567. *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part VI.* The Reaction over Rhodium and Iridium.*

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The reaction between acetylene and hydrogen proceeds over rhodium and iridium very similarly to that over other group-VIII metals. In the reaction over rhodium, which is a fairly active catalyst, the yields of C_2 hydrocarbons (ethylene, ethane) are 70—80% of the acetylene removed, the rest of the removed acetylene appearing as partially hydrogenated polymers. The C_2 hydrocarbon yield is somewhat greater at large hydrogen : acetylene ratios, but the dependence on this ratio is very slight. The orders of reaction (first with respect to hydrogen, zero with respect to acetylene) therefore apply to both the simple hydrogenation and the hydropolymerisation. The effect of temperature on the total initial rate corresponds to an apparent activation energy of 15·5 kcals. Iridium is rather weakly active, and produces largely simple hydrogenation, with a small amount of hydropolymerisation. The orders of reaction over iridium are similar to those over rhodium. Ruthenium and osmium are only very slightly active as catalysts. The catalytic effects of all the metals of group VIII are briefly discussed and compared.

In recent years importance has been attached to comparisons of the kinetics of a given catalytic process over series of related catalysts. The acetylene–hydrogen reaction has been investigated over a variety of metals, and, with nickel, palladium, platinum, and iron, some details of its behaviour have been elucidated (Parts I—V, *J.*, 1944, 373; 1945, 133, 301, 305, 470). Although in this reaction there are two stages of hydrogenation, and also production, to varying extents, of reduced polymers of acetylene, these complexities make possible the ready detection of differences in the behaviour of different metals as catalysts. Apart from possessing clear differences in activity, metals differ in the relative extents to which they produce polymerisation and hydrogenation, and in the extents to which the latter is selective in yielding ethylene rather than ethane while any appreciable amount of acetylene remains. These variations are superimposed on a significant similarity in kinetic behaviour over all catalysts studied, which indicates always a very strong adsorption of acetylene, this being stronger than the adsorption of ethylene on the same catalyst. Variations in activation energies with different metals are observed, but are not very marked.

In view of the results reported for the hydrogenation of ethylene, and in particular of the great activity of rhodium in this reaction (Beeck, *Rev. Mod. Physics*, 1945, **17**, 61), it was felt desirable to extend work on the acetylene–hydrogen reaction to the use of those group-VIII metals not previously studied. This would make possible a wider comparison between the actions of various metals and assist the ultimate understanding of their actions in terms of their electronic and crystal structures. In the present paper, therefore, results are reported for rhodium, iridium, ruthenium, and osmium catalysts. Since this work was completed (1949) we have learnt of experiments by Beeck and Wheeler (cf. Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 122) on the hydrogenation of acetylene over rhodium, as well as over other catalysts previously studied. Details of their results, however, have not yet been given.

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* Part V, *J.*, 1945, 470.

EXPERIMENTAL

Apparatus.—This was essentially as described in Part I.

Gases.—Cylinder acetylene was purified by passage through the reagents described by Conn, Kistiakowsky, and Smith (*J. Amer. Chem. Soc.*, 1939, **61**, 1868), but was not dried other than by passage over anhydrous calcium chloride. Cylinder hydrogen was freed from oxygen by passage through alkaline sodium hydrosulphite (dithionite) solution.

Catalysts.—All catalysts were carried on well cleaned pumice granules, and had metal : pumice ratios of 1 : 20. Ruthenium, rhodium, and iridium catalysts were made by evaporating solutions of ruthenium trichloride, rhodium trichloride, and ammonium hexachloroiridate on to the pumice with continuous stirring, and then drying them at 120°. Required amounts of ruthenium and rhodium catalysts were finally reduced with hydrogen in the reaction vessel at 240—250° for at least 2 hours (reduction was then complete). The ammonium hexachloroiridate was first decomposed at 120° in a stream of hydrogen, ammonium and hydrogen chlorides being evolved, and the residue finally reduced in hydrogen at 240° as before. Osmium catalysts were made by reduction of aqueous osmium tetroxide with alkaline formaldehyde in the presence of pumice. Water-soluble compounds were removed by washing the product, and the residual water was then evaporated, with stirring. The catalyst was heated in hydrogen to 150° immediately before use.

Approximately 2 g. of catalyst, including carrier, were used in each experiment.

Analysis of Products.—Gaseous products were analysed in a Bone–Newitt apparatus, the methods described in Part I being used.

RESULTS

Ruthenium.—Prepared as described, ruthenium had an extremely small activity as a catalyst. A slow reaction occurred at 288° but did not reach a rate convenient for study below temperatures at which the ordinary thermal reactions of acetylene in glass are known to begin. Therefore, though a definite slight catalytic effect is probable, no detailed study could be made.

Osmium.—Though slightly more active than ruthenium, osmium also had very little catalytic effect. With 400 mm. of hydrogen and 200 mm. of acetylene a pressure fall of 46 mm. occurred in 2 hours at 210°. Though this change is definitely faster than any reaction in the absence of osmium at this temperature, a convenient study could again not be made except at such temperatures that non-catalysed thermal reactions were also likely. Analysis, after a relatively small pressure fall, indicated that reaction was largely polymerisation, though accompanied by some hydrogenation.

Rhodium.—This metal was quite an active catalyst, and reaction over it could be conveniently studied at 50—100°. The fall in pressure with time followed courses similar to those obtained with nickel catalysts (Part I).

Some typical examples of analyses of products are given in the table (Δp = fall in pressure in time t; C_mH_n represents olefins higher than C_2 detected in the gas). With such initial mixtures, some 70% of the acetylene used undergoes hydrogenation, giving ethylene with fair selectivity, and the remaining 30% is converted, with about an equal amount of hydrogen, into reduced polymers of acetylene. Since the pressures of higher olefins detected in the gas phase are about 40% of the pressures of acetylene removed as reduced polymers, these must be largely low polymers, *e.g.*, of the C_4 and C_6 series.

	Initial press. (mm.)				Press. in product (mm.)					Yield (as % of C_2H_2 removed)	
T °	C_2H_2	H_2	Δp (mm.)	t (mins.)	C_2H_2	C_mH_n	C_2H_4	H_2	C_2H_6	C_2H_4	C_2H_6
84·5	196	223	187	60	60	15	84	54	16	61	13
84·5	400	169	169	130	266	15	85	22	12	63	9
84	101	203	100	17	28	8	40	116	12	55	16
88	201	404	201	18	62	19	56	228	40	40	29

Variations in initial hydrogen : acetylene ratio affect the yields in the manner shown in Fig. 1. In these experiments the larger of the initial partial pressures was near 400 mm. A sixteenfold increase in initial hydrogen : acetylene ratio causes an increase in the yield of C_2 hydrocarbons from about 70% to about 85% of the removed acetylene. This relatively small change for such a wide change in ratio must mean that the orders of reaction for the hydrogenation are very similar to those for the polymerisation. Production of ethane, at the stages at which analyses were made (where Δp = initial pressure of the less rich component), was small when acetylene was in a large excess, but increased about fourfold for a sixteenfold increase in hydrogen : acetylene ratio, while the yield of ethylene simultaneously fell slightly.

The orders of reaction were studied by the method of initial rates (Fig. 2); the reaction is of first order with respect to hydrogen and of zero order (or somewhat lower) with respect to acetylene. Hence the kinetics of the reactions over rhodium closely resemble those over all other metals studied. Strong adsorption of acetylene is again indicated, and it seems very probable that the mechanism of reaction is essentially similar to that postulated for other catalysts in previous papers in this series.

The effect of temperature on the initial rate of pressure-fall was studied between 17° and 110°. A good straight line is obtained for the plot of the logarithm of the initial rate against the reciprocal of the temperature, the slope corresponding to an apparent activation energy of 15·5 ± 0·5 kcal.

Iridium.—This metal had a smaller but distinct activity, and could be used conveniently at about 175°. The pressure–time curves obtained were again similar to those for nickel catalysis.

The effects of variation of partial pressures on the initial rate were systematically studied; the results were very similar to those found for rhodium. Therefore the reaction is of first order with respect to hydrogen and of zero order with respect to acetylene, in resemblance to that over other metals.

