The Hydrogenation of Acetylene

V. The Reaction of Acetylene with Hydrogen and Deuterium Catalyzed by Alumina-Supported Ruthenium and Osmium

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The reaction of acetylene with hydrogen and deuterium has been studied using alumina-supported ruthenium (92–192°C) and osmium (144–202°C). The kinetics, activation energies, and selectivities have been determined. Under comparable conditions, ruthenium was always more selective than osmium for ethylene production.

In the reaction with deuterium, appreciable amounts of acetylene exchange were observed and evidence is presented which suggests that acetylene exchange and deuteration occur independently. The deuteroethylene distributions have been interpreted in terms of the theoretical scheme discussed in Part IV. The chance of adsorbed species acquiring a deuterium atom rather than a hydrogen atom is approximately the same over each metal, although the chance of vinyl undergoing hydrogenation rather than dehydrogenation is lower over Ru than Os. The mechanism is discussed in terms of the successive addition of two "hydrogen" atoms to adsorbed acetylene.

INTRODUCTION

Although the catalytic hydrogenation of acetylene has been studied using rhodium, iridium, palladium, and platinum catalysts (1, 2), the other noble Group VIII metals, ruthenium and osmium, have received but little attention. Sheridan and Reid (3) reported that pumice-supported ruthenium and osmium were inactive for acetylene hydrogenation below 250°C. Subsequent work has shown that, in aqueous solution, charcoal-supported ruthenium catalysts are active for the hydrogenation of diphenylacetylene (4), and alumina-supported ruthenium and osmium are active for 2-butyne hydrogenation (5).

This paper reports the hydrogenation of acetylene over alumina-supported ruthenium and osmium catalysts. This study was carried out with a view to comparing the

catalytic properties of ruthenium and osmium with those of the other Group VIII metals. We also hoped to determine whether the crystal structure of the metal noticeably influenced its activity or selectivity as a hydrogenation catalyst (ruthenium and osmium crystallize in the close-packed hexagonal form, whereas the other noble Group VIII metals have a face-centered cubic structure).

EXPERIMENTAL

Catalysts. The preparation of the catalyst stocks has been described elsewhere (5). Ruthenium and osmium were supported on 10–12 mesh Peter Spence Type "A" alumina (surface area ∼ 200 m²g⁻¹) at a concentration of 1% (Ru-A and Os-A) or 5% w/w (Ru-B and Os-B).

Materials. The purification of commercial acetylene and the preparation of deuterium containing 99.3 atom % D were carried out as described in Parts I and IV, respectively. Hydrogen (British Oxygen Co.) was freed of trace amounts of oxygen by passage

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through palladized asbestos at 200°C and then through a cold trap maintained at −196°C.

Apparatus and experimental procedure. Descriptions of the apparatus and analytical procedures have been reported (*2, 5*); the following is a summary. Reactants were expanded into an evacuated 100-ml Pyrex reaction vessel containing the catalysts which was connected to a conventional high-vacuum apparatus. Reactions were followed by the pressure fall observed on a mercury manometer. After the desired degree of hydrogenation, the reaction mixture was pumped from the vessel through the spiral trap, which was cooled in liquid nitrogen; the hydrocarbons were thus freed of hydrogen and their chemical composition was determined by gas chromatography using a 4-ft column of activated silica gel (40–60 mesh) operated at 80° ± 2°C. When the pure hydrocarbon components were required for mass spectrometric or infrared analysis, they were frozen out of the carrier gas stream on elution from the chromatograph. The mass spectrometric and infra-

red analyses were conducted exactly as reported in Part IV of this series (*2*).

RESULTS

Pressure against time curves. Typical curves are shown in Fig. 1. With initial hydrogen:acetylene ratios of 2 or greater, the reaction over ruthenium proceeded in two stages (a), whereas over osmium only one stage was discernible (b). The acceleration point (denoted by $-\Delta p_a$) of curve (a) was independent of the initial hydrogen pressure and of the temperature, occurring at a pressure fall equal to 1.40 ± 0.05 times the initial acetylene pressure; i.e., at a pressure fall corresponding to the nearly complete removal of acetylene. The second stage thus represents olefin hydrogenation only. The absence of an acceleration point over osmium indicates that the transition from acetylene hydrogenation to olefin hydrogenation was not sudden.

