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Patterns of Behavior in Catalysis by Metals

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The relative merits of "technical" and "clean" metal catalysts for the study of the hydrogenation of unsaturated hydrocarbons are discussed, and it is concluded that the former have substantial advantages provided that there are parameters which are essentially independent of the precise physical form of the catalyst. A survey of the literature shows that (a) the degree of selectivity shown in the hydrogenation of multiply unsaturated hydrocarbons and (b) the tendency to give olefin isomerization and exchange during hydrogenation constitute such parameters. The information in the literature is supplemented by new experimental work on the noble, Group VIII, metals (reported in outline); it is shown that the second row metals (Ru, Rh, Pd) all give substantial isomerization and exchange, whereas the third row metals (Os, Ir, Pt) give little. These results are used to explain the selectivity sequence observed in the hydrogenation of actylenes and diolefins.

I. INTRODUCTION

Progress in our understanding of the catalytic properties of metals has been severely hampered by the difficulty of preparing reproducible metal surfaces. It is well known that "technical" metal catalysts (that is, supported metals and metal powders) show not only notoriously variable activities, but also variable activation energies, and even kinetics (1), for a given reaction. Several reasons may be advanced to account for the irreproducibility of such catalysts: (a) variation in the state of reduction and cleanliness of the surface (probably the single most important factor); (b) variation in the concentration of surface defects; (c) variation in the extent to which different crystallographic planes are exposed; and (d) variation in the distribution of particle sizes. With so many potentially variable (and uncontrollable) factors, it is small wonder that the behavior of technical metal catalysts is not reproducible.

Evaporated metal films have been widely used in an attempt to overcome these difficulties; there are, however, two related disadvantages in using them as catalysts. First, their inherent reactivity sometimes causes reactants to be strongly and irreversibly adsorbed. Thus, for example, acetylene is irreversibly adsorbed by evaporated metal films (2) but not by supported metals (3); diethylether is decomposed by rhodium films at moderate temperatures with the formation of poisonous residues (4), whereas alumina-supported rhodium does not act this way (5). Second, the high activity of metal films when compared with other metal forms means either that (a) reactions performed near room temperature proceed so rapidly that intermediate products cannot be detected (6) or that (b) reactions must be performed at much lower temperatures than are required with other forms (7), thus limiting the range of molecules which may be investigated; or that (c) flow systems must be resorted to in order to minimize contact times (8). The use of very light films is unsatisfactory because they are rapidly inactivated by adventitious poisons.

In purely practical terms, technical metal catalysts are undoubtedly the easier to employ, and we must, therefore, examine whether the variable factors just listed constitute an insuperable objection to their use. An assessment of the literature several years ago suggested that there are certain properties of metal catalysts which seem to be substantially independent of their physical form; that certain features of catalytic reactions are shown by many kinds of technical catalysts and also sometimes by films; and that these features (which do not include activity and activation energy) cannot, therefore, depend critically on the above-listed variable quantities, but are mainly characteristic of the metal in question. These common features are shown in the hydrogenation of unsaturated hydrocarbons over the metals of Group VIII and are largely independent of the hydrocarbon used. Examples elaborating this statement will be given in the following. The very variable activities and kinetics shown by various kinds of metal catalysts, while understandable, undoubtedly retard the progress of our knowledge of catalysis. It, therefore, seems worth emphasizing that *there are nevertheless certain other properties which exhibit some regularity and which are characteristic mainly of the metal,* and the regularities thus revealed may be of some help in introducing further order into this subject.

II. The Hydrogenation of Unsaturated Hydrocarbons on the Metals of Group VIII—A Survey of the Literature

The Selective Hydrogenation of Multiply Unsaturated Hydrocarbons

It was claimed in the preceding that certain features of the hydrogenation of unsaturated hydrocarbons on the metals of Group VIII are independent of the physical form of the metal. The purpose of this section is to review the information which was available some three years ago to foster this belief, and to present further information which has since appeared in the literature. Our own contribution to this subject is summarized in the next section.

