THE SELECTIVE HYDROGENATION OF ACETYLENE

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A study has been made of the degree of selectivity of ethylene formation in the hydrogenation of acetylene catalyzed by rhodium, palladium, platinum and some palladium + silver mixtures supported on α -Al₂O₃. Analyses were performed by gasliquid chromatography.

Palladium is the most active of the pure metals: prolonged exposure to hydrogen at room temperature decreases its activity for acetylene hydrogenation and completely destroys its activity for ethylene hydrogenation. The selectivity, before the onset of the generally more rapid ethylene hydrogenation, falls in the order Pd > Rh > Pt. Palladium + silver catalysts containing 10 to 30 % silver show notably higher initial selectivities than pure palladium and are also highly active.

Thermodynamic and mechanistic factors in selectivity are discussed, and the probable role of dissolved hydrogen in determining the selectivity of palladium catalysts is outlined.

The selective hydrogenation of acetylene to ethylene and the selective removal of small amounts of acetylene from gas streams containing large excesses of ethylene constitute problems of considerable technical interest. The relevant literature has recently been reviewed; ¹ previous research has, however, been largely of an applied nature, and the fundamental causes underlying selectivity in this system are as yet not well understood.

Of the metals which catalyze the hydrogenation of acetylene, palladium has an outstanding ability to give a highly selective production of ethylene.¹ Industrial experience shows that the selectivity of palladium catalysts increases with use, and the present work has provided a possible explanation of this. The behaviour of platinum, rhodium, palladium and some silver + palladium mixtures supported on α -Al₂O₃ has been studied with emphasis on determining the factors governing the extent of ethane formation from acetylene in the absence of added ethylene.

EXPERIMENTAL

APPARATUS, MATERIALS AND PROCEDURE

Reactions were carried out in a cylindrical Pyrex vessel (capacity 125 ml), the catalyst granules resting on the bottom of the vessel. "Oxygen-free" hydrogen was purified by passage through a cooled charcoal trap: cylinder acetylene was degassed and purified by repeated fractional distillation from a solid CO_2 + methanol bath.

Each new catalyst sample (normally 0.25 to 0.30 g) was evacuated while the temperature was raised to 200° C and kept at this temperature until a hard vacuum was obtained (15-30 min). Hydrogen (~ 100 mm) was then admitted and the temperature adjusted to that required for the first experiment after 30 min. The hydrogen was pumped off and the reactants admitted in sequence, acetylene normally being added first. The progress of the reaction was followed manometrically, and after the desired conversion the contents of the reaction vessel were transferred to the analytical section of the apparatus.

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CATALYSTS

Standard catalysts consisted of the reduced metal or mixture of metals supported on α -Al₂O₃ (B.S.S. 8-16 mesh) at a concentration of 5 molar %. These were p.epared by impregnating the alumina with the appropriate quantity of a solution of a convenient salt or mixture of salts, drying, and reducing in a stream of hydrogen at 400°C. Palladium + silver catalysts were prepared containing 4.5 % Pd + 0.5 % Ag (Pd + Ag, I), 4.0 % Pd + 1.0 % Ag (Pd + Ag, II) and 3.5 % Pd + 1.5 % Ag (Pd + Ag, III). They were subjected to X-ray examination but the results were inconclusive, and no evidence of solid solution formation was found.

ANALYSIS

Estimation of the ethylene/ethane ratio in the products was carried out by means of gas-liquid chromatography. Separation was effected by means of a 16 ft. column containing tetra-*iso*butylene on firebrick as the stationary phase and hydrogen (flowing at about 1 l/h) as the moving phase. The components were detected by their thermal conductivity; the column and the thermal conductivity cells were at room temperature. Under these conditions, acetylene was incompletely separated from ethylene (difference in retention times ~ 0.5 min), but calibrations showed that up to 20 % acetylene in an acetylene + ethylene mixture had no effect on the apparent ethylene sensitivity factor (peak height/ pressure of sample). Experimental conditions were therefore chosen so that as far as possible the gas to be analyzed contained less than 20 % acetylene. The difference between the retention times of ethylene and ethane was about 1.25 min and gas mixtures containing 0.5 to 20 % ethane could be analyzed with an accuracy of about ± 0.3 %.

Peak heights were then converted into partial pressures using sensitivity factors obtained from calibrations with the separate components. The results are expressed in terms of the degree of selectivity, defined as $P_{C_2H_4}/(P_{C_2H_4} + P_{C_2H_6})$. Calibrations with the separate components and with standard mixtures were made at regular intervals.