Initial rate orders and activation energies. Orders of reaction measured by the initial rate method were unity in hydrogen (Ru at 112° and 139°C and Os at 165°C), and zero in acetylene (Ru at 112° and Os at 165°C). Activation energies were 10.5 ± 1.0 kcal mole^{-1} over Ru between 92° and 145°C and 8.0 ± 1.0 kcal mole^{-1} over Os between 144° and 202°C.

Dependence of selectivity upon experimental variables. Selectivity, S, is defined as $P_{C_2H_4}/(P_{C_2H_4} + P_{C_2H_6})$. During the first stage of the reaction, acetylene was hydrogenated to ethylene *and* ethane. With ruthenium at 135°C, the selectivity during reaction of 50 mm of acetylene with 100 mm of hydrogen was independent of pressure fall over the range 4 to 40 mm, the value being 0.80 ± 0.01. However, over osmium at 123°C, during the reaction of 50 mm of acetylene with 250 mm of hydrogen, the selectivity declined continuously with conversion:

Pressure fall (mm):	7.0	13.7	26.7	43.8
Selectivity:	0.54	0.52	0.49	0.47

Over both metals, selectivity decreased as the initial hydrogen pressure was increased (see Fig. 2) and as the temperature was lowered (see Fig. 3).
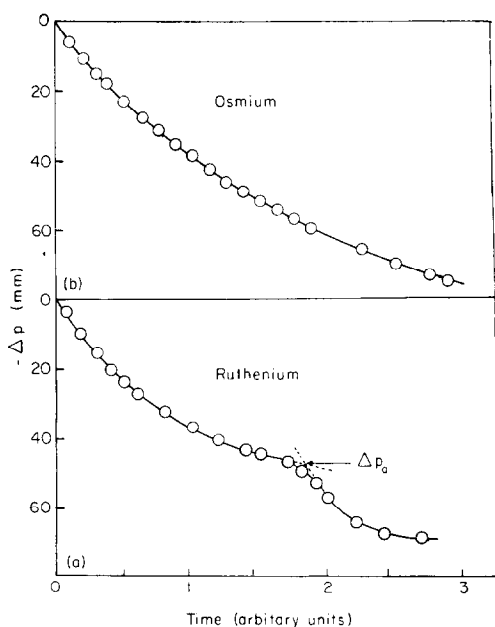

FIG. 1. Typical pressure fall, $-\Delta p$, against time curves for the complete hydrogenation of 40 mm of acetylene. (a) Ru-A at 135°C, $(P_{H_2})_0$ = 97 mm; (b), Os-A at 150°C, $(P_{H_2})_0$ = 162 mm.
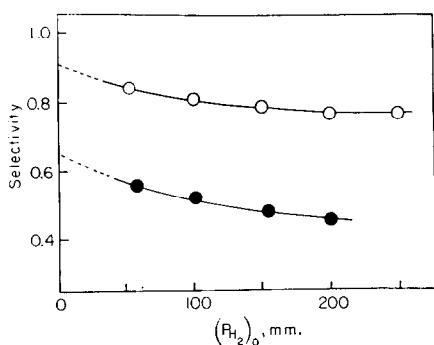
FIG. 2. Dependence of selectivity upon initial hydrogen pressure for Ru-A (○) [$(P_{C_2H_2})_0 = 50$ mm; temp., 139°C] and for Os-A (●) [$(P_{C_2H_2})_0 = 50$ mm; temp., 165°C].

Formation of C_4 hydrocarbons. In common with the other Group VIII metals, ruthenium and osmium catalyze the dimerization of acetylene to C_4 hydrocarbons. Eight percent of the acetylene was consumed in this way when using Ru-A [166°C, $(P_{C_2H_2})_0 = 50$ mm; $(P_{H_2})_0 = 100$ mm; pressure fall, 80 mm], and 16% when using Os-A [123°C; $(P_{C_2H_2})_0 = 50$ mm; $(P_{H_2})_0 = 200$ mm; pressure fall, 80 mm]. The C_4 hydrocarbons consisted of n-butane, 1-butene, and cis- and trans-2-butene. No higher hydrocarbons were detected.