FIG. 1. *Effect of initial hydrogen : acetylene ratio on yields over rhodium at 84·5°.*

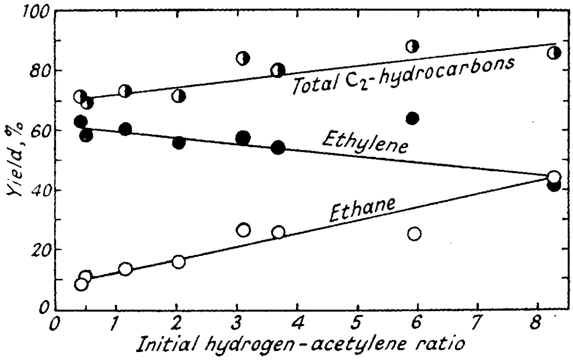
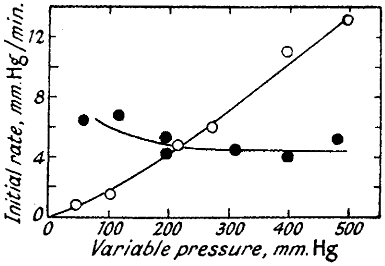


FIG. 2. *Effect of variation of partial pressure on the initial rate over rhodium at 85·5°.*



Open circles: 200 mm. of acetylene; hydrogen pressure varied.
Filled circles: 200 mm. of hydrogen; acetylene pressure varied.

Iridium catalysts were readily deactivated, and the products were analysed only for the reaction over partially deactivated catalysts. While considerable unchanged acetylene still remained, about 25% of the used acetylene appeared as ethylene and about 60% of it as ethane, the remaining 15% being removed (with an approximately equal amount of hydrogen) as reduced polymers. The high yield of ethane indicates a poor selectivity of hydrogenation, which is unexpected in view of the strong adsorption of acetylene indicated by the reaction orders. The effect may, however, be connected with the deactivated state of the catalyst, since a similar ethane predominance was also observed over highly deactivated palladium (Part V).

DISCUSSION

Since experiments have now been made on all the metals of group VIII, and also copper, as catalysts for the acetylene–hydrogen reaction, it is convenient to discuss the results of the current experiments as part of a brief review of the differences in catalytic action shown by different metals.

Activity of Catalysts.—Considering catalysts in the most active forms which we have used, palladium is the most active, weight for weight, followed by platinum and then by nickel and rhodium, which are about equally active. Iron, copper, cobalt, and iridium are weakly active, and ruthenium and osmium almost inactive. In the absence of data on the specific surfaces of our catalysts such results must be very approximate, but there is good qualitative agreement with Beeck and Wheeler's results (Beeck, *loc. cit.*) for platinum, palladium, nickel, rhodium, and iron catalysts, in which surface areas are allowed for. New copper catalysts have quite definite activity, comparable with that of iron.

All the appreciably active metals are of face-centred cubic structure (nickel, palladium, platinum, rhodium, iridium, and copper), while the least active (osmium and ruthenium) are of close-packed hexagonal structure. As cobalt may contain crystals of both these types (Hofer and Peebles, *J. Amer. Chem. Soc.*, 1947, **69**, 2497), it is not impossible that such activity as it shows is due to the cubic form, the close-packed hexagonal form being again inactive. Iron, with a body-centred cubic lattice, has a definite though small activity.

Reaction Orders and Energies of Activation.—In all cases where orders could be measured (nickel, palladium, platinum, iron, rhodium, and iridium) a remarkable consistency is found, indicative of very strong acetylene adsorption. In these circumstances the apparent activation energies, which would not require correction for the heat of adsorption of acetylene, should reflect any deep-seated differences in reaction mechanism, and they are found to be all rather similar in the cases measured. For nickel, platinum, palladium, iron, and rhodium the mean activation energies for the overall reaction are in the range 12—16 kcals.; only for nickel was it possible to estimate separate activation energies for hydrogenation and hydropolymerisation, but it seems probable that in general the activation energies are all close to the mean values. These facts all support a close general similarity in the mechanism of the reactions over these metals.

Beeck and Wheeler (*loc. cit.*) also find a constant energy of activation of the hydrogenation for nickel, rhodium, palladium, and platinum, but their figure (6—7 kcals.) is much lower than ours. This discrepancy, though presumably due to differences between our catalysts and Beeck and Wheeler's evaporated films, is somewhat puzzling.

Extent of Hydropolymerisation.—At comparable temperatures and gas pressures, this is greatest in the first horizontal row of metals—iron, cobalt, nickel, and copper. Copper readily produces a peculiarly specific polymerisation, relatively little hydrogen entering into the polymers. Of this set of metals, iron causes least polymerisation. In the second row of group VIII, rhodium and palladium are alike in producing considerably less polymer, but this still normally constitutes some 20—30% of the removed acetylene. With iridium and platinum (the third row of the group) the polymer yield has fallen to less than 20%. Polymerisation, therefore, seems chiefly associated with metals of smaller atomic radii. The situation was discussed in Part III.

Selectivity of Hydrogenation to Ethylene.—This can be assessed by comparison of the ethane : ethylene ratios, in the early stages of reaction, with comparable acetylene : hydrogen ratios. It is greatest with palladium, somewhat lower with nickel, and lower still with rhodium, platinum, and probably iridium. Over cobalt, selectivity is quite high, and with iron it shows variations with different samples of catalyst (Part V).

It is clearly not possible at present to give a full interpretation of comparisons of the above types in terms of the electronic and crystal structures of the metals concerned, but the following points may be noted.

Activity is mainly associated with face-centred cubic metals, close-packed hexagonal structures being scarcely active. This is possibly related to differences in interatomic distances in certain crystal faces. In particular, the longer spacings in the (110) faces of nickel, palladium, platinum, rhodium, and iridium are in the range 3·5—3·9 Å, and would all (as was shown for nickel, palladium, and platinum in Part I) be stereochemically suitable for associative chemisorption of acetylene, whereas in hexagonal cobalt, ruthenium, and osmium the $(10\bar{1}0)$ planes, which resemble the (110) case most closely, have longer metal–metal distances (4·11, 4·27, and 4·31 Å), which are probably too long to be spanned by adsorbed acetylene without considerable strain.

Maximum activity in each horizontal row of group VIII occurs in the column nickel, palladium, platinum, and this is parallel to a similar maximum in paramagnetic susceptibility in this column (cf. Maxted, *J.*, 1949, 1990). Palladium, with the highest susceptibility per gram-atom of those listed by Maxted, is in fact the most active catalyst in the present reaction, and the sequence of activities resembles the sequence of susceptibilities. Palladium is also the catalyst producing the most selective hydrogenation of acetylene. A parallel with magnetic properties in this case, however, may well be fortuitous, since the factors affecting selectivity must involve complex adsorption relationships, and it is certainly not valid to regard selectivity as a measure of the relative activities of a catalyst for the hydrogenation of acetylene and of ethylene on the same surface, since acetylene is always able to displace ethylene strongly. In general, however, the parallel between activity and magnetic susceptibility reflects an undoubted influence of the electronic structure of the metal. The clear differences, electronically, between metals of the copper group and those of group VIII are also reflected in the specific polymerizing action of copper in the acetylene–hydrogen reaction (cf. Reynolds, *J.*, 1950, 266).

For the hydrogenation of ethylene a relationship has been proposed (Beeck, *loc. cit.*, 1950) between the activity of the catalyst and the percentage of *d*-character in the metallic bonding of the metal, as estimated by Pauling (*Proc. Roy. Soc.*, 1949, *A*, **196**, 343). Since the percentage of *d*-character reaches maxima at ruthenium and osmium, any influence purely of *d*-character ought to show parallel maxima. Actually these metals have virtually no activity for acetylene hydrogenation; in the hydrogenation of ethylene, where activity is thought to increase with *d*-character, they might be expected to be very active, but have not been tested. There appears to be no clear influence purely of *d*-character detectable on any characteristic of the acetylene–hydrogen reaction.

It might, however, be expected that any influence of *d*-character would be clearer within cases of a definite crystal type, such as the face-centred cubic metals. This seems to be so in the hydrogenation of ethylene, where activity in nickel, platinum, palladium, and rhodium increases steadily in that order, which is the order of increasing *d*-character. For the acetylene-hydrogen reaction, on the other hand, activity and selectivity, plotted against *d*-character, reach maxima at palladium, since iridium and rhodium, both with more *d*-character than palladium, are less active and less selective than that metal. Iridium, in particular, probably falls out of any smooth sequence, and it would be interesting to know if iridium has the high activity for the hydrogenation of ethylene which is predicted for a face-centred cubic metal with bonds containing nearly as much *d*-character as those in rhodium. Until data are obtained on a wider variety of metals than hitherto, it would seem wise to interpret with caution relationships between *d*-character and catalytic action, particularly where different types of crystal lattice are under consideration.

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