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The Hydrogenation of Ethylacetylene

III. Reaction of Ethylacetylene with Hydrogen Catalyzed by Platinum and Iridium

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The reaction between ethylacetylene and hydrogen over pumice supported and unsupported platinum and iridium catalysts was investigated between 20 and 80°C for a wide range of reactant ratios. The order of reaction with respect to ethylacetylene was zero, and one with respect to hydrogen. The overall apparent activation energies were for supported and unsupported platinum and iridium 9.4, 7.9, 7.8, and 10.8 kcal/mole, respectively. Changes in selectivity and activity of the catalyst are discussed in relation with its physical properties.

INTRODUCTION

In parts I and II of this series, we reported the kinetics and products obtained from the reaction of ethylacetylene with hydrogen, catalyzed by supported and unsupported nickel (*1*), cobalt, and iron (*2*). In the present paper, we report the reaction of ethylacetylene with hydrogen, catalyzed by supported and unsupported platinum and iridium, and discuss the activity and selectivity of these catalysts.

EXPERIMENTAL METHODS

The apparatus, purification and specification of the reactants, experimental procedure, preparation of the catalysts, and the method of analysis of the products were described earlier (*1*, *3*). The initial rates ($-dp/dt$) were obtained from manometric measurements. The mercury manometer was separated from the reaction vessel by means of a trap, which was opened only when the reading was to be taken. The platinum, iridium, and osmium metal catalysts were prepared from $PtCl_4$, $(NH_4)_2IrCl_6$, and osmium ammonium chloride supplied by K and K Laboratories Inc.

RESULTS

All catalysts were active in the temperature range 26–80°C, with the exception of osmium. In the case of osmium, the pressure drop was 10 mm in 40 min at 195°C (P_{H_2} = 138 and $P_{C_4H_6}$ = 50 mm). The catalyst deactivated quite rapidly. Therefore, the kinetics of the reaction over osmium could not be studied.

(a) **The pressure fall–time (*P–t*) curves.** The pressure fall–time curves observed in the hydrogenation of ethylacetylene over nickel, cobalt, and iron catalysts were discussed in detail earlier (*1*, *2*). The kinetic form of the pressure–time curves observed in case of all catalysts studied were bilinear Type I, when the hydrogen/ethylacetylene ratio was less than 2. But when the ratio was greater than 2, the curves observed in case supported and unsupported planinum and iridium catalysts were of Type IV and Type III, respectively.

(b) **Order in ethylacetylene and hydrogen obtained by initial rate method.** Using a fixed ethylacetylene pressure of 50 mm and a wide range of hydrogen pressures (45–200 mm) the order of reaction with respect to

TABLE 1

ORDERS OF REACTION AND ACTIVATION ENERGIES FOR CATALYSTS[a]

Temp (°C)	m^b	n^b	E (kcal/mole)	k at 60° (g mm^{-1})	Temp (°C)	m	n	E (kcal/mole)	R at 60° (g mm^{-1})
Pt-pumice					Pt powder				
30	0.00	1.0			34	0.00	1.10		
35	0.00	1.01	9.4	4.46	50	0.00	1.04		
								7.9	0.96
40	−0.43	1.10			60	−0.33	0.99		
50	−0.55	1.10			70	−0.51	1.00		
					80	−0.60	0.99		
Ir-pumice					Ir powder				
30	0.00	1.01			26	0.00	1.10		
41	0.00	1.03			35	0.00	1.10		
			7.8	3.10				10.8	4.0
46	0.00	1.03			40	−0.33	1.08		
54	0.00	0.99			50	−0.51	1.00		
63	0.00	1.01			57	−0.61	1.06		

[a] Wt of catalysts = 0.025 g.

[b] m and n are orders of reaction with respect to ethylacetylene and hydrogen, respectively.

hydrogen was determined at several temperatures. Similarly the order of ethylacetylene was obtained at several temperatures by using a fixed hydrogen pressure (50 mm). The results are given in Table 1. The order of reaction with respect to hydrogen (Table 1) was about one and temperature independent. The order of the reaction with respect to ethylacetylene was temperature dependent and became negative with increased temperatures for supported and unsupported platinum and supported iridium. However, in the case of iridium powder, it was zero and independent of temperature. Similar results were obtained in case of nickel, iron, and cobalt catalysts (*1*, *2*).

(c) Temperature dependence of rate constants. Specific rates were obtained from initial rate measurements for the reaction of 50 mm of ethylacetylene with 35–150 mm of hydrogen between 25 and 80°C. Plots of $\log_{10}$ (specific rates) against the reciprocal of absolute temperature were good straight lines over a wide range of temperatures for the supported and unsupported platinum and iridium catalyst, satisfying the Arrhenius equation. The apparent activation energies thus evaluated are given in Table 1.

(d) Dependence of selectivity upon pressure fall or conversion. The course of the reaction for hydrogen/ethylacetylene ratios of 1 ($P_{H_2} = P_{C_4H_6} = 50$ mm) and more than 2 ($P_{C_4H_6} = 50$ mm, P_{H_2} greater than 100 mm) was followed by analyzing the reaction products after various pressure falls. The selectivity (S) is defined as the ratio of α-butylene to α-butylene plus n-butane:

$$S = \frac{\text{conc of } \alpha\text{-butylene (mm pressure)}}{\text{conc of } \alpha\text{-butylene (mm pressure)} + \text{conc of } n\text{-butane (mm pressure)}}.$$

Conversion (X) is the ratio of ethylacetylene reacted (consumed) to ethylacetylene admitted into the reaction vessel. No *cis*- and *trans*-butene formed over these catalysts under experimental conditions. In the case of platinum–pumice, these isomers were in trace amounts which were negligible in comparison with α-butylene and n-butane. Figure 1a and b shows the distribution of the products and the unreacted ethylacetylene against the percentage conversion of ethylacetylene over the catalysts investigated for equimolar quantities of the reactants. The selectivity was independent of conversion for all catalysts. The dependence of the selectivity upon the percentage conversion of ethylacetylene for hydrogen/ethylacety-

TABLE 2

Dependence of Selectivity and Reaction Products on Pressure Fall

Catalyst	Temp (°C)	H_2 pressure (mm Hg)	C_4H_6 pressure (mm Hg) at room temp	Pressure drop (mm)	Products (mm)			Polymer (%)[a]	Selectivity
					$P_{C_4H_{10}}$	$P_{C_4H_8}$	$P_{C_4H_6}$		
Pt powder	63	140	46.5	20.0	2.0	17.0	26.5	2.1	0.894
				62.0	22.5	3.0	11.5	20.0	0.117
Pt-pumice[b]	35	120	49.0	20.0	4.5	12.0	30.0	5.1	0.722
				62.0	29.5	2.5	15.0	4.1	0.078
Ir-powder	26	101	49.5	20.0	10.5	1.0	31.0	13.1	0.104
				60.5	28.0	2.0	14.5	10.1	0.066
Ir-pumice	30	120	49.0	20.0	7.5	6.0	28.0	15.3	0.481
				71.0	24.5	2.5	8.5	27.5	0.090

[a] Polymer (%) was calculated from the difference between the initial pressure of ethylacetylene and the sum of pressures of products (butane and butenes) and unreacted ethylacetylene.

[b] Traces of *cis*- and *trans*-2-butene were also formed which were in negligible amounts.

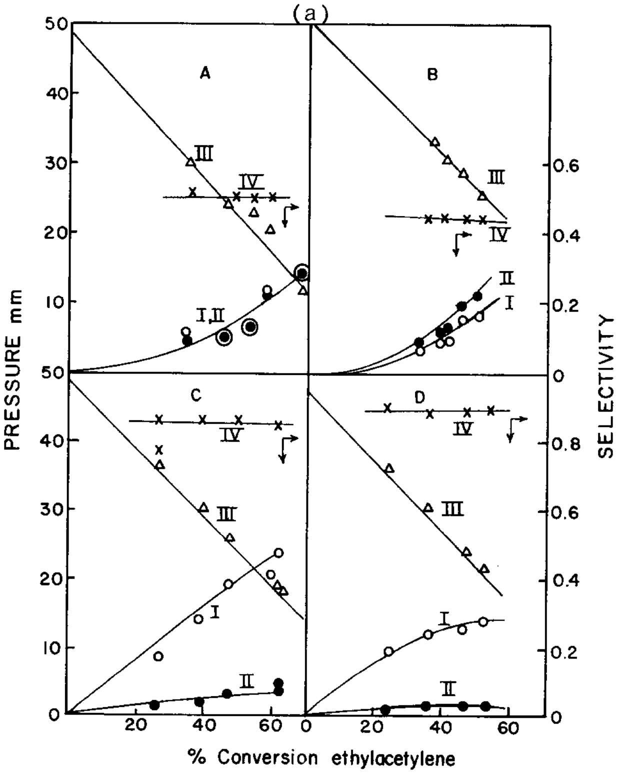

Fig. 1. Course of reaction: (a) $P_{H_2} = P_{C_4H_6} = 50 \pm 2$ mm; I, α-butylene; II, butane, III, unreacted ethyl acetylene; IV, selectivity vs. conversion; (A) Ir–pumice, $T = 30°C$; (B) Ir powder, $T = 25°C$; (C) Pt–pumice, $T = 35°C$; (D) Pt powder, $T = 63°C$. (b) $P_{C_4H_6} = 50 \pm 2$ mm; I, α-butylene; II, butane; III, unreacted ethylacetylene; IV, selectivity vs. conversion; (A) Ir–pumice, $T = 52°C$; $P_{H_2} = 120 \pm 1$ mm; (B) Ir powder, $T = 25°C$, $P_{H_2} = 101 \pm 1$ mm; (C) Pt–pumice, $T = 35°C$, $P_{H_2} = 120 \pm 2$ mm; (D) Pt powder, $T = 63°C$, $P_{H_2} = 140 \pm 2$ mm.

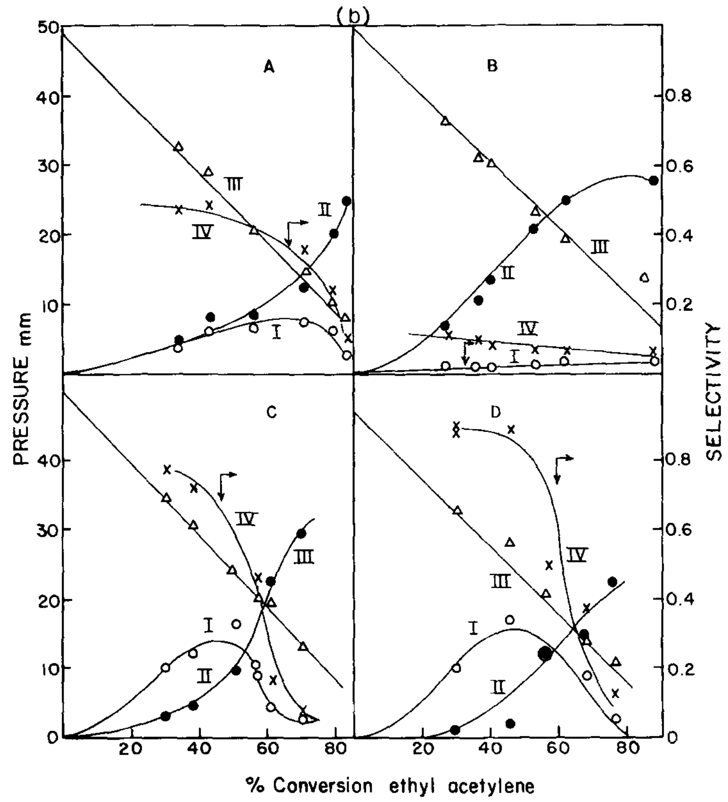

FIG. 1b

lene ratios greater than two is shown in Fig. 1b for different catalysts. The activity was independent of the percentage conversion until about more than half of the ethylacetylene had reacted, after which the selectivity started falling for all catalysts, except in the case of iridium powder where it decreased very slowly.