The features in question were twofold: first, the degree of selectivity shown in the formation of a monoolefin in the hydrogenation of an acetylenic compound or a diolefin, and, second, the degree of olefin exchange shown in the interaction of an olefin with deuterium. Two separate kinds of selectivity in catalytic reactions are recognized. In the first the reaction sequence is written

$$\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{C}$$

and the extent to which B is formed selectively is determined by how much more strongly A is adsorbed than B. Thus if A is so strongly adsorbed that it prevents the readsorption of B once formed, then the process B → C cannot proceed, and B is the only product until the pressure of A is insufficient to maintain complete coverage. Since selectivity is here determined by the relative free energies of adsorption of A and B, it has been termed "thermodynamic selectivity" (9). A second reaction sequence is

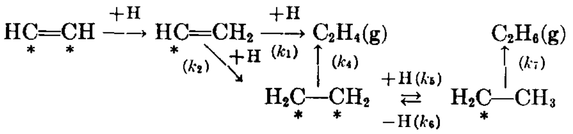
$$\mathrm{A}\begin{array}{l}\nearrow \mathrm{B}\\ \searrow \mathrm{C}\end{array}$$

and here the two products are formed through two simultaneously available reaction paths; the selective formation of either is thus dependent only on the mechanism of the reaction, and this has been termed "mechanistic selectivity" (9).

In the hydrogenation of unsaturated hydrocarbons, it is commonly found that an acetylene or diolefin is more strongly adsorbed than the corresponding monoolefin, so that the degree of thermodynamic selectivity is usually high—for this reason we need not discuss it further here. However mechanistic selectivity varies widely, and we must briefly enquire into its causes. We define the degree of mechanistic selectivity S_m as

$$S_m = \frac{\text{yield of olefin}}{\text{yield of olefin + paraffin}}$$

When the thermodynamic selectivity is high, S_m will remain constant until high conversions are reached. *The appearance of a fully saturated product in the early stages of reaction must arise through the* *further hydrogenation of adsorbed olefin which has never left the surface.* In its simplest form the reaction for acetylene may be written as in Scheme 1. Analogous schemes are readily written for other acetylenes, for allene, and for butadiene. Since similar unit processes are involved in each case, we might expect to find that *the mechanistic selectivity shown in the hydrogenation of any multiply unsaturated is about the same over a given metal (under comparable operating conditions).* Unfortunately it is not possible directly to assign the cause of high mechanistic selectivity in terms of the foregoing scheme. We readily see that it will arise if either k_1/k_2 or k_4/k_5 is large, and will be aided by a high value of k_6/k_7 if k_4/k_5 is not large. Additional possible reaction paths not included in this simplified scheme further complicate the problem (9).



SCHEME 1

TABLE 1

MECHANISTIC SELECTIVITIES (S_m) SHOWN BY PUMICE-SUPPORTED IRON, COBALT, AND NICKEL

Metal	Hydrocarbon	Initial P_{H_2}/P_{hc}	Temp. (°C)	S_m	Ref.
Fe	Acetylene	1	156	0.91	10
Co	Acetylene	1	197	0.90	10
Ni	Acetylene	1	99	0.89	10
Ni	Acetylene	3.5	99	0.86	11
Ni	Methylacetylene	1	91	0.93	12
Ni	Allene	1	73	0.93	12

We now review the information in the literature on the mechanistic selectivity shown by the metals of Group VIII. Some values for the first row metals are shown in Table 1, with notes on the operating conditions. Ignoring the differences in temperature, all three metals show about the same values, and, over nickel, closely similar values are given by different hydrocarbons. Raney nickel, however, has the reputation of behaving very selectively in liquid-phase reactions.

Table 2 gives the same information for the noble metals of Group VIII. These results refer to catalysts operating in a steady and reproducible manner. Some palladium catalysts show a selectivity much less than the usual high value (16), and it sometimes increases with use of the catalyst (15). This behavior is also shown by palladium catalysts used industrially for the removal of acetylene and diolefins from gas streams consisting mainly of olefins and seems to be characteristic of catalysts in which the metal/support ratio is low. This is qualitatively explained if it is assumed that with such catalysts much of the reaction proceeds in the pores of the granules and that these pores become filled or blocked at the mouth by polymeric products. Palladium catalysts have the ability to become selectively poisoned, by, for example, mercury (19) and dimethylsulfide (15), so that the hydrogenation of olefins no longer proceeds. The prime example of this behavior is the Lindlar catalyst, but this kind of poisoning does not necessarily affect the mechanistic selectivity (19). The other metals do not appear to have the same propensity for selective poisoning.

The information in Table 2 shows that the metals can be placed in a sequence of decreasing selectivity:

$$\text{Pd} > \text{Rh} \geq \text{Pt} > \text{Ir} \qquad \text{(i)}$$

Information on rhodium and iridium is sparse, and on ruthenium and osmium almost nonexistent; but it has been reported (20) that in the hydrogenation of tall-oil fatty acids (a mixture of linoleic and oleic acids, with small amounts of linolenic and stearic acids), the tendency to give selective formation of oleic acid falls in the sequence:

$$\text{Pd} > \text{Rh} > \text{Pt} > \text{Ru} > \text{Ir} \qquad \text{(ii)}$$

This sequence is, therefore, in harmony with that given in sequence (i).

TABLE 2

Mechanistic Selectivities Shown by the Noble Metals of Group VIII

Metal	Support	Hydrocarbon	Initial P_{H_2}/P_{Ac}	Temp. (°C)	S_m	Ref.
Rh	Pumice	Acetylene	1	85	0.86	13
Rh	Alumina	Acetylene	2	133	0.92	9
Pd	Pumice	Acetylene	2	36	0.92	10
Pd	Alumina	Acetylene	2	22	0.95	9
Pd	Silica	Acetylene	3.75	181	0.97	14
Pd	Pumice	Methylacetylene	1	80	0.97	12
Pd	Alumina	Dimethylacetylene	2.1	20	1.0	15
Pd	(film)	Dimethylacetylene	2.1	20	1	15
Pd	Pumice	Allene	1	116	1.0	12
Pd	—	Butadiene	[a]	−12	0.94	16
Pd	—	Isoprene	[a]	?	0.98	17
Pd	—	2,5-dimethyl-2,4-hexadiene	[a]	20	0.93	18
Ir	Pumice	Acetylene	1	175	0.30	13
Pt	Pumice	Acetylene	1	163	0.82	19
Pt	Alumina	Acetylene	2	105	0.86	9
Pt	Pumice	Methylacetylene	1	75	0.89	12
Pt	Pumice	Allene	1	89	0.80	12
Pt	—	Butadiene	[a]	−12	0.61	16
Pt	—	Isoprene	[a]	?	0.65	17
Pt	—	2,5-dimethyl-2,4-hexadiene	[a]	20	0.76	18

[a] Reactions carried out in the liquid phase.

The Isomerization and Exchange of Unsaturated Hydrocarbons

The mechanisms of these processes is, it is thought, quite well understood. If we consider the interaction of, say, ethylene with deuterium, the appearance of deuterated ethylene in the gas phase may arise through the following sequence of processes:

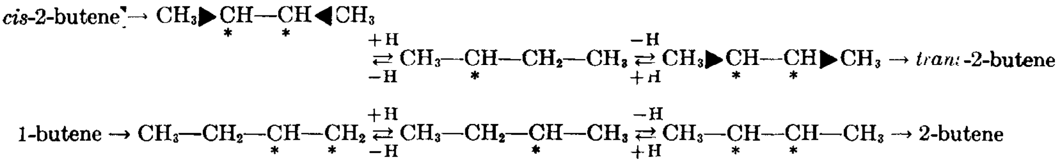
$$C_2H_4 \rightarrow \underset{*}{H_2C}—\underset{*}{CH_2}$$

$$\xrightarrow{+D} \underset{*}{H_2C}—CH_2D \xrightarrow{-H} \underset{*}{H_2C}—\underset{*}{CHD} \rightarrow C_2H_3D$$

More highly deuterated ethylenes may be formed by further reaction of either the adsorbed or the gaseous ethylene-d_1. This *olefin exchange reaction* is accompanied by a *hydrogen exchange reaction* in which HD and H_2 are returned to the gas phase, but the extent of these two exchange processes are not necessarily equal. It is evident in the case of the butenes and higher olefins that this cycle of processes can lead to *cis-trans isomerization* and *double-bond migration* (see Scheme 2). Because of the close similarities in mechanism, we may expect to find close connections between the amounts of isomerization and olefin exchange shown by a given metal. The alternative fates of the adsorbed radicals are, thus,

(a) $$\underset{*}{C_4H_9} \rightarrow \underset{*\,*}{C_4H_8} + \underset{*}{H}$$

(b) $$\underset{*}{C_4H_9} + \underset{*}{H} \rightarrow C_4H_{10}$$



$$cis\text{-2-butene} \rightarrow CH_3▶\underset{*}{CH}—\underset{*}{CH}◀CH_3 \underset{-H}{\overset{+H}{\rightleftarrows}} CH_3—\underset{*}{CH}—CH_2—CH_3 \underset{+H}{\overset{-H}{\rightleftarrows}} CH_3▶\underset{*}{CH}—\underset{*}{CH}▶CH_3 \rightarrow trans\text{-2-butene}$$

$$\text{1-butene} \rightarrow CH_3—CH_2—\underset{*}{CH}—\underset{*}{CH_2} \underset{-H}{\overset{+H}{\rightleftarrows}} CH_3—CH_2—\underset{*}{CH}—CH_3 \underset{+H}{\overset{-H}{\rightleftarrows}} CH_3—\underset{*}{CH}—\underset{*}{CH}—CH_3 \rightarrow \text{2-butene}$$

Scheme 2

and the amount of exchange or isomerization shown is a measure of the extent to which (a) is favored with respect to (b).

We now survey the relevant literature. Nickel is well-known to give extensive isomerization, both in the hydrogenation of the butenes (21,22) and of unsaturated glyceride oils. There is evidence that every isomerized butene molecule contains at least one deuterium atom (22). Nickel is generally also found to give extensive olefin exchange (7,22,23). Some of the available results are plotted in Fig. 1. The function ϕ is defined, following Kemball (7),

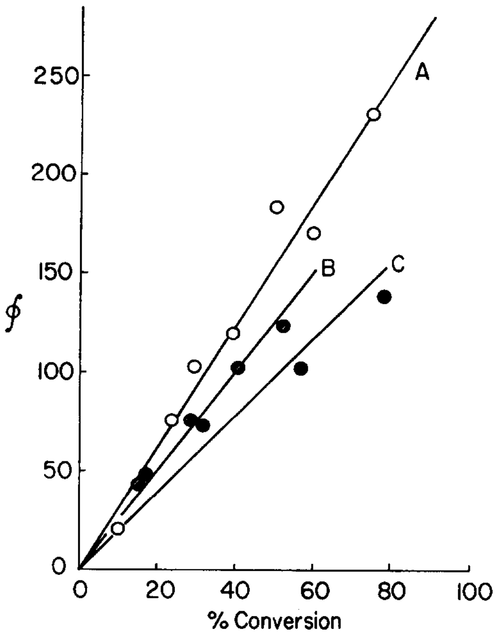


Fig. 1. Plots of ϕ(deuterium content of olefin) against percentage conversion for the interaction of olefins with deuterium over nickel catalysts. (A) Reaction of ethylene with deuterium over nickel wire at 90°C; (B) reaction of 1-butene with deuterium over nickel wire at 90°C; and (C) reaction of ethylene with deuterium over nickel film at −100°C.

$$\phi = a + 2b + 3c + 4d \ldots$$

where a, b, etc. are the percentages which monodeutero-, dideuteroolefins, etc., are of the total olefin. In the absence of significant hydrogen exchange, this function should increase linearly with conversion, and within experimental error it seems generally to do so. It is interesting to note that the rate of increase of ϕ with conversion is almost the same for 1-butene as for ethylene under identical conditions, and that a difference of almost 200°C has relatively little effect.

Iron is also known to give extensive olefin exchange (6,7), although its behavior in isomerization seems to be unknown. Figure 2 presents the available results. Cyclopentene shows more exchange than cyclohexene on sintered iron films at similar temperatures, whereas that given by ethylene at −100°C is very closely the same as it gives over nickel films at this temperature. Unfortunately there are, as yet, no data for cobalt, but we may provisionally conclude that iron, cobalt, and nickel have similar tendencies to give extensive isomerization and exchange. Table 1 showed that they gave similar selectivities.

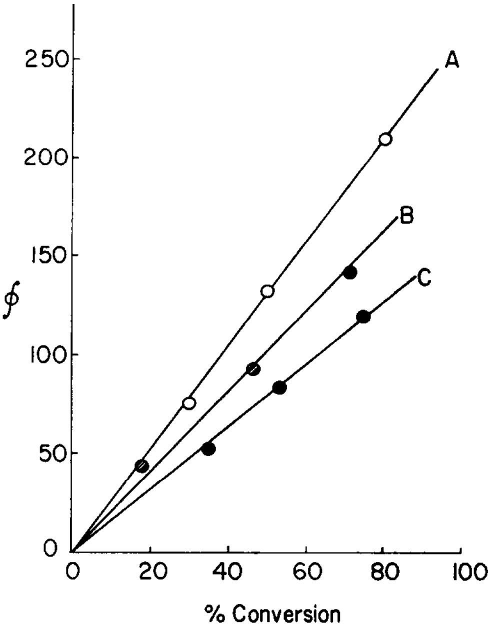


Fig. 2. Plots of ϕ(deuterium content of olefin) against percentage conversion for the interaction of olefins with deuterium over iron films. (A) Reaction of cyclopentene with deuterium at −35°C; (B) reaction of ethylene with deuterium at −100°C; and (C) reaction of cyclohexene with deuterium at 0°C.

We come finally to palladium and platinum. Platinum appears to give little olefin exchange (24,25). With ethylene over a variety of platinum catalysts, the exchange rate is never more than 4% of the addition rate (24), and with propylene over platinum-pumice, the exchange is suppressed completely on increasing the initial D_2/olefin ratio from 0.9 to 1.4. Over palladium-pumice, however, olefin exchange with propylene is much more marked (26). This difference also appears in the hydrogenations of unsaturated cyclic compounds (27,28). Little isomerization is observed during the hydrogenation of 2,3-dimethylcyclohexene and of 2-methyl-methylenecyclohexane on platinum, but in the hydrogenation of the latter over palladium-charcoal its concentration has fallen to its low equilibrium value after about 30% conversion (see Fig. 3); palladium-alumina behaves similarly (27). A variety of substituted cyclohexenes and methylenecyclohexanes do not isomerize appreciably when hydrogenated over platinum (28). Palladium on barium sulfate causes rapid equilibration of 1-butene in ethanol solution at −8°C (16). The results on isomerization and on olefin exchange are, therefore, quite consistent and point to palladium being much more active for these processes than platinum.

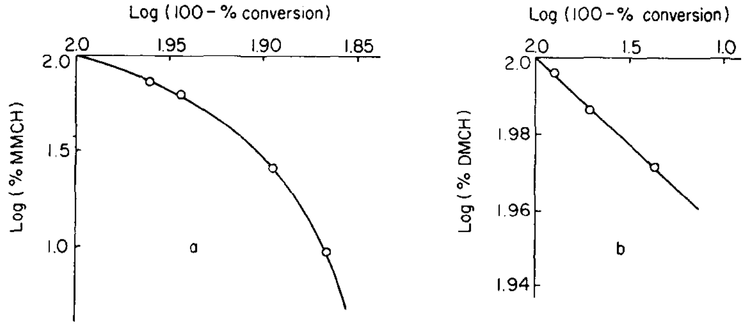


FIG. 3. Plots of log(100% − conversion) against log(% reactant olefin remaining) for the isomerization of cyclic olefins during their hydrogenation at 25°C. (a) 2-Methylmethylenecyclohexane (MMCH) over Pd-charcoal; (b) 2,3-dimethylcyclohexene (DMCH) over Pt (note different scales).

The only information in the literature concerning the other Group VIII metals refers to ther propensity to cause *cis-trans* isomerization during the hydrogenation of tall-oil fatty acids; the sequence is

$$\mathrm{Pd} > \mathrm{Rh} > \mathrm{Ru} > \mathrm{Ir} > \mathrm{Pt} \qquad \text{(iii)}$$

which, therefore, confirms the observations in the last paragraph.

III. *The Hydrogenation of Unsaturated Hydrocarbons over the Noble Metals of Group VIII—Some New Results*

We have studied the selective hydrogenation of acetylene, allene, and butadiene, the isomerization of butene-1, and the exchange of propylene with deuterium over alumina-supported ruthenium, rhodium, palladium, osmium, iridium, and platinum catalysts. The following results and discussion summarize a large body of work, a detailed exposition and discussion of which will be presented for publication in due course. This section is concerned with the magnitude of the selectivities shown by these metals and with their efficiency for isomerization and exchange as opposed to hydrogen (or deuterium) addition. Our results are compared with previous work, where possible, and a general relationship among exchange, isomerization, and selectivity is developed.

All experimental work was carried out in the gas phase in a static system. Each metal was supported on 8 to 16-mesh α-alumina; the platinum, palladium, rhodium, and iridium being present to the extent of 5 molar per cent by weight, and ruthenium and osmium to the extent of 1 molar per cent. Reaction products were analyzed by gas chromatography, and the deuterium content of exchanged propylenes was estimated by mass spectrometry.

The Selective Hydrogenation of Acetylene, Allene, and Butadiene

Selectivity was defined in Section II. This function decreased with increasing initial hydrogen pressure, increased with increasing temperature, and was independent of acetylene pressure. Thus, it is not a simple matter to decide upon a "standard state" in which to compare the selectivities given by the six metals. The values shown in Table 3 for any given metal refer to a common percentage conversion, and the temperatures quoted are those at which the rates of hydrogenation of each hydrocarbon were easily measurable.

TABLE 3

MECHANISTIC SELECTIVITIES (S_m) SHOWN BY ALUMINA-SUPPORTED RUTHENIUM, RHODIUM, PALLADIUM, OSMIUM, IRIDIUM AND PLATINUM CATALYSTS

Metal	Hydrocarbon	Initial P_{H_2}/P_{hc}	Temp. (°C)	S_m
Ruthenium	Acetylene	2.0	133	0.82
Ruthenium	Allene	3.1	51	0.84
Ruthenium	Butadiene	2.0	0	0.73
Rhodium	Acetylene	2.0	132	0.93
Rhodium	Allene	3.0	61	0.92
Rhodium	Butadiene	1.0	56	0.92
Palladium	Acetylene	2.0	30	0.97
Palladium	Allene	1.5	19	0.99
Palladium	Butadiene	2.0	21	1.00
Osmium	Acetylene	2.3	153	0.67
Osmium	Allene	6.0	130	0.73
Osmium	Butadiene	2.0	69	0.69
Iridium	Acetylene	2.0	62	0.22
Iridium	Allene	1.8	28	0.36
Iridium	Butadiene	3.0	24	0.25
Platinum	Acetylene	2.0	97	0.83
Platinum	Allene	1.8	79	0.89
Platinum	Butadiene	2.0	108	0.81

The metals can be placed in the following sequence of decreasing selectivity:

$$\text{Pd} > \text{Rh} \geq \text{Pt} > \text{Ru} > \text{Os} > \text{Ir} \qquad \text{(iv)}$$

This order confirms the order derived from the literature [sequences (i) and (ii), Section II] including the isolated report for iridium, and extends it to include ruthenium and osmium. It is important to emphasize that *the selectivity exhibited is primarily a function of the metal and is substantially independent of the hydrocarbon undergoing reaction and of the conditions under which the reaction was carried out.*

Previous workers have reported that ruthenium and osmium were inactive for acetylene hydrogenation (13), but our work refutes this report and is being commented upon elsewhere (29).

Before turning to a discussion of these results it is necessary to establish that sequence (4) is a true one and has not arisen through a fortuitous selection of conditions. The selectivity afforded by each metal was studied using several catalyst samples and embraced the entire accessible range of hydrogen pressure and temperature; Table 4 shows the maximum and minimum selectivities given by each metal irrespective of conditions. The order of selectivity derived from Table 3 is confirmed by the results shown in Table 4.

TABLE 4

MAXIMUM AND MINIMUM VALUES OF S_m RECORDED FOR THE SIX METALS IRRESPECTIVE OF THE REACTION OR CONDITIONS EMPLOYED

Metal	S_m
Palladium	0.90–1.00
Rhodium	0.65–0.95
Platinum	0.65–0.95
Ruthenium	0.55–0.85
Osmium	0.40–0.70
Iridium	0.10–0.60

Discussion of the Selectivity Sequence

The reaction scheme shown in Section II for acetylene hydrogenation constitutes a satisfactory basis for the following discussion.

