butyne-diol reduction, the effect on the butene-diol hydrogenation was much greater. So much so, in fact, that with the addition of 0.18 moles lead per mole palladium reduction was not completed within the three hour duration of the experiment.

The lead poisoning of a palladium catalyst is generally assumed to be due to an alloy containing metallic lead on the palladium surface. However, in our conditions (pH 2.3 $[Pb^{2+}] \sim 10^{-5}M$) the redox potential for metallic lead formation at -150 mV relative to the reversible hydrogenation potential is considerably more cathodic than we can achieve in our reaction system. It only becomes zero at or above pH 5 (7). Indeed we ascribe the **absence** of a poisoning effect above pH 5 to deposition of metallic lead and conversely the selective poisoning of the palladium surface to the adsorption of a **divalent lead cation.** Remembering that, as we showed earlier, the surface intermediate in butene-diol hydrogenation is a cationic species under these low pH conditions we conclude that it is the more favourable adsorption of the dicationic lead ion that poisons the sites normally active in forming the monocationic butene-diol hydrogenation intermediate. The relative reductions in the stabilities of these intermediates are reflected in the relative reductions in their half wave redox potentials.

Conclusions

It has been our purpose in this article to indicate the effectiveness of the electrochemical technique when applied to a real working catalytic system. We think it is important to recognise the distinction that must be made between electronic reduction and hydrogenation even in the case of simple double bond saturation reactions. We have stressed comparative studies of compounds having different redox potentials and studies made under different acidity conditions. Although these conditions are relatively easy to specify in liquid phase hydrogenation systems, we believe that the same parameters apply in gas phase hydrogenation reactions and that if we are to understand properly support-metal interactions both the acidity and redox potential of the whole catalytic system must be taken into account. Our results indicate that in some conditions ionically charged reaction intermediates occur on the catalyst surface and that at least in the case of a lead poisoned palladium catalyst this has been invoked to explain the observed selective poisoning of the mono olefin hydrogenation reaction.

The ability to quantify the free energy of formation of the surface reaction intermediates by means of the half wave reduction potential presents us with a powerful tool for comparing catalysts of different metals and the effects of alloying and multimetallic composite catalysts.

Finally, there is much useful background information in this area contained in a recent review (8) and in the results obtained by Russian workers who originated and developed the electrochemical technique that has been publicised by D. V. Sokolskii (3, 4). Particularly we would refer the reader to the latter for information on how different metals affect the half wave reduction potential and for some of the linear free energy correlations between half wave reduction potentials and activation energy on the one hand and the effects of electrophilic benzene substituents in hydrogenation substrates on the other.

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Glassy Alloys Containing Platinum Group Metals

Amorphous Metallic Alloys, EDITED BY F. E. LUBORSKY
Butterworth & Co. (Publishers) Limited, London, 1983, 534 pages, £35

Amorphous metallic alloys have great scientific and technological importance in the field of materials science. The above-named book, one of the Butterworth's Monographs in Materials series, brings together much of our basic knowledge and understanding of the atomic, electronic and structural behaviour of such materials with emphasis on magnetic, superconducting, thermal and chemical properties and techniques of production.

In the section dealing with chemical properties of amorphous metallic systems, a series of palladium-phosphorus alloys are mentioned which have been specifically designed as anode materials for the electrolysis of sodium chloride solutions. These materials have shown high catalytic activity for chlorine evolution with low activity for oxygen evolution while maintaining good corrosion resistance in the hot aqueous environment. Surface-activated amorphous palladium-phosphorus alloys for use as fuel cell electrodes are also described where it has been observed that these systems show higher catalytic activity for the oxidation of methanol and its derivatives than either platinised platinum or surface-activated crystalline palladium.

Refractory metal-metalloid superconducting glasses, particularly those of molybdenum-ruthenium-phosphorus and molybdenum-rhodium-phosphorus, show unusually high transition temperatures compared with their crystalline counterparts which is in contrast to normally expected behaviour. In the readily formed glass systems of the early transition-late transition alloys where the late transition metal is one of the platinum group elements, eutectic temperatures are generally high (>1500°C). However, with devitrification temperatures in excess of 725°C it is surprising that few systems have been investigated; those reported include 55 niobium–45 iridium and 55 tantalum–45 rhodium.

The book contains references to 193 amorphous metallic alloys of which 39 involve one or more of the platinum group metals. It is evident, however, that glassy alloys which contain a platinum group metal are still at the level of scientific interest with few systems being examined for technological application.

With the knowledge that a great deal of work is continuing in this field, our increasing understanding of amorphous alloy behaviour should lead to novel products.   I.R.M.