Table 2 gives the selectivity and reaction products at different percentages of conversion. The amount of polymerization was calculated as the difference between the initial pressure of ethylacetylene and the sum of ethylacetylene reacted to form α-butylene and n-butane and unreacted ethyl acetylene. The polymers may be in a gaseous form, which could not be detected by the hexamethylphosphoramide or molecular sieve columns, under experimental conditions.

(e) **Dependence of selectivity upon initial pressure and hydrogen and ethylacetylene.** Measurements were made of the selectivity of metals at different temperatures as a function of initial hydrogen pressure by using a fixed ethylacetylene pressure (50 mm) and varying the hydrogen pressure between 45 and 200 mm. Products were analyzed when the total pressure fall was equal to 20 mm of total pressure. The selectivity of platinum powder was nearly independent of hydrogen pressure (Fig. 2). In other cases, the selectivity was dependent on the initial hydrogen pressures. No significant variation in the selectivity with initial ethylacetylene pressures (45–160 mm) for a fixed hydrogen pressure (50 mm) was observed for platinum catalysts. However, it increased slowly in case of iridium catalysts (Fig. 3).

(f) **Dependence of selectivity upon temperature.** The temperature dependence of selectivity for hydrogen/ethylacetylene ratio of 1 and more than 2 was studied at several temperatures for a total pressure fall of 20 mm. The results are given in Fig. 4A

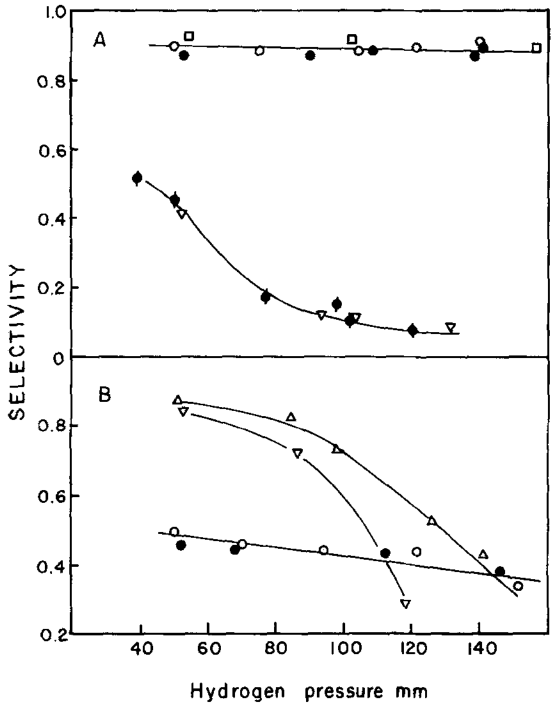

FIG. 2. Dependence of selectivity upon the initial pressure of hydrogen, $P_{C_4H_6} = 50$ mm. (A) Pt powder, ○, $T = 63°C$; ●, $T = 73°C$; □, $T = 82°C$; Ir powder, ◆, $T = 25°C$; ▽, $T = 45°C$; (B) Pt-pumice, △, $T = 43°C$; ▽, $T = 48°C$; Ir-pumice, ○, $T = 30°C$; ●, $T = 41°C$.

and B. For equimolal amount of reactants, selectivity decreased with increasing temperatures in the case of all catalysts, except for platinum-pumice, for which it remained constant. For a hydrogen/ethylacetylene ratio of 2 or more, the selectivity decreased rapidly in case of platinum-pumice and iridium-pumice. However, in the case of platinum and iridium powders, no significant variation in the selectivity was observed.

DISCUSSION

The experimental results of the hydrogenation of ethylacetylene over supported and unsupported platinum and iridium catalysts were similar to those obtained in our previous studies over nickel, cobalt, and iron catalysts. In all the cases where reaction orders could be measured (supported Ni, Co, Fe, Pt, and Ir, and unsupported Ni, Co, Pt, and Ir) a remarkable consistency was found, indicative of a very strong ethylacetylene adsorption. The differences in the apparent activation energies, which do not require correction for the heat of adsorption of ethylacetylene, in these circumstances should reflect any deep-seated differences in the reaction mechanism. In the present investigation, the activation energies for all the catalysts except nickel powder were in the order of 7–10 kcal/mole. The kinetic similarities of the hydrogenation over various metals suggest that the mechanism of reaction over platinum and iridium is the same as suggested for nickel, cobalt, and iron previously (*2*). The implication of the various types of pressure–time curves observed in this reaction is also similar to

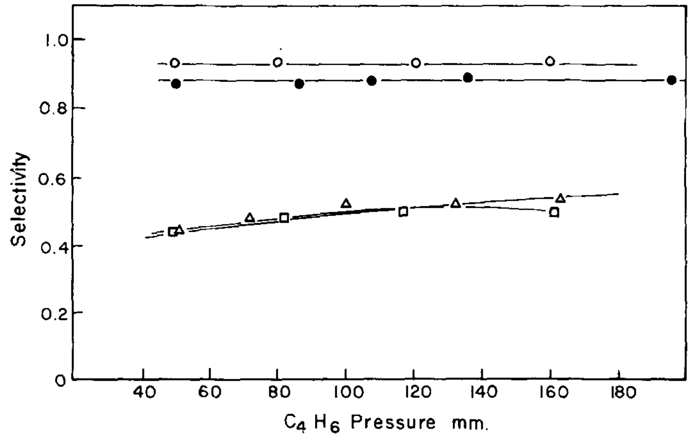

FIG. 3. Dependence of selectivity upon the initial pressure of ethylacetylene, $P_{H_2} = 50 \pm$ mm. ○, Pt powder, $T = 73°C$; ●, Pt-pumice, $T = 43°C$; △, Ir powder, $T = 35°C$; □, Ir-pumice, $T = 73°C$.

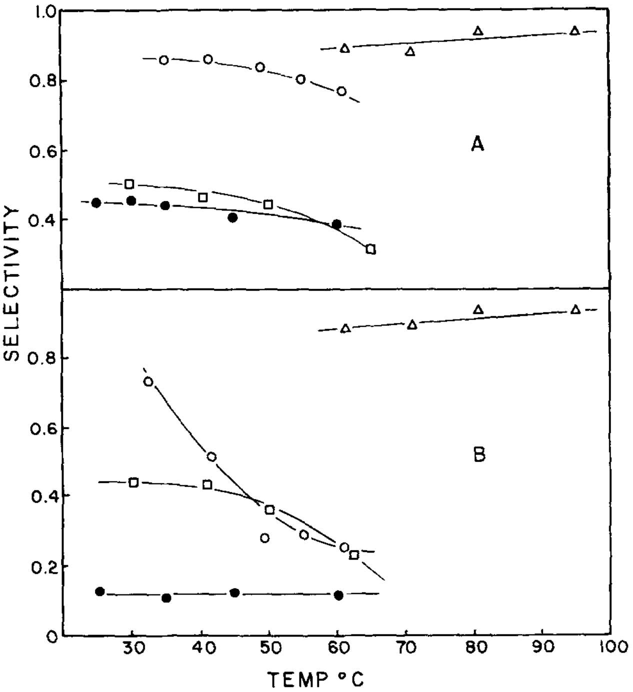

FIG. 4. Dependency of selectivity upon the temperature: (A) $P_{C_4H_6} = P_{H_2} = 50 \pm 2$ mm. △, Pt powder, ○, Pt-pumice, □, Ir-pumice, ●, Ir powder; (B) $P_{C_4H_6} = 50 \pm 2$ mm. △, Pt powder, $P_{H_2} = 101 \pm 2$ mm; ○, Pt-pumice, $P_{H_2} = 120 \pm 2$ mm; □, Ir-pumice, $P_{H_2} = 120 \pm 2$ mm; ●, Ir powder, $P_{H_2} = 101 \pm 2$ mm.

that observed for nickel, cobalt, and iron. This has been discussed in detail previously.

From Fig. 1b it is clear that the hydrogenation of ethylacetylene over supported and unsupported platinum and supported iridium is a consecutive first-order reaction ($A \rightarrow B \rightarrow C$). In the case of iridium powder, it appears that the reaction might be proceeding by two simultaneously available reaction paths $\left(A \begin{smallmatrix} \nearrow B \\ \searrow C \end{smallmatrix}\right)$. For all the catalysts, except iridium powder, the α-butylene hydrogenation does not start until the bulk of ethylacetylene has been converted. This selectiveness of the reaction must be due to the poisoning effect of ethylacetylene in the α-butylene hydrogenation, because it is much more strongly adsorbed on the catalyst surface than the α-butylene. In the case of iridium powder, ethylacetylene does not seem to poison the catalyst surface for the further hydrogenation of α-butylene. Furthermore, the rate of hydrogenation of α-butylene was faster than the rate of hydrogenation of ethylacetylene, which may be indicative of some slightly different reaction mechanism. The order with respect to ethylacetylene was zero and slightly negative with the increase of temperature. In the case of iridium-pumice, it was temperature independent (Table 1). It appears that the negative orders (in some cases) with respect to ethylacetylene imply the heat of adsorption does contribute to the activation energy.

The rate of the selective reduction of the reaction ($C_4H_6 \xrightarrow{H_2} C_4H_8$) depends significantly on the metal, the catalyst support, reaction conditions, and on various catalyst promoters. Since a properly supported catalyst invariably shows a higher activity on a metal weight basis, as compared to an unsupported catalyst, the use of a support is always recommended to obtain the maximum efficiency of the metal. In addition to this, supported catalysts show greater resistances to poisoning.

According to Dowden (*4*) the catalytic

activity of the transition metals is due to *d* holes in the *d* band. The findings of Gwathemy *et al.* (*5–8*) also indicate that the Dowden's theory does not completely explain the catalytic activity of the transition metals. In some cases Gwathemy *et al.* found greater differences between the catalytic activities of the different crystal faces of the same metal than between the two metals having different electronic configuration. The results of Mann and Khulbe (*9*), Hall and Emmett (*10*), and Takai and Yamanka (*11*) cast some doubt on the suggestion of Dowden, that the catalytic activity is directly related to the *d* holes. As suggested earlier, the mechanism of the reaction over platinum, iridium, nickel, cobalt, and iron is the same, and the results reported in Table 3 do not support the views of Dowden. However, in the absence of data on the specific surfaces of the catalysts listed, such results and conclusions arrived thereon must be approximate. The results of the hydrogenation of ethylacetylene over iron, cobalt, nickel, platinum, and iridium (except supported iridium and unsupported nickel) supported the hypothesis that the catalytic activity of the metals is directly related to the Pauling's percentage δ-character (*12*). In the case of iridium, the discrepancy may be due to the support material. A similar behavior was observed by Mann and Khulbe (*13*) in the hydrogenation of methylacetylene over these catalysts. It is possible that under similar experimental conditions of preparation and activations of catalysts, the number of lattice defects, which play an important role in enhancing the activity of the catalysts, is greater in the unsupported iridium catalyst.

On the other hand, the work of Sheridan and Reid (*14*) showed that there was no clear influence of percentage δ-character detectable on any characteristics of the acetylene hydrogenation reaction over group VIII transition metals. Maximum activity in each horizontal row of group VIII occurs in the column for nickel and platinum, supported catalysts (Table 3). This is parallel to a similar maximum in paramagnetic susceptibility in this column as pointed out by Maxted (*15*), and also similar to the results of Sheridan and Reid. The parallel between the catalytic activity and magnetic susceptibility undoubtedly reflects the influence of electronic structure of the metal on its catalytic activity. Recently, Toyosaburo (*16*) studied a number of nickel–copper alloy catalysts prepared by

TABLE 3

CHARACTERISTICS OF THE CATALYSTS

Catalyst	δ-character (%)[a]	Specific rate at 60°C (per min^{-1})	Temp (°C)	Selectivity at 20 mm pressure drop ($H_2 = C_4H_6 =$ 50 mm)	*d* hole[d]
Fe pumice[b]	39.5	0.026	117	0.838	2.2
Fe powder[c]	39.5	—	130	0.884	2.2
Co-pumice[b]	39.7	0.84	50	0.823	1.7[d]
Co powder[b]	39.7	0.026	35	0.777	1.7
Ni-pumice[b]	40.0	1.38	50	0.695	0.6
Ni powder	40.00	1.48	40	0.615	0.6
Pt pumice	44.00	4.46	35	0.722	0.55–0.6
Pt powder	44.00	0.96	63	0.894	0.55–0.6
Ir pumice	49.0	3.10	30	0.104	1.7[d]
Ir powder	49.0	4.00	26	0.481	1.7

[a] G. C. Bond, "Catalysis by Metals" Academic Press, New York, 1962.

[b] Value of specific reaction rate constant was evaluated from the curve $\log_{10} K$ vs. $1/T$ (*1, 2*).

[c] The rate was very slow even at 180°C.

[d] A. Damjanovic and J. O. M. Bockris, *J. Phys. Chem.* **67**, 2508 (1963).

different methods and suggested that the catalytic activity is mainly due to the imperfection of the crystal. It seems to us that besides these factors, the structure and the properties of the reductant (hydrocarbon) also play an important role in determining the catalytic activity for a particular hydrocarbon.

Bond *et al.* (*17*) defined two types of selectivity; (i) thermodynamic and (ii) mechanistic. Thermodynamic selectivity is determined by the relative free energies of adsorption of A and B in the reaction sequence $A \rightarrow B \rightarrow C$. Where two products are formed through two simultaneously available reaction paths, the relative formation of either is thus dependent only on the mechanism of the reaction and is designated mechanistic selectivity. It is clear from Fig. 1 that in the case of platinum and iridium (except unsupported iridium) and from our previous work (*1*, *2*) on ethylacetylene hydrogenation over nickel, cobalt, and iron that the thermodynamic selectivity is most important. In the case of iridium powder, it is the mechanistic selectivity that plays the dominant role.

It may be concluded from Table 1 that while the activity pattern for supported catalysts is

$$\mathrm{Pt} > \mathrm{Ir} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Fe} \qquad (1)$$

and for unsupported catalysts is

$$\mathrm{Ir} > \mathrm{Ni} > \mathrm{Pt} > \mathrm{Co}, \qquad (2)$$

the selectivity pattern for supported catalysts is

$$\mathrm{Fe} > \mathrm{Co} > \mathrm{Pt} > \mathrm{Ni} > \mathrm{Ir} \qquad (3)$$

and for unsupported catalysts is

$$\mathrm{Pt} > \mathrm{Co} > \mathrm{Ni} > \mathrm{Ir}. \qquad (4)$$

From comparison of patterns (1) and (3) and (2) and (4), it seems that the activity factor is generally the governing factor for the selectivity as well, except for the platinum catalyst.

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