REACTION OF ACETYLENE WITH DEUTERIUM

The deuteroethylenes formed by the reaction of acetylene with deuterium, the residual acetylene, and the residual deuterium were each analyzed mass spectro-
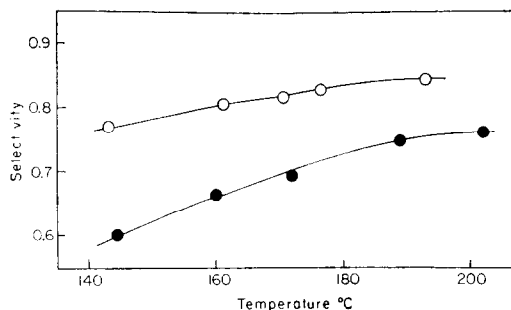

FIG. 3. Dependence of selectivity upon temperature for Ru-A (○) [$(P_{C_2H_2})_0 = 50$ mm; $(P_{H_2})_0 = 100$ mm; $-\Delta p$ at analysis = 12.5 mm] and for Os-A (●) [$(P_{C_2H_2})_0 = 30$ mm; $(P_{H_2})_0 = 150$ mm; $-\Delta p$ at analysis = 7.5 mm].

metrically. The deuteroethylenes were also examined by infrared spectroscopy to determine the cis–trans ratio in dideuteroethylene, denoted by (c/t), and the yield of asymmetric dideuteroethylene (α) as a percentage of the total dideuteroethylene yield.

In the following tables the *deuterium number* (x_e) of the ethylene, or (x_a) of the acetylene is defined as the mean number of deuterium atoms per hydrocarbon molecule, and the *hydrogen number* (y) of the "deuterium" is the mean number of hydrogen atoms present per molecule. Both of these quantities have been corrected for the initial hydrogen impurity in the deuterium.

In the theory presented in the discussion, the distributions of deuterium in the ethylene and the yield of asymmetric dideuteroethylene (α) have been calculated using the method described in Part IV (2). For convenience, some of the calculated deuteroethylene distributions, calculated values of (α_e), and values of p, q, and s are included in the tables of experimental results.

Effect of increasing pressure fall. The variation of the distribution of deuterium in the ethylenes and acetylenes was determined as a function of deuterium uptake at 173°C over Ru-B and 150°C over Os-B. The results are shown in Tables 1 and 2, respectively. With both catalysts, as the pressure fall increased, the deuterium number of the ethylenes decreased and the amount of hydrogen exchange increased. Over ruthenium, the amount of acetylene exchange was independent of pressure fall, while over osmium it decreased slightly as the reaction proceeded.

Variation of deuterium pressure. The effect of increasing initial deuterium pressure using Ru-B at 144°C (see Table 1) was to decrease the deuterium number of the ethylenes and to increase the extent of hydrogen exchange. With Os-B at 167°C (see Table 2) increasing initial deuterium pressure increased the deuterium number of the ethylenes and the extent of hydrogen exchange. Over both metals the relative yields of asymmetric and trans-dideuteroethylene decreased as the initial deuterium pressure was increased.

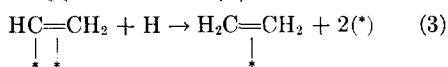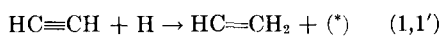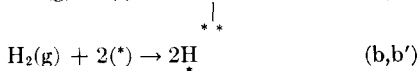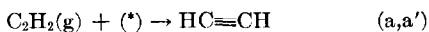**Variation of temperature.** The deuterium

TABLE 1

REACTION OF ACETYLENE WITH DEUTERIUM OVER RUTHENIUM (Ru-B)