RESULTS

Pressure against time curves were generally first order in hydrogen pressure when the initial hydrogen/acetylene ratio was less than about two, and (except for rhodium) zero order when this ratio was greater than about two. Except in the case of the "poisoned" palladium catalyst, rates began to accelerate after a pressure fall depending on conditions, sometimes attaining immeasurably high values, thereafter falling rapidly to zero. The pressure fall at which the acceleration starts is termed $-\Delta p_a$ and there is an uncertainty of about ± 2 mm in quoted values for this quantity. Samples were generally extracted for analysis after a pressure fall ($-\Delta p_e$) equal to between 0.8 and 1.0 times the initial acetylene pressure.

RHODIUM, PLATINUM AND PALLADIUM CATALYSTS

Table 1 indicates the temperatures at which these catalysts were satisfactorily active (col. 2) and the degree of deactivation they underwent before settling down to a fairly steady activity (col. 3). Column 4 shows the observed orders in hydrogen measured at the temperatures given in column 2. In all cases, the total pressure falls which resulted in experiments where a greater than two-fold excess of hydrogen over acetylene was used corresponded closely to the values expected for the stoichiometric conversion of acetylene to ethane.

TABLE 1.—KINETIC CHARACTERISTICS SHOWN BY RHODIUM, PLATINUM AND PALLADIUM CATALYSTS

catalyst	temp. at which satisfactorily active 130°	final activity	order in hydrogen	selectivity
Rh		0.3	~ 1	1.0
Pt	105°	1.0	1.5	0.86
Pd	20°	0.4	1.42	0.96

Fig. 1 shows the dependence of selectivity on hydrogen pressure for the three catalysts, the experimental conditions being detailed below the diagram. Column 5 of table 1 gives the selectivities extrapolated to zero hydrogen pressure and these may be in error

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by ± 0.01 . Over rhodium, $-\Delta p_a$ was invariably 1.23 ± 0.05 times the initial acetylene pressure, so that the selectivities recorded in fig. 1 were obtained well before the onset of the acceleration. With platinum, extractions from runs using less than 175 mm hydrogen were made before the start of the acceleration, and from those using more than this pressure, after the acceleration had started. With palladium, all the extractions were made after the beginning of the acceleration; $-\Delta p_a$ was inversely proportional to the hydrogen pressure, having a value of about 44 mm at 100 mm hydrogen pressure. The selectivity obtaining earlier was calculated in the following empirical manner. A quantity β is defined as the difference between $-\Delta p_e$ and the pressure fall expected at that time if no increase in rate had occurred; on plotting the selectivity against β (fig. 2), a straight line is obtained which when extrapolated to $\beta = 0$ yields an initial selectivity S_{β} of 0.965. Results other than those corresponding to the values in fig. 1 are included in this graph.



FIG. 1.—The dependence of selectivity on initial hydrogen pressure for palladium, rhodium and platinum.

⊙, Pd at 22°C; $P_{C_2H_2}$, 49·6 ± 1 mm; $-\Delta p_e/P_{C_2H_2}$, 0·80; Ø, Rh at 133°C; $P_{C_2H_2}$, 51·0 ± 2 mm; $-\Delta p_e/P_{C_2H_2}$, 0·95; ●, Pt at 105°C; $P_{C_1H_2}$, 51·5 ± 2 mm; $-\Delta p_e/P_{C_2H_2}$, 0·80.

The reason for the dependence of $-\Delta p_a$ on hydrogen pressure is briefly as follows. Acetylene is more strongly adsorbed than either ethylene or hydrogen: increasing the partial pressure of either of the latter therefore serves to secure the entry of ethylene into the reactive layer. Calculations based on the experiments described in the last paragraph show that the ratio of the sum of the ethylene and hydrogen pressures to the acetylene pressure at $-\Delta p_a$ is within error constant and independent of hydrogen pressure. Acceleration always starts when this ratio exceeds a value of about 9.

If the onset of the acceleration over rhodium occurs when conditions permit the entry of gaseous ethylene into the reactive layer, then the acetylene pressure at this time must be quite low (~ 1 to 2 mm) and hence it must be much more strongly adsorbed than ethylene on this catalyst. Ethane formed in the early stages must therefore arise directly from acetylene without the intervention of gaseous ethylene, this process being favoured by increasing hydrogen pressure.

The selectivity over rhodium was independent of temperature between 132 and 162°C, but over platinum with a fixed hydrogen/acetylene ratio both $-\Delta p_a$ and the selectivity decreased with rising temperature in the range 77 to 161°C. Apparent activation energies over rhodium and platinum are 10.6 \pm 0.3 and 17.6 \pm 0.3 kcal/mole respectively.

