The Platinum Metals as Selective Hydrogenation Catalysts

A BASIC APPROACH

By Peter B. Wells, B.Sc., Ph.D.

Department of Chemistry, University of Hull

At the present time the consumption of catalytic materials by industry is increasing rapidly, and the demand is growing for catalysts that are able to promote specific or selective reactions. In practice, however, the formulation of a catalyst for a particular function is frequently empirical, at least in part. We are not yet in the position of being able to design a catalyst "on the drawing-board" for a specific complex operation with any high degree of confidence, although this is a situation which we may reasonably hope to achieve at some time in the future.

Recent research at the University of Hull, most of which is unpublished as yet, has indicated that a considerable rationalisation may soon be possible in the field of the metal-catalysed hydrogenation of multiply unsaturated hydrocarbons and the hydroisomerisation of olefins. It is the purpose of this paper to present a preview of this work and to advance some of its tentative conclusions.

The Pattern of Selectivity

All of the metals of Group VIII may be used as catalysts for the hydrogenation of acetylenes and di-olefins, although the extent to which mono-olefin is produced as an initial product varies widely from metal to metal. Metals that produce high yields of mono-

olefin are referred to as highly selective, using the definition:

$$\text{Selectivity} = \frac{\text{yield of mono-olefin}}{\text{yield of mono-olefin} + \text{paraffin}}$$

Results in the literature indicate, and our own work confirms and extends the generalisation, that the selectivity shown by a given metal is characteristic of that metal and is substantially independent of the physical form of the catalyst and of the multiply-unsaturated hydrocarbon that is undergoing hydrogenation. A selection of the available results for the noble Group VIII metals is shown in Table 1.

Selectivity is found to decrease with increasing hydrogen pressure and decreasing temperature, and the selectivities quoted in the table must be examined with that in mind. It is apparent from the table that the metals may be placed in a sequence of decreasingly selective behaviour thus:

Pd > Rh > Pt > Ru > Os > Ir
.... sequence (i)
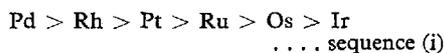
It is interesting that this is exactly the series reported recently by Zajcew for the selectivity of these metals (except osmium, which was not studied) in the hydrogenation of tall-oil fatty acids to give selective formation of oleic acid (14).

So different are the conditions of experiment, the catalysts, and the molecular species involved, that a sequence such as this demands an explanation.
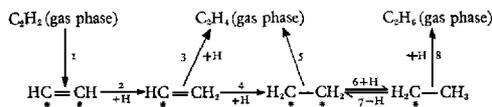
Unfortunately, the hydrogenation of an acetylene or a di-olefin is not a simple reaction.

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| | | | | **Table I** | | | |
			Selectivities Shown by the Noble Metals of Group VIII			
Metal	Support	Hydrocarbon	Initial P_{H_2}/P_{hc}	Temperature °C	Selectivity	Reference
Ru	alumina	acetylene	2.0	133	0.82	1, 2
Ru	alumina	allene	3.1	51	0.84	1
Ru	alumina	butadiene	2.0	0	0.73	1, 2
Rh	alumina	acetylene	2.0	132	0.93	1
Rh	alumina	allene	3.0	61	0.92	1
Rh	alumina	butadiene	1.0	56	0.92	1
Rh	pumice	acetylene	1	85	0.86	3
Rh	carbon	pent-2-yne	*	18	0.84	4
Pd	alumina	acetylene	2.0	22	0.95	1, 5
Pd	pumice	acetylene	2.0	36	0.92	6
Pd	silica	acetylene	3.7	181	0.97	7
Pd	pumice	allene	1	116	1.00	8
Pd	alumina	butadiene	2.0	21	1.00	1
Pd	(wire)	butadiene	2.0	150	1.00	9
Pd	(film)	butadiene	2.0	19	0.99	9
Pd	—	butadiene	*	—12	0.94	10
Pd	pumice	propyne	1.0	80	0.97	8
Pd	alumina	but-2-yne	2.1	20	1.00	11
Pd	carbon	pent-2-yne	*	18	0.99	4
Pd	carbon	piperylene	*	18	0.99	4
Pd	—	isoprene	*	?	0.98	12
Os	alumina	acetylene	2.3	153	0.67	1, 2
Os	alumina	allene	6.0	130	0.73	1
Os	alumina	butadiene	2.0	69	0.69	1, 2
Ir	alumina	acetylene	2.0	62	0.22	1, 5
Ir	pumice	acetylene	1	175	0.30	3
Ir	alumina	allene	1.8	28	0.36	1
Ir	alumina	butadiene	3.0	24	0.25	1
Pt	alumina	acetylene	2.0	97	0.83	1, 5
Pt	pumice	acetylene	1	163	0.82	13
Pt	alumina	allene	1.8	79	0.89	1
Pt	pumice	allene	1	89	0.80	8
Pt	alumina	butadiene	2.0	108	0.81	1
Pt	—	butadiene	*	—12	0.61	10
Pt	carbon	piperylene	*	18	0.82	4
Pt	carbon	pent-2-yne	*	18	0.92	4
Pt	—	isoprene	*	?	0.65	12

* denotes liquid phase hydrogenation

Let us consider the simplest case, the reaction of acetylene itself with hydrogen; the reaction may be written as follows:

$$C_2H_2 \text{ (gas phase)} \qquad C_2H_4 \text{ (gas phase)} \qquad C_2H_6 \text{ (gas phase)}$$

$$HC \underset{*}{\equiv} CH \xrightarrow[+H]{2} HC \underset{*}{=} CH_2 \xrightarrow[+H]{4} H_2C \underset{*}{-} CH_2 \underset{7-H}{\overset{6+H}{\rightleftharpoons}} H_2C \underset{*}{-} CH_3$$

An asterisk denotes an adsorption site on the surface of the catalyst.

Variants on this mechanism may be written for other acetylenes and di-olefins. It has been well established (1, 5) that the paraffin formed in selective hydrogenation is produced during one residence of the hydrocarbon species on the surface, and not by the re-adsorption and reaction of olefin that has been returned to the gas phase. Therefore, to understand selectivity we must pay attention to steps 5, 6, 7 and 8 of the above scheme. Since these are also the steps which operate in ethylene hydrogenation, it is with olefin hydrogenation that we must first be concerned.

Factor One: Activity for Olefin Hydrogenation

Consider two extreme hypothetical cases. First, a catalyst which has no ability to promote the hydrogenation of ethylene would be perfectly selective for the hydrogenation of acetylene to ethylene. Secondly, a catalyst which is extremely active for ethylene hydrogenation would catalyse steps 6 and 8 at the expense of step 5, and the absolute value of the selectivity would then be governed by the amount of ethylene formed by step 3. Thus, the first important factor to assess is the relative activities of these metals for ethylene hydrogenation.

Two determinations have been made of the relative activities of rhodium, palladium and platinum for ethylene hydrogenation, one by Beeck who used evaporated metal films (15) and the other by Schuit and van Reijen who used silica-supported metals (16). The work by Beeck has been discussed in this journal by Bond (17). In both reports rhodium was found to be more active than palladium, and palladium more active than platinum. Moreover, the activities of these metals vary linearly with the percentage d-character of the metallic bond (18). Results from the literature are shown in Table II.

The metallic bonds in iridium, ruthenium and osmium have either the same or nearly the same d-character as those in rhodium, and it is to be expected, therefore, that their activities in olefin hydrogenation will be similar to that of rhodium. Unfortunately, the measurement for iridium by Schuit and van Reijen does not support this, although there is fair agreement between the values for rhodium and ruthenium. Our own qualitative comparison, based merely on measurements of reaction rates, have shown rhodium, ruthenium and iridium to have similar activity for ethylene hydrogenation, at least to within an order of magnitude. Another quantitative comparison of the activities of all of the noble Group VIII metals for this reaction, or indeed for the hydrogenation of any other olefin, would be very valuable in this connection.