$(P_{C_2H_2})_0$ (mm)	$(P_{D_2})_0$ (mm)	Temp. (°C)	$-\Delta p$ at analysis (mm)	Acetylene composition (%)						Ethylene composition (%)						$C_2H_2D_2$			(α_e)	p	q	s
				C_2H_2	C_2HD	C_2D_2	(z_a)	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4	(z_e)	(y)	cis	trans	(α)				
75	160	173	29	50.7	41.3	9.0	0.60	1.4	6.7	32.9	33.9	25.2	2.77	0.18	—	—	—	—	—	—	—
75	160	173	55	52.9	43.1	4.0	0.53	1.1	8.7	31.6	34.2	24.4	2.75	0.26	—	—	—	—	—	—	—
75	160	173	78	33.8	48.3	17.7	0.85	2.1	8.9	31.6	34.4	22.9	2.69	0.31	—	—	—	—	—	—	—
75	75	144	42	69.8	27.5	2.7	0.34	0.2	7.2	31.3	36.3	25.0	2.81	0.19	39.7	43.6	16.7	—	—	—	—
—	—	—	—	—	—	—	—	*1.5*	*10.4*	*31.3*	*36.9*	*19.9*	*2.63*	—	—	—	—	*27.6*	*0.04*	*0.70*	*0.75*
75	252	144	42	71.5	25.7	2.8	0.32	1.5	10.0	37.7	30.4	20.4	2.60	0.14	44.8	39.6	15.6	—	—	—	—
—	—	—	—	—	—	—	—	*2.0*	*15.2*	*37.2*	*30.0*	*15.5*	*2.42*	—	—	—	—	*25.3*	*0.15*	*0.80*	*0.70*
75	172	133	42	66.6	29.7	3.6	0.38	1.4	10.5	37.2	31.1	19.9	2.58	0.21	44.0	39.6	16.4	—	—	—	—
75	172	153	42	62.5	33.1	4.4	0.42	1.8	10.7	37.2	30.2	20.0	2.58	0.18	41.6	42.0	16.4	—	—	—	—
75	172	183	42	64.4	26.8	8.9	0.46	1.6	8.3	29.1	35.0	25.9	2.75	0.30	37.0	48.6	14.4	—	—	—	—
—	—	—	—	—	—	—	—	*1.1*	*9.8*	*29.2*	*38.0*	*21.8*	*2.9*	—	—	—	—	*26.6*	*0.05*	*0.72*	*0.80*
100	100	124	5	40.6	46.1	13.3	0.73	0.0	4.5	30.7	39.9	24.9	2.85	0.21	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	*0.6*	*7.8*	*27.7*	*39.4*	*24.6*	*2.80*	—	—	—	—	*26.9*	*0.05*	*0.72*	*0.90*
100	100	185	5	35.1	48.1	16.8	0.83	5.4	9.6	30.4	35.5	19.1	2.55	0.36	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	*1.9*	*12.4*	*30.9*	*36.2*	*18.5*	*2.57*	—	—	—	—	*25.8*	*0.04*	*0.70*	*0.70*

TABLE 2

REACTION OF ACETYLENE WITH DEUTERIUM OVER OSMIUM (Os-B)

$(P_{C_2H_2})_0$ (mm)	$(P_{D_2})_0$ (mm)	Temp. (°C)	$-\Delta p$ at analysis (mm)	Acetylene composition (%)				Ethylene composition (%)							$C_2H_2D_2$				p	q	s
				C_2H_2	C_2HD	C_2D_2	(x_a)	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4	(x_e)	(y)	cis	$trans$	(α)	(α_c)			
75	160	150	20	61.0	34.4	4.6	0.44	6.4	24.2	39.9	22.6	7.0	2.00	0.58	—	—	—	—	—	—	—
75	160	150	41	66.0	29.5	4.5	0.39	10.7	28.4	38.8	17.5	4.6	1.77	0.67	—	—	—	—	—	—	—
75	160	150	74	76.0	22.0	2.0	0.27	13.4	31.5	36.4	15.0	3.7	1.65	0.78	—	—	—	—	—	—	—
75	99	167	40	34.2	47.7	18.1	0.84	8.6	25.1	34.4	21.9	10.0	2.00	0.75	52.4	34.3	13.3	—	—	—	—
75	176	167	40	43.6	44.7	11.7	0.69	6.3	22.4	37.4	26.2	7.8	2.07	0.64	55.9	33.3	10.8	—	—	—	—
—	—	—	—	—	—	—	—	*6.2*	*25.1*	*37.0*	*24.6*	*7.1*	*2.01*	—	—	—	—	*27.5*	*0.10*	*0.6*	*0.6*
75	320	167	40	51.7	40.8	7.5	0.56	2.5	16.2	39.8	31.0	12.5	2.38	0.35	58.2	32.0	9.8	—	—	—	—
—	—	—	—	—	—	—	—	*1.2*	*14.5*	*38.8*	*32.2*	*13.3*	*2.42*	—	—	—	—	*22.9*	*0.15*	*0.7*	*0.9*
80	210	148	40	50.1	41.4	9.5	0.61	10.5	28.2	38.9	18.2	5.0	1.81	0.28	68.4	22.7	8.9	—	—	—	—
—	—	—	—	—	—	—	—	*6.2*	*28.2*	*39.9*	*20.6*	*5.0*	*1.90*	—	—	—	—	*20.8*	*0.20*	*0.6*	*0.7*
80	210	187	40	26.8	49.8	23.4	0.97	3.0	13.1	32.7	35.3	15.9	2.48	0.50	43.8	45.1	11.1	—	—	—	—
—	—	—	—	—	—	—	—	*2.0*	*14.5*	*32.4*	*34.7*	*15.9*	*2.47*	—	—	—	—	*26.3*	*0.05*	*0.7*	*0.7*
80	210	202	40	20.3	49.6	30.1	1.10	2.7	11.6	30.8	37.2	17.7	2.56	0.57	40.7	46.7	12.6	—	—	—	—

numbers of the ethylene and acetylene, and the hydrogen number of the deuterium increased with increasing temperature over both Ru-B (Table 1) and Os-B (Table 2). Increasing temperature also led to increased yields of *trans*-dideuteroethylene over each catalyst.

DISCUSSION

The order of zero in acetylene observed with either metal indicates that this reactant was strongly adsorbed and that hydrogen adsorbed comparatively weakly or noncompetitively on the sites unavailable for acetylene adsorption. This may have been due to geometrical restrictions for acetylene adsorption. The hydrogen order of unity is consistent with either (a) the reaction of adsorbed acetylene with molecular hydrogen, or (b) the successive addition of two hydrogen atoms to adsorbed acetylene. Both of these mechanisms have been discussed in detail in Part III of this series (2) and for reasons similar to those considered for the rhodium-catalyzed reaction the second mechanism,

$$C_2H_2(g) + (^*) \rightarrow HC\!\equiv\!CH \qquad (a,a')$$
$$\underset{^*\;^*}{|}$$

$$H_2(g) + 2(^*) \rightarrow 2H \qquad (b,b')$$
$$\underset{^*}{|}$$

$$HC\!\equiv\!CH + H \rightarrow HC\!=\!CH_2 + (^*) \qquad (1,1')$$
$$\underset{^*\;^*}{|} \qquad\qquad \underset{^*\;^*}{|\;|}$$

$$HC\!=\!CH_2 + H \rightarrow H_2C\!=\!CH_2 + 2(^*) \qquad (3)$$
$$\underset{^*\;^*}{|\;|} \qquad\qquad\qquad \underset{^*}{|}$$

is considered to apply to the ruthenium and osmium-catalyzed reactions.

With both ruthenium and osmium the rate of pressure fall decreased continuously as the reaction proceeded for all values of $(P_{H_2})_0/(P_{C_2H_2})_0$. When $(P_{H_2})_0/(P_{C_2H_2})_0 \geqslant 2$, the ruthenium-catalyzed reaction showed an acceleration point. This occurred when the acetylene pressure had fallen to approximately 2 mm and the value of $(P_{C_2H_4}/P_{C_2H_2})$ was around 18. With osmium, however, no increase in rate was observed during the reaction, although the activity of this catalyst for ethylene hydrogenation was greater than for acetylene hydrogenation (6). The low selectivity observed with osmium indicates that ethylene

successfully competed with acetylene throughout the reaction. Consequently, the $(P_{C_2H_4}/P_{C_2H_2})$ ratio never attained a value sufficiently high for the increased rate of ethylene hydrogenation to become detectable.

Ruthenium invariably gave a higher selectivity than did osmium under comparable conditions. This is a consequence of two factors. First, over ruthenium the selectivity was independent of pressure fall, whereas over osmium the selectivity decreased as the reaction proceeded; ruthenium, therefore, has a higher thermodynamic selectivity (see Part I). Second, extrapolation of the curve in Fig. 3 to zero hydrogen pressure shows that $S_0 < 1$ with either metal and thus a mechanistic factor is also operative. Considering the reaction scheme

$$HC\!\equiv\!CH \xrightarrow{2H} H_2C\!=\!CH_2 \xrightarrow{k_1} C_2H_4 \qquad (g)$$
$$\underset{^*\;^*}{|} \qquad\qquad \underset{^*}{|}$$

$$+H \Big\downarrow k_2 \quad \Big\uparrow -H \Big\downarrow k_{-2}$$
$$\xrightarrow{+H}$$
$$H_2C\!-\!CH_3 \xrightarrow{k_3} C_2H_6 \qquad (g)$$
$$\underset{^*}{|}$$
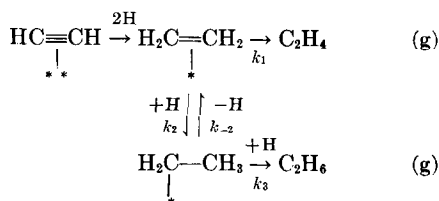
the mechanistic selectivity depends upon two factors: (i) the ratio (k_1/k_2), and (ii) the ratio (k_{-2}/k_3). If these are both large the mechanistic selectivity will be high. From studies of the ethylene/deuterium reaction over catalysts from the same stocks (7) we have found that (a) the equilibrium, $C_2H_4(ads) + H(ads \rightleftharpoons C_2H_5(ads)$ lies somewhat to the left with each metal, more particularly with ruthenium, and (b) the ratio (k_1/k_2) is greater over ruthenium than over osmium. Consequently, since both these factors operate together, it is reasonable to expect that the mechanistic selectivity will also be higher over ruthenium than over osmium.

The selectivity increased with increasing temperature over both ruthenium and osmium; similar behavior was reported for platinum (2b), rhodium and iridium (2c).

The Reaction of Acetylene with Deuterium

Unlike the other noble Group VIII metals (2d), ruthenium and osmium produced

large quantities of exchanged acetylenes. This severely complicates the interpretation of results. However, the results suggest that the acquisition of deuterium by acetylene occurred independently of the addition reaction and consequently attempts were made to overcome the former. It was thought that the acetylene exchange was rapid compared with the deuteration reaction and involved residual deuterium on the catalyst which was not removed by the pumping procedure immediately before a reaction was performed.* Experiments were therefore carried out in which the catalyst was treated with acetylene (50 mm) alone for a predetermined time ($\sim$20 min) immediately before a reaction was performed. The acetylene from the pretreatment and the residual acetylene from the subsequent reaction were then analyzed for deuterium content and compared. For example, using ruthenium at 173°C, a pretreatment with 50 mm C_2H_2 for 19 min, followed by reaction of 75 mm C_2H_2 with 165 mm D_2 yielded the following distributions:

	Pretreatment			Residual acetylene from reaction	
C_2D_2	C_2HD	C_2H_2	C_2D_2	C_2HD	C_2H_2
6.2	35.1	58.7	6.3	37.2	56.5

From these results it can be seen that, within experimental error, the deuteroacetylene distributions are the same. Furthermore the deuteroacetylenes are in their equilibrium ratios of $1:6:9::C_2D_2:$ $C_2HD:C_2H_2$. From these results we conclude that the formation of deuteroacetylenes occurred independently of the addition reaction.

Experiments with alumina in place of the catalyst showed that the support alone was not active for acetylene exchange under the experimental conditions used.

Owing to the complicating feature of the acetylene exchange, satisfactory hydrogen/
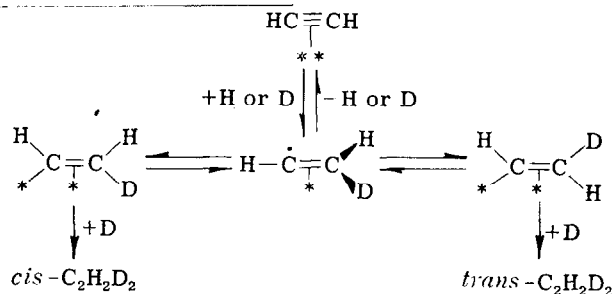
* Although it was not realized at the time this work was carried out, from more recent work (8, 9, 10) it is evident that the acetylene exchange involved the interaction of acetylene with deuterium associated with the alumina support.

deuterium mass balances between reactants and products were not obtained in most cases.

The Deuteroethylene Distributions

Quantitative interpretation of the ethylene distributions has been made using the treatment described in Part IV of this series (2d), with the modification that a third parameter, q, was introduced. The three parameters, s, p, and q used in the calculations are defined as follows:

s	chance of acetylene acquiring a D atom to form vinyl
$(1-s)$	chance of acetylene acquiring a H atom to form vinyl
p	chance of vinyl undergoing hydrogenation to ethylene
$(1-p)$	chance of vinyl reverting to acetylene by loss of H or D
q	chance of vinyl acquiring a D atom to form ethylene
$(1-q)$	chance of vinyl acquiring a H atom to form ethylene

For the reasons given above, it was assumed that, as with the other noble Group VIII metals, desorption of acetylene during the addition reaction was absent, and that the three isotopic acetylenes were adsorbed on the surface in the ratio given by their final gas-phase composition. The steady state concentrations of C_2H_2, C_2HD, and C_2D_2 were then calculated as described in Part IV (2d).

By carrying out some 40 calculations, systematically varying p, q, and s, it was found possible to reproduce the experimental deuteroethylene distributions fairly accurately. Tables 1 and 2 show the agreement obtained between experimental and calculated distributions for each metal. With ruthenium the results show that in general the yield of C_2D_4 was underestimated and the yield of C_2H_3D was overestimated; the yields of C_2HD_3, $\Sigma(C_2H_2D_2)$, and C_2H_4 agree well. With osmium, good agreement was obtained throughout the entire distribution. With each metal, the calculated value of (α) was approximately twice the observed value. This discrepancy

may arise from the assumptions made in determining the yield of asymmetric dideuteroethylene by infrared analysis and also from assumptions made in the mathematical scheme. However, the calculated and observed values of (α_c) showed the same trends of (i) increasing with increasing temperature and (ii) decreasing with increasing deuterium pressure.

Variation of s, p, and q with the Experimental Variables

Both ruthenium and osmium give an approximately 35% yield of dideuteroethylene of which the asymmetric isomer accounts for 10% to 16%. This relatively low yield of $C_2H_2D_2$ is a consequence of a very high chance (80–90%) that a vinyl will revert to an acetylene, rather than react to form ethylene, together with an approximately 70% chance that adsorbed acetylene and vinyl will add a deuterium atom rather than a hydrogen atom.

Increasing the initial deuterium pressure

parison of these values with those given in Tables 1 and 2 shows that the surface and gas-phase acetylene concentrations are not simply related. This we take to indicate that, as we previously assumed, acetylene desorption was absent during the addition reaction.

Stereospecificity: the cis:trans Ratio in the $C_2H_2D_2$

The cis:trans ratio varied between 0.7 and 1.2 over ruthenium and between 0.9 and 3.0 over osmium. It is noticeable that, like the other four noble metals, the relative yields of cis-, trans-, and asymmetric $C_2H_2D_2$ were a function of the total $C_2H_2D_2$ yield, expressed as a percentage of the total ethylene yield, in the sense that the lower the $C_2H_2D_2$ yield the greater were the proportions of the trans and asymmetric isomers. This indicates clearly that the mechanism for the formation of trans-ethylene-d_2 is essentially the same over all six metals, i.e.

increased the chance of adsorbed vinyl reacting to form ethylene, and also increased the chance of adsorbed acetylene or vinyl acquiring a D atom, rather than an H atom.

The probability of vinyl groups reverting to acetylene increased with increasing temperature. Since this process liberates hydrogen atoms to the surface, the slight decrease in s, observed with each metal, is expected, although q appears to remain approximately constant.

The steady state surface concentrations of C_2D_2, C_2HD, and C_2H_2 as a percentage of the total surface acetylene concentration were approximately 20.0, 41.5, and 38.5, respectively, over ruthenium, and 51.0, 37.0, and 12.0, respectively, over osmium. Com-

The lower degree of specificity exhibited by ruthenium and osmium, compared with palladium, platinum, rhodium, or iridium, is a reflection of the lower value of p, i.e., a greater chance of vinyl reversal, which is an essential step for the formation of trans and asymmetric ethylene-d_2. In this context it should be noted that when compared with the other Group VIII metals, Ru and Os also exhibit a lower specificity in 2-butyne hydrogenation (5, 7).

The general similarity in catalytic behavior of ruthenium and osmium with that of the other noble Group VIII metals for acetylene hydrogenation, leads us to believe that the crystal structure of the metal is relatively unimportant in these reactions.

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