During the first five runs performed over the palladium catalyst at 23°C (using a fixed initial hydrogen/acetylene ratio), the selectivity rose regularly from 0.85 to 0.95. Allowing

acetylene to remain in the reaction vessel for 15 min before adding hydrogen resulted in a rate 14 % faster than in the previous standard experiment using the same gas pressures; the effect on the selectivity was small, and no further significant change was found after a 16-h acetylene pretreatment. Prolonged (65 h) exposure of the catalyst to hydrogen at room temperature reduced the rate of the following reaction to about half the value observed in the previous comparable experiment.

"POISONED " PALLADIUM CATALYST

The results for palladium already presented refer to a catalyst reduced in the standard manner and studied immediately thereafter. A second sample of the same catalyst was similarly reduced, but left under 100 mm hydrogen for 11 days before being studied. It showed no activity below 95°C and only slight activity at this temperature : all further work was carried out at 137 \pm 2°C. No increase in rate was found in any experiment;



FIG. 2.—The dependence of selectivity on β over palladium at 22°C.

pressure against time curves showed constant rates until $-\Delta p/P_{C_2H_2} \sim 0.8$, after which time rates slowly decreased to zero. Final pressure falls were 28 ± 5 % greater than expected for the stoichiometric conversion of acetylene to ethylene, indicating the occurrence of considerable polymerization. The selectivity rose in the first three experiments from 0.83 to 0.96, thereafter remaining constant. After six experiments the catalyst was shown to catalyze the hydrogenation of ethylene alone only extremely slowly. The dependence of rate and selectivity on hydrogen pressure was not studied in detail, but there was no change in selectivity on increasing the hydrogen pressure from 142 to 268 mm.

It therefore appears as if the prolonged initial exposure of the catalyst to hydrogen at room temperature had the effect of poisoning the catalyst's activity for converting ethylene to ethane while leaving relatively unaffected its ability to hydrogenate acetylene to ethylene.

PALLADIUM + SILVER CATALYSTS

The palladium + silver catalysts were all active at room temperature : approximate relative activities for catalysts containing 0, 10, 20 and 30 % silver were respectively 10:1:15:5. All showed the usual types of pressure against time curves. The dependence

of $-\Delta p_a$ on hydrogen pressure was the same in all cases, and the results are shown in fig. 3: this graph includes without discrimination values obtained from three different samples of catalyst Pd + Ag, I. $-\Delta p_a$ is again inversely proportional to the initial hydrogen pressure, and for a given hydrogen pressure, it declined rapidly with increasing temperature. Total pressure falls were never more than 5 % more than the stoichiometric-ally expected value. All catalysts showed constant activity and selectivity from the beginning of their use.



FIG. 3.—The dependence of $-\Delta p_a$ on hydrogen pressure for palladium + silver catalysts at room temperature.

 \bigcirc , Pd + Ag, I; \emptyset , Pd + Ag, II; \bigcirc , Pd + Ag, III.

Table 2 summarizes some of the results for the palladium + silver catalysts, while fig. 4 shows their dependence of selectivity on hydrogen pressure at 20°C. In table 2, S is the selectivity extrapolated to zero hydrogen pressure from fig. 4 while S_{β} is the initial selectivity obtained from selectivity against β plots. Fig. 5 shows the dependence of selectivity on hydrogen pressure for catalyst Pd + Ag, I at various temperatures. The very rapid decrease in selectivity with rising temperature with hydrogen pressures greater than about 50 mm reflects a corresponding decrease of $-\Delta p_{a}$. The activation energy between 20 and 80°C was estimated as 20·1 \pm 0·5 kcal/mole.

Table 2.—Kinetic characteristics of palladium + silver catalysts at $20^{\circ}C$

catalyst	order in hydrogen	S	S_{β}
Pd + Ag, I	1.68	0.985	1.00
Pd + Ag, II	1.68	0.980	0.980
Pd + Ag, III	1.80	0.975	0.983

Some experiments were performed over catalyst Pd + Ag, III to determine the effect on pressure against time curves of adding ethylene to the reaction mixture. It was admitted to the reaction vessel after the acetylene and before the hydrogen: the results are shown in table 3. The addition of ethylene caused an increase in the rate, and column 4 gives the ratio of the observed rate to that expected if no ethylene had been added. The increase is roughly proportional to the added ethylene pressure. $-\Delta p_a$ decreases linearly with increasing ethylene pressure, and also falls much more rapidly with increasing hydrogen pressure in the presence of added ethylene than in its absence (compare fig. 4). Column 6



FIG. 4.—The dependence of selectivity on initial hydrogen pressure for palladium + silver catalysts at room temperature; symbols are as in fig. 3. The dotted line refers to [Pd + Ag, I], the points for which are shown in fig. 5.



FIG. 5.—The dependence of selectivity on hydrogen pressure at various temperatures over catalyