Ruthenium and Osmium as Hydrogenation Catalysts

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It has been shown in a previous article in this journal that the hitherto little studied metals ruthenium and osmium possess catalytic activities which are comparable with those of the other noble Group VIII metals for the hydrogenation of the n-butenes, buta-1,3-diene and acetylene. Further studies have now been made using alumina-supported ruthenium and osmium catalysts for the hydrogenation and deuteration of dimethylacetylene and for the deuteration of ethylene and acetylene. Some of the results from these more recent studies are given in this article and the catalytic properties of ruthenium and osmium are discussed in relation to their position in the periodic table.

The preparation and activation of alumina-supported ruthenium and osmium catalysts and the apparatus used to follow reactions in a static system were described fully in a previous article (1). The analysis of reaction products was achieved using gas chromatography, mass spectrometry and infra-red spectrometry.

Reaction of Dimethylacetylene with Hydrogen and Deuterium

The only previous study of this reaction was reported by Hamilton and Burwell (2). They studied the reaction in a flow system over a palladium on alumina catalyst and found that up to the point in the reaction corresponding to the uptake of one mole of hydrogen per mole of butyne, cis-but-2-ene was the sole product.

The reaction has been studied over ruthenium and osmium to measure the degree of specificity for cis-but-2-ene formation which these metals promote and to compare the selectivity observed in this reaction with that observed in the hydrogenation of other di-unsaturated hydrocarbons.

A 1 per cent ruthenium-alumina catalyst was used to study the reaction in the temperature range 85 to 130°C. The variation of the butene distribution and of the selectivity with the number of moles of hydrogen consumed per mole of butyne, when a twofold excess of hydrogen was used, is shown in Fig. 1. From this figure, it can be seen that the butene distribution was constant until about 0.75 moles of hydrogen had been consumed and as the reaction proceeded beyond this point, the butenes isomerised, attaining their thermodynamic equilibrium proportions when about 1.4 moles of hydrogen had been consumed.

The initial butene distribution was independent of the initial hydrogen pressure and the only effect of increasing temperature was to increase slightly the yield of but-1-ene and decrease the yield of cis-but-2-ene. The selectivity showed the same trends to decrease with increasing initial hydrogen pressure and to increase with increasing temperature as were observed for acetylene and buta-1,3-diene (1). Orders of unity in hydrogen and zero in dimethylacetylene were obtained by the initial rate method at 100°C. The activation energy using hydrogen was 10 ± 1 kcal. mole^{-1} and using deuterium was 12.5 ± 1 kcal. mole^{-1}.

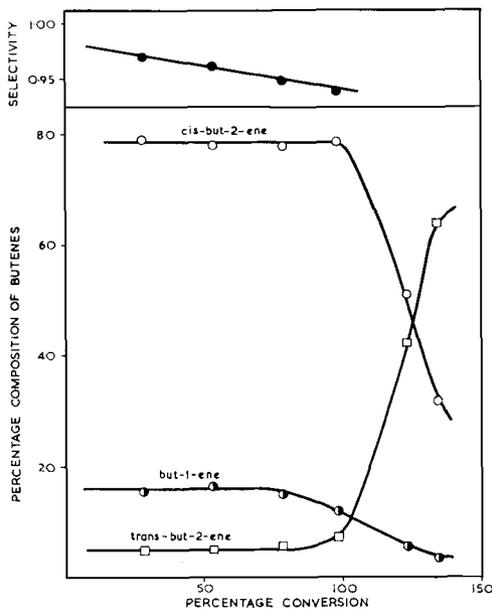The distribution of deuterium in each of the butenes was determined and the residual

Fig. 1 *Hydrogenation of dimethylacetylene over Ru/Al₂O₃; variation of butene distribution and of selectivity with conversion*

Fig. 2 *Reaction of dimethylacetylene with deuterium over Ru/Al₂O₃; variation of mean deuterium contents of butenes with conversion*

dimethylacetylene and deuterium were analysed for deuterium and hydrogen respectively. Under all conditions used, no deuterium was found in the dimethylacetylene. Table I shows a typical set of deutero-butene distributions. From these results it can be seen that the *cis-* and *trans*-but-2-ene distributions were very similar, whereas the but-1-ene had a much broader distribution. Fig. 2 shows the variation of the deuterium number, defined as the mean number of deuterium atoms per molecule of butene, for each of the butenes with the number of
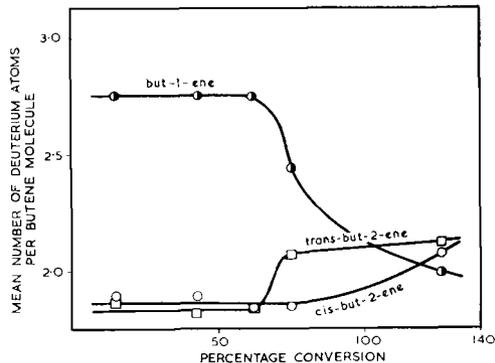
moles of deuterium consumed. It is of interest to compare this figure with Fig. 1, when it can be seen that at the point in Fig. 1 where the butenes start to isomerise, there is a rapid redistribution of deuterium in the but-1-ene and the *trans*-but-2-ene.

The reaction was studied between 100 and 155°C using 1 per cent osmium-alumina catalyst. Fig. 3 shows the variation of the butene distribution and selectivity with the number of moles of hydrogen consumed, for the reaction using a twofold excess of hydrogen. Unlike ruthenium, the butene distribution was dependent upon the extent of the reaction, the yield of but-1-ene decreasing and that of *trans*-but-2-ene increasing as the reaction proceeded, although the *cis*-but-2-ene yield remained approximately constant. The selectivity decreased as the reaction proceeded. The butene distribu-

Table I

Deutero-butene Distributions obtained from the Dimethylacetylene-Deuterium Reaction over Ru/Al₂O₃ at 83°C and over Os/Al₂O₃ at 100°C

Metal	Hydrocarbon	$-d_0$	$-d_1$	$-d_2$	$-d_3$	$-d_4$	$-d_5$	$-d_6$	$-d_7$	$-d_8$	M
Ru	But-1-ene	0.0	4.7	40.1	39.1	10.0	6.1	0.0	0.0	0.0	2.72
	trans-but-2-ene	0.7	16.1	72.3	9.4	1.5	0.0	0.0	0.0	0.0	1.94
	cis-but-2-ene	0.5	11.7	85.2	2.1	0.5	0.0	0.0	0.0	0.0	1.89
Os	But-1-ene	0.2	8.0	22.1	39.2	12.0	8.5	4.8	2.8	2.4	3.29
	trans-but-2-ene	2.1	17.0	55.9	7.9	6.4	6.0	2.2	1.5	1.0	2.41
	cis-but-2-ene	2.5	21.8	63.9	4.9	3.1	2.2	0.7	0.6	0.3	2.00

tion was independent of the initial hydrogen pressure and, with increasing temperature, the same trends were observed as were found with ruthenium. The initial rate kinetics were unity in hydrogen and zero in dimethylacetylene at 135°C. A value of 11 ± 1 kcal. mole^{-1} was obtained for the activation energy when hydrogen was used.

As with ruthenium, no dimethylacetylene exchange was observed in the reaction with deuterium. Table I shows a typical set of deutero-butene distributions. The but-1-ene was more heavily deuterated than the but-2-enes, as was observed with ruthenium, although the *trans*-but-2-ene distribution was somewhat broader than that of the *cis*-but-2-ene. Comparison of these results with those for ruthenium shows that the most highly deuterated butene contained eight deuterium atoms when an osmium catalyst was used, but only five when a ruthenium catalyst was used.

Reaction of Ethylene with Deuterium

A mathematical analysis has been carried out to interpret the observed distributions of deuterium in the product and the reactant as a result of the interaction of ethylene with deuterium.

A 1 per cent ruthenium-alumina catalyst was used to study the reaction between 32 and 79°C. Orders of reaction of unity in deuterium and –0.2 in ethylene were observed
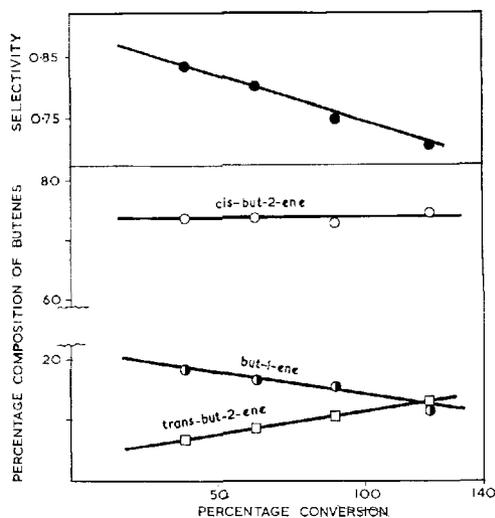

Fig. 3 *Hydrogenation of dimethylacetylene over Os/Al_2O_3; variation of butene distribution and of selectivity with conversion*

at 53°C and a value of 8.7 ± 0.5 kcal. mole^{-1} was obtained for the activation energy. Table II shows a product distribution obtained after 5 per cent reaction at 32°C: the deuterated ethanes and ethylenes (excluding ethylene-d_0) are expressed as a percentage of their sum: the ethylene-d_0 formed in the reaction cannot of course be distinguished from reactant ethylene which has not been in contact with the surface. The parameter F is defined as $\Sigma C_2 X_4 / \Sigma C_2 X_6$, where X may be either H or D, and constitutes a measure of the amount of olefin exchange.

A 1 per cent osmium-alumina catalyst was used and the reaction was studied between

Table II

Product Distributions from the Ethylene-Deuterium Reaction over Ru/Al_2O_3 (5 per cent reaction, 32°C) and over Os/Al_2O_3 (7.5 per cent reaction, 17°C)

Metal	Ethylene				Ethanes							F
	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6	
Ru	39.8	0.0	0.0	0.0	2.2	10.4	45.3	2.1	0.0	0.0	0.0	0.66
—	*36.7*	*1.6*	*0.1*	*0.0*	*0.6*	*10.5*	*47.7*	*2.7*	*0.1*	*0.0*	*0.0*	*0.62*
Os	18.9	0.4	0.0	0.0	1.0	9.8	59.0	6.4	3.0	0.7	0.7	0.24
—	*20.1*	*2.1*	*0.2*	*0.0*	*0.7*	*12.3*	*56.4*	*7.4*	*0.8*	*0.1*	*0.0*	*0.29*

The italicised figures are the theoretical distributions

17 and 49°C. An order of unity in deuterium was obtained at 24°C and the activation energy was found to be 8.5 ± 0.5 kcal. mole^{-1}. Table II shows a product distribution obtained after 7.5 per cent reaction at 17°C.

Comparison of these results with those obtained for ruthenium shows that, as was found with the deutero-butene distributions obtained from dimethylacetylene, the distributions were broader over osmium than over ruthenium.

Also shown in Table II are theoretical distributions which are in good agreement with those observed experimentally. These distributions were computed according to the theory originally put forward by Kemball (3). This theory is a steady state analysis of the reaction scheme:

$$C_2X_4(g) \rightleftharpoons C_2X_4(a) \xrightleftharpoons[-X]{+X} C_2X_5(a) \xrightarrow{+X} C_2X_6(g)$$
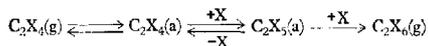
where X may be either H or D, their origins and fates being unspecified.

The results obtained from this mathematical analysis show that the ratio of the chance of ethylene becoming ethyl to the chance of ethylene desorbing is higher for osmium than for ruthenium. Furthermore, this parameter is independent of the reaction conditions, variations in the experimental distributions being accounted for by variations in the parameter which gives the ratio of the chance of ethyl reverting to ethylene to the chance of ethyl becoming ethane. Over both metals, this latter parameter increases with increasing temperature and decreases with increasing initial deuterium pressure. The value for ruthenium was higher than for osmium, under comparable conditions, i.e. there was a greater chance of "ethyl reversal" over ruthenium.

Table III

Deutero-ethylene Distributions observed in the Acetylene-Deuterium Reaction over Ru/Al$_2$O$_3$ at 133°C and over Os/Al$_2$O$_3$ at 146°C

Metal	d_0	d_1	d_2	d_3	d_4	α	cis/trans	M
Ru	1.4	10.5	37.2	31.1	19.9	16.4	1.10	2.58
—	1.2	14.5	38.8	30.2	15.3	26.6	—	2.44
Os	10.5	28.2	38.9	18.2	5.0	8.9	3.00	1.81
—	6.2	28.2	39.9	20.6	5.0	20.8	—	1.90

The italicised distributions are those calculated from the scheme shown in the text

Reaction of Acetylene with Deuterium

This reaction was studied primarily to examine the distribution of deuterium in the deutero-ethylenes and to determine the yields of cis-, trans- and asymmetric dideutero-ethylene by infra-red analysis. The residual acetylene and deuterium were also analysed to determine respectively the deuterium and hydrogen content.