Table II						
Values of the log of the velocity constant for ethylene hydrogenation and the percentage d-character of metal-metal bonds as calculated by Pauling						
	Pt	Pd	Rh	Ir	Ru	Os
$Log_{10}(Kc_2H_4)$ (15)	−1.6	−0.8	0.0	—	—	—
$Log_{10}(Kc_2H_4)$ (16)	−1.5	−0.9	0.0	−2.0	−0.3	—
d-character of metal	44	46	50	49	50	49

For the purpose of this discussion, the order of activity for ethylene hydrogenation will be based on the d-character of the metallic bond. Thus, relative activities may be placed in the following sequence:

$$Rh = Ru \geqslant Ir = Os > Pd > Pt$$
$$\ldots \ldots \text{sequence (ii)}$$
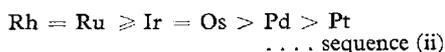
This sequence must now be considered in connection with the reaction scheme. It has been shown that the selectivity will be higher the lower the activity for ethylene hydrogenation; thus, if this is the only factor operating, the order of selectivity should be the reverse of sequence (ii), that is:
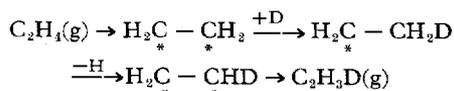
$$Pt > Pd > Os = Ir \geqslant Ru = Rh$$
$$\ldots \ldots \text{sequence (iii)}$$
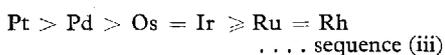
However, this bears only a little resemblance to sequence (i) and some other competing factor or factors must be present in the system.

Factor Two: The Reversal of Alkyl Formation

The competing factor is step 7. In this step the ethyl group loses a hydrogen atom to reform diadsorbed ethylene, which has a finite chance of undergoing desorption to give gas phase ethylene. The greater the importance of step 7 the higher will be the ethylene yield, and the higher the selectivity. It is necessary, therefore, to examine experimental evidence for the presence or absence of step 7, which will be referred to as **the reversal of ethyl formation.** The processes which give this information are **olefin exchange** and **olefin isomerisation.**

The interaction of an olefin with deuterium will yield deutero-paraffins and also, possibly, deutero-olefins and HD. Deutero-olefins may arise by the reversal of ethyl formation thus:

$$C_2H_4(g) \rightarrow H_2\overset{*}{C} - \overset{*}{C}H_2 \xrightarrow{+D} H_2\overset{*}{C} - CH_2D$$
$$\xrightarrow{-H} H_2\overset{*}{C} - \overset{*}{C}HD \rightarrow C_2H_3D(g)$$

This series of steps is termed an olefin exchange reaction.

When an olefin contains four or more carbon atoms, the same series of steps, in which a hydrogen atom is first added and then a different hydrogen atom removed, leads to *cis-trans* isomerisation or to double bond migration. Thus it is expected that a metal that gives olefin exchange would give isomerisation with the same parent olefin, under the same conditions.

The isomerisation of each of the three normal butenes has been studied over all of the noble Group VIII metals (2, 19) and that of pent-1-ene and pent-2-ene over rhodium, palladium, iridium and platinum (4). The pattern of behaviour that has emerged is that the elements of the second transition metal series in Group VIII are good catalysts for isomerisation reactions, whereas the metals of the third series are poorer catalysts; indeed, iridium and platinum have shown only the slightest isomerisation ability. Several workers in the United States have studied the isomerisation and hydrogenation of di-substituted cyclohexenes, *exo*-olefinic di-substituted cyclohexanes and certain octalins (20). These experiments were carried out in the liquid phase, using palladium supported on charcoal and reduced platinum oxide catalysts. Almost without exception, isomerisation of the parent hydrocarbon was found to be an important reaction over palladium, but to be almost absent over platinum. These results agree with ours, and indicate that this may be a general feature of the catalytic properties of these metals.

The reactions of olefins with deuterium have only been carried out using rhodium, palladium, iridium and platinum, as yet (19). Considerable propylene and butene exchange was observed over the second row metals, but it occurred only to a negligible extent over the third row metals. This repeats the pattern established in isomerisation and lends support to the generally accepted mechanism for these reactions.

In order to discuss the relevance of alkyl reversal to our examination of selective behaviour it is necessary that some numerical comparison be made between the metals regarding their activities for isomerisation and

Table III		
Typical F Values given by the Noble Metals of Group VIII		
Metal	Temp. (°C)	F
Ruthenium	24	1.05
Rhodium	69	5.70
Palladium	37	1.90
Osmium	25	0.23
Iridium	0	0.01
Platinum	107	0.03

Table IV		
Typical F' Values given by some Noble Metals of Group VIII		
Metal	Temp. (°C)	F'
Rhodium	88	1.6
Palladium	−20	1.1
Iridium	78	0.03
Platinum	72	0.06

exchange. For the purposes of this paper it is sufficient to define two quantities, F and F'. Consider first the reaction of but-1-ene with hydrogen. The quantity F may be defined so that:

$$F = \frac{\text{pressure of } cis\text{-} + trans\text{-but-2-ene produced}}{\text{pressure of } n\text{-butane produced}}$$

Secondly, consider the analogous quantity, F', that can be obtained from the reaction of propylene with deuterium.

$$F' = \frac{\text{pressure of exchanged propylenes produced}}{\text{pressure of deutero-propanes produced}}$$

Values of F and F' are given in tables III and IV.

Thus, we may write the sequence of activity for these metals as follows:

Rh > Pd > Ru > Os > Ir ≈ Pt
.... sequence (iv)
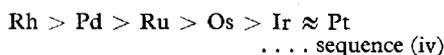
These results may be interpreted in one of two ways. It may be that alkyl reversal is efficient over the second row metals but not over those of the third row. A second possibility is that the reversal of alkyl formation takes place over all of the metals, but that in the case of the third row metals the equilibrium is so much on the side of the alkyl radical that virtually no adsorbed olefin is present to desorb and appear in the gas phase. An analysis of results published in 1956 by Bond (21), using an electronic computer, has shown that, for the reaction of ethylene with

deuterium over platinum, the second of the two possibilities given above is the true one. A study of the ethylene-deuterium reaction over the other metals is now in progress in order to provide comparable data. If therefore we define the usual equilibrium constant K, such that:

$$C_2H_4 + H \rightleftharpoons C_2H_5 \; ; \; K = \frac{[C_2H_5]}{[C_2H_4][H]}$$
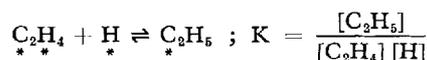
then the variation of K among the metals is the reverse of that given in sequence (iv):

Pt ≈ Ir > Os > Ru > Pd > Rh
.... sequence (v)
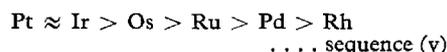
A Synthesis of the Factors

It now remains to attempt a synthesis of the factors which govern sequences (ii) and (v). Osmium, iridium, ruthenium and rhodium are expected to possess similar activity for ethylene hydrogenation. Thus the selectivity in this quartet will be governed by and will be inversely proportional to K; that is, the selectivity will be expected to decrease in the sequence

Rh > Ru > Os > Ir .... sequence (vi)
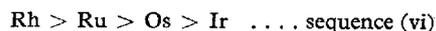
That this is the observed order (see sequence (i)) is very encouraging. Platinum is less active for olefin hydrogenation than rhodium, but K for platinum is higher than that for rhodium. Here there are two opposing factors and the higher selectivities shown by rhodium

must indicate that the latter is of the greater importance. Palladium exhibits a lower activity for ethylene hydrogenation than rhodium and a slightly lower value of K. Thus it is to be expected that the selectivity over palladium will be higher than that over rhodium, as is observed. This synthesis of the two factors, therefore, gives a sequence that is identical to that observed experimentally and it would appear that an understanding of selective behaviour has been achieved.

Some Remaining Problems

Several problems remain. Why are the values of K higher for the third row metals than for the second row metals ? May not the ability of the metals to promote isomerisation be a function of temperature such that no truly fundamental difference in catalytic behaviour exists ?

Another difficulty may be introduced into discussions of olefin isomerisation in the near future. In this paper the mechanism of isomerisation has been assumed to involve the alkyl radical. A report has recently been made that intermediates may be present in certain catalytic reactions which are π-bonded to the surface (22). Such intermediates could be formed by the **loss** of a hydrogen atom from, say, a but-2-ene to form a π-allylic species in which the π-electrons overlap with the d-orbitals of a metal atom or atoms, with the formation of a chemical bond. The addition of a hydrogen atom to this species could then give but-1-ene or but-2-ene, depending upon the point of addition, that is, isomerisation could thus be achieved. While it is not envisaged that this mechanism would be totally responsible for the observed isomerisation, its possible existence as a contributary mechanism may well serve to cloud the picture. On the other hand, it is a new concept, and as such it offers a challenge to experimentation and hypothesis that must be welcomed.

A discussion has not been given here of the isomer distribution obtained in isomerisation reactions or of the principle underlying the stereo-determining step. It is probable that the alkyl radicals will take up those conformations which are of lowest energy and thus an estimation of these conformations is all important. A study of the preferred conformations of the butyl group $CH_3CH_2\overset{\centerdot}{C}HCH_3$ has led to an understanding of the isomerised butenes observed in our studies, while a similar approach, in principle, has been used by Siegel to understand the paraffinic isomers that arise by the hydrogenation of di-substituted cyclohexenes (20). This approach should allow an understanding of the initial isomer distribution that is obtained both in olefin isomerisation and in the hydrogenation of multiply unsaturated hydrocarbons such as butadiene which give a distribution of isomers.

Another problem concerns the importance of step 3 as an olefin-forming step (see the general mechanism). This step is not present in mechanisms for di-ene hydrogenation and yet such systems fit into the general classification along with the acetylenes. A complete predominance of step 3 over step 4 could lead to perfectly selective behaviour in which none of the factors discussed above is applicable. No such system has yet been identified.

In Conclusion

The value of this discussion of selectivity and isomerisation is twofold. It has allowed an understanding of experimental results, but also it should furnish a basis on which predictions can be made for systems as yet unstudied. Factors such as the inherent activities of the metals, and the energetically favourable conformations of alkyl groups, are sufficiently fundamental, once established, for predictions to be made for a wide range of systems. At the present time these factors and their synthesis present a new approach and they may, as time passes, need revision or amplification. However, it is only by establishing such fundamental factors and by testing their validity over as wide a range of experimental conditions as possible that a rationalisation of catalytic behaviour will eventually be achieved.

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RHODIUM PLATING IN LIGHTHOUSE BEACONS

An unusual example of the corrosion resistance and reflectivity of electroplated rhodium is found in the AGA Sunvalve manufactured by the lighthouse engineers, Gas Accumulator Co., (U.K.) Limited. This ingenious device controls the operation of lighthouse beacons.

The valve consists of three copper rods, rhodium plated to give a highly reflective surface, and a fourth copper rod with a mat black surface. At dawn, sunlight falling on the mat black surface warms the copper rod and it expands, while at dusk, when the light intensity falls, the rod cools and contracts. The movement in the rod caused by longitudinal expansion works a valve cut-off mechanism, interrupting the flow of acetylene gas to the beacon and extinguishing the light during daylight hours.

The high reflectivity of the rhodium plated rods ensures that their expansion is independent of the light intensity and they serve to compensate for expansion or contraction in the mat black rod due to changes in ambient temperature. In service, Sunvalves are exposed to the corrosive attack of marine atmospheres in all climates yet the rhodium plate retains its reflectivity for very long periods. The average service life of the valve is fifteen years but some have been in operation for over thirty.