It was seen there that the yield of saturated hydrocarbon given by a catalyst will depend on at least two factors: (*a*) the activity of the catalyst for olefin hydrogenation, i.e., k_4/k_5, and (*b*) the extent to which the formation of adsorbed alkyl groups is reversible, i.e., k_6/k_7.

Beeck (2) and Schuit and van Reijen (30) have reported relative activities for ethylene hydrogenation using, respectively,

TABLE 5

VALUES OF $\mathrm{Log}_{10}\, k_{C_2H_4}$ AND δ FOR THE NOBLE GROUP VIII METALS

	Pt	Pd	Rh	Ir	Ru	Os
$\mathrm{Log}_{10}\, k_{C_2H_4}$ [Beeck (2)]	−1.6	−0.8	0.0	—	—	—
$\mathrm{Log}_{10}\, k_{C_2H_4}$ [Schuit and van Reijen (30)]	−1.5	−0.9	0.0	−2.0	—	—
Percentage *d*-character of metallic bond [Pauling (31)]	44	46	50	49	50	49

evaporated metal films and silica-supported metals. Table 5 contains their results and also the percentage *d*-character of the metallic bonds, δ, of the elements in question as calculated by Pauling (31).

The results of Beeck (2) and of Schuit and van Reijen (30) agree closely, and $\log_{10} k_{C_2H_4}$ increases linearly with δ as pointed out by Beeck (2). The low value of $\log_{10} k_{C_2H_4}$ for iridium is surprising in view of the high value of δ calculated for this metal. In spite of this report, the order of activity for ethylene hydrogenation accepted for the purposes of this discussion will be that based on δ, since this definitely assists an understanding of the experimental results. This order is

$$\mathrm{Rh} \approx \mathrm{Ru} \geq \mathrm{Ir} \approx \mathrm{Os} > \mathrm{Pd} > \mathrm{Pt} \qquad \text{(v)}$$

Thus if the activity for ethylene hydrogenation was the only factor governing selectivity, the observed order of selectivity would be

$$\mathrm{Pt} > \mathrm{Pd} > \mathrm{Os} \approx \mathrm{Ir} \geq \mathrm{Ru} \approx \mathrm{Rh} \qquad \text{(vi)}$$

Sequences (iv) and (vi) differ because in the former case the olefin produced is reacting in the presence of the acetylene or diolefin from which it was formed and which is more strongly adsorbed. Under these conditions, readsorption of the olefin from the gas phase cannot occur (which is shown by the independence of selectivity upon percentage reaction), and, thus, the reversal of alkyl formation reduces the rate of formation of saturated hydrocarbon. If we consider two metals having the same activity for olefin hydrogenation, the one which is efficient for the reversal of alkyl formation will show a higher selectivity than one that is inefficient.

Unfortunately, the ethylene that arises in the hydrogenation of acetylene from steps [2] and [4] is indistinguishable from that which undergoes steps [2], [5], [6], and finally [4]. The situation is different in the hydrogenation of butadiene, where the relative abundances of the three butene isomers can be understood in terms of the two possible routes for olefin production. However, the situation here is complex, and the necessary information concerning the reversibility of alkyl radical formation can be obtained more simply from a study of the hydroisomerization and hydrogenation of butene-1 and of the exchange and deuteration of propylene.

Isomerization and Exchange of Unsaturated Hydrocarbons during Hydrogenation: Reversible Formation of Alkyl Radicals

In the presence of hydrogen, butene-1 is converted to *cis*- and *trans*-butene-2 and to *n*-butane. For the purposes of this paper it is sufficient to define a quantity *F* so that

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

Values of *F* over the six metals are shown in Table 6.

TABLE 6

TYPICAL *F* VALUES GIVEN BY THE NOBLE METALS OF GROUP VIII

Metal	Temp. (°C)	*F*
Ruthenium	24	1.05
Rhodium	69.3	5.70
Palladium	37.1	1.90
Osmium	25	0.23
Iridium	0	0.01
Platinum	107.5	0.03

Analogous information can be obtained from a study of the reaction of propylene with deuterium. The quantity F' can be defined,

$$F' = \frac{\text{Pressure of exchanged propylenes produced}}{\text{Pressure of deuteropropanes produced}}$$

Values of F' over rhodium, palladium, iridium, and platinum are shown in Table 7.