The reaction was studied between 133 and 183°C using 5 per cent ruthenium-alumina catalyst and between 148 and 201°C using 5 per cent osmium-alumina catalyst. Table III shows the deutero-ethylene distributions at the lowest temperatures used, the yield of asymmetric dideutero-ethylene as a percentage of the total dideutero-ethylene yield (α) and the cis/trans ratio in the dideutero-ethylene. Table III also shows theoretical deutero-ethylene distributions which show satisfactory agreement with those observed experimentally. These theoretical distributions were calculated in a manner similar to that used to calculate the ethylene-deuterium product distributions, i.e. by carrying out a steady state analysis of the reaction scheme:

$$C_2X_2(a) \xrightleftharpoons[-X]{+X} C_2X_3(a) \xrightarrow{+X} C_2X_4$$
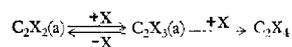
where X may be either H or D, their origins and fates not being specified.

Table IV

Table IV

Selectivity Values for the Noble Group VIII Metals

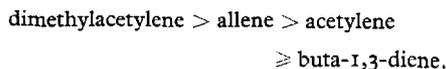| Metal	Dimethylacetylene	Allene	Acetylene	Buta-1,3-diene	References
Ru	0.98 at 88.5°	0.8 at 51°	0.8 at 135°	0.75 at 0°	—
Os	0.9 at 120°	0.7 at 130°	0.5 at 123°	0.7 at 67°	—
Rh	0.99 at 153°	0.9 at 61°	0.9 at 132°	0.9 at 132°	4, 5, 6
Ir	0.96 at 153°	0.4 at 23°	0.2 at 24°	0.3 at 108°	4, 5, 6
Pd	1.0 at 20°	0.99 at 19°	0.97 at 30°	0.99 at 21°	2, 5, 6
Pt	0.96 at 153°	0.9 at 110°	0.8 at 97°	0.8 at 108°	4, 5, 6

The results obtained from the mathematical analysis show that the chance of the vinyl group reverting to adsorbed acetylene is higher over ruthenium than over osmium, and that with increasing temperature and decreasing deuterium pressure, the chance of "vinyl reversal" increases.

Discussion

The results presented in this and the previous article (1) show that invariably the selectivity for olefin formation, observed in the hydrogenation of di-unsaturated hydrocarbons, is higher over ruthenium than over osmium. This tendency for the selectivity to decrease from the second to the third transition metal series appears to be a common feature of all the noble Group VIII metals, as can be seen from the values quoted in Table IV. From this table two distinct trends emerge; first, the selectivity for a given

reaction decreases from the second to the third transition metal row and, secondly, for a given metal, the selectivity decreases in the order:

dimethylacetylene > allene > acetylene

$$\geqslant \text{buta-1,3-diene.}$$

Further correlations between catalytic properties and the position of the metal in the periodic table can be found by considering the degree of specificity for *cis*-but-2-ene formation observed in dimethylacetylene hydrogenation, as shown in Table V. The degree of specificity increases from left to right across each series and decreases from the second to the third row.

The results obtained from studies of the hydroisomerisation of the *n*-butenes show that ruthenium possesses a higher isomerisation activity than osmium. Again this is a general feature of the noble Group VIII metals, since the second row metals ruthenium, rhodium and palladium possess higher isomerisation activities than the third row metals, osmium, iridium and platinum (6). The sequence of decreasing isomerisation activity is:

$$Pd > Rh > Ru > Os \gg Pt \simeq Ir$$
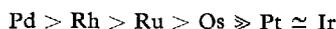
Similarly, the second row metals promote more olefin exchange than the third row metals, as can been seen from the F values observed in the ethylene-deuterium reaction (7):

Ru	Rh	Pd	Os	Pt	Ir
1.38	1.60	1.23	0.40	0.13	0.13

Table V

Yield of cis-but-2-ene observed in the Hydrogenation of Dimethylacetylene over the Noble Group VIII metals

Metal	Temperature °C	Per cent cis-but-2-ene	Reference
Ru	88.5	79.5	—
Os	120.0	74.0	—
Rh	153.0	84.4	4
Ir	153.0	87.0	4
Pd	20.0	100.0	2
Pt	153.0	87.5	4

From the foregoing discussion, it can be seen that ruthenium and osmium exhibit similar catalytic properties to those of the other noble Group VIII metals and furthermore, the changes from ruthenium to osmium appear to be consistent with a general systematic variation in certain catalytic properties with the position of the metal in the periodic table.

While it is unlikely that there is a single simple interpretation of the trends outlined above, it is possible that the mode of chemisorption of olefins and acetylenes on metal surfaces may be of some importance in this context. Up to the present time, it has generally been assumed that olefins and acetylenes chemisorb by the rupture of the olefinic or acetylenic π-bond and the formation of two carbon-metal σ-bonds.

It has recently been suggested (8), however, that the chemisorption of olefins could occur by the formation of an olefin-metal complex similar to the complexes encountered in organometallic chemistry. The bonding in organometallic complexes of this type has been described in some detail by Chatt and co-workers (9). Similar complexes could arise with acetylenes which, having two mutually perpendicular sets of π-orbitals could bond to one or two surface metal atoms, both mono- and binuclear complexes having been reported in organometallic chemistry (10). If chemisorption of olefins and acetylenes occurs by the formation of π-complexes it might be expected that the stabilities of the complexes in catalytic reactions would be similar to those of the corresponding organometallic complexes. Unfortunately, very few organometallic complexes relevant to the present discussion have as yet been reported, although the few details that are available suggest that the stabilities of the olefin complexes increase from the second to the third transition metal row. Thus, for example, ferrocene, ruthenocene and osmocene increase in stability in that order (11) while the ethylene complexes of nickel, palladium and platinum

show a similar trend (11). Assuming that these trends are applicable to intermediates in catalytic reactions it can be readily seen that the ability of the second row metals to promote more isomerisation and olefin exchange than the third row metals can be explained by the difference in the stabilities of the olefin-metal complex, since the less stable this complex the more easily will desorption of reacted olefins occur.

The decrease in selectivity from the second to the third transition metal row can also be explained in terms of the concept of chemisorption of acetylenes and olefins by π-complex formation. Consider the hydrogenation of acetylene;

The ethylene is formed as a π-olefin-metal complex and must undergo desorption before appearing in the gas-phase. Consequently, the selectivity will be a function of the ability of the olefin to desorb rather than undergo further hydrogenation to alkane. Since the stability of the π-olefin-metal complexes increases from the second to the third row and, therefore, the ease of desorption decreases, it might be expected that the selectivity would decrease from the second to the third row, in agreement with the experimental observations.

The close similarity between the catalytic properties of ruthenium and osmium and those of the other noble Group VIII metals may indicate that the geometric factor is of little importance in catalysis. Ruthenium and osmium have a close packed hexagonal structure while the other noble Group VIII metals crystallise in the face centred cubic form. The chemisorption of acetylene by the formation of two carbon-metal σ-bonds

involves only the longer interatomic spacings (12) and although such spacings do exist in the c.p.h. metals (1), they are less commonly available than in the f.c.c. metals. Consequently, it might be expected that the c.p.h. metals would show a significantly lower activity for acetylene hydrogenation than the f.c.c. metals. This has been found not to be the case and these observations may also support the postulate that acetylene chemisorbs as a binuclear π-complex, rather than as a σ-1,2-diadsorbed species, since the former state will have less severe geometric restrictions. Such a conclusion may be substantiated by the observation that acetylene and ethylene when adsorbed on nickel films show positive surface potentials (13).

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High Temperature Resistance Furnaces

40 PER CENT RHODIUM-PLATINUM VERSUS RHODIUM

The rhodium-platinum equilibrium diagram has been known since about 1930, but metallurgists in general have been somewhat slow to appreciate its significance when they need to choose a material for winding resistance furnaces for operation at high temperatures.

For the last 20 years whenever it has been necessary to construct small furnaces operating in air at temperatures up to about 1800°C, rhodium has invariably been the first choice.

The original proposal to use rhodium for this purpose is to be found in a pamphlet issued by the National Physical Laboratory in August 1942, describing the technique of calibrating platinum : 13 per cent rhodium-platinum thermocouples for use in liquid steel.

A furnace was needed in which the tip of the couple could be heated slowly until the platinum arm melted, the molten bead gradually moving down the other arm of the couple. The furnace, which was rated at only about $\frac{1}{4}$ kilowatt, was made by winding rhodium strip on a sintered alumina tube, the winding being protected by a layer of pure alumina from the outer lagging.

The reason for the choice of rhodium as a winding is its high melting point, 1960°C. Rhodium wire or strip, however, is not particularly easy to make, it tends to be fibrous in structure, and is expensive. A brief reference to the rhodium-platinum diagram indicates that the melting point of rhodium is lowered only very slowly by additions of platinum; even with 60 per cent of platinum the liquidus temperature is lowered by only 25°C. It is thus possible to make very considerable economies with little sacrifice in performance by employing a 40 per cent rhodium-platinum alloy in place of rhodium whenever high temperature furnaces are to be constructed.

Recently attention has been given to improving the uniformity and ductility of 40 per cent rhodium-platinum wire and strip. Methods of manufacture have been developed which ensure a fine grain size even after long service at elevated temperatures, and as the characteristics of this alloy are more widely appreciated, it will find increased use for making small high temperature furnaces for operation in air.

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