TABLE 7

TYPICAL F' VALUES GIVEN BY RHODIUM, PALLADIUM, IRIDIUM, AND PLATINUM CATALYSTS

Metal	Temp. (°C)	F'
Rhodium	88.5	1.6
Palladium	−20	1.1
Iridium	78.2	0.03
Platinum	72.6	0.06

The data in Tables 6 and 7 are consistent. They indicate that the metals of the second row of Group VIII are very efficient for the reversal of alkyl formation and that, in all cases, more alkyl reverts to adsorbed olefin *and undergoes desorption* than is hydrogenated further to saturated hydrocarbon. Third-row metals are much less efficient for alkyl reversal, although the behavior of osmium is intermediate between that of platinum and iridium, on the one hand, and, say, ruthenium, on the other. Thus, if the activities of all six metals for olefin hydrogenation were identical, then the order of selectivity, based on their efficiency for alkyl reversal, would be

$$\text{Rh} \geq \text{Ru} \approx \text{Pd} > \text{Os} > \text{Ir} \approx \text{Pt} \qquad \text{(vii)}$$

It now remains to attempt a synthesis of the factors which determine sequences (vi) and (vii).

A Synthesis of the Factors Governing Selectivity

Iridium, osmium, ruthenium, and rhodium are expected to possess a similar activity for ethylene hydrogenation, on the basis of Pauling's values of δ. Thus the selectivity in this quartet is expected to be proportional to the extent to which these metals promote the reversal of alkyl formation in the order iridium, osmium, ruthenium, rhodium. That this is precisely the observed order is very gratifying, indeed.

Platinum is less active for olefin hydrogenation than rhodium, but virtually all of the alkyl formed is hydrogenated to ethane. The similarity of the selectivity over platinum and rhodium must, therefore, arise through a balancing of these factors.

Palladium exhibits a lower activity for olefin hydrogenation than rhodium, yet it is (like rhodium) an efficient catalyst for the reversal of alkyl formation. Thus palladium is expected to give a higher selectivity than rhodium, which, again, is in complete accordance with observation.

Thus a synthesis of the factors governing selectivity is seen to predict an order of the metals for increasing selectivity which is in agreement with experiment, only the precise relation of platinum to rhodium is slightly uncertain. It appears, therefore, that a qualitative understanding of selectivity has been achieved.

IV. DISCUSSION

The new results given in the last section confirm the selectivity sequence shown in the literature survey, and provide the first information on the relative tendencies of ruthenium, osmium, rhodium, and iridium to give exchange or isomerization. It now appears that high selectivity accompanies (and is perhaps caused by) a high tendency to give exchange and isomerization, and that these phenomena neither depend critically on molecular type nor on the physical nature of the catalyst. There is a clear difference in behavior between the second-row metals (Ru, Rh, Pd) and the third-row metals (Os, Ir, Pt). This distinction is unrelated to the crystal structure of the metals (Ru and Os are hexagonal, close packed, and the rest cubic, close packed) and to quantities such as percentage *d*-bond character.

The source of this distinction lies in the relative tendencies of the metals to promote the dehydrogenation of an adsorbed alkyl radical in preference to its further hydrogenation. This tendency is of profound importance since it determines not only the course of the hydrogenation of olefins, but also, in some measure, the selectivity observed in the hydrogenation of multiply unsaturated hydrocarbons. The reason why this tendency is systematically greater in the second-row metals than in the third remains a question for further study.

The first-row metals (Fe, Co, Ni) seem to show high activity in exchange and isomerization (see Section II) and to be less active than the noble Group VIII metals in olefin hydrogenation (2, 30); on both these scores, therefore, we should expect them to show high selectivities. The values quoted in Table 1 are all close to 0.9 and, moreover, Raney nickel is well known to be highly selective (16–18). On the available evidence we would judge that the foregoing arguments apply as much to the first-row metals as to the remainder.

Correlations of the type developed in this paper have some practical value. Thus we can now predict with some confidence the course of certain catalytic reactions as yet unstudied, and this is, indeed, an unusual situation. For example, we should expect that in the hydrogenation of substituted olefins iridium would never give much isomerization, whereas with rhodium it would be extensive. The correlations, though firmly based, remain empirical; but empirical correlations are better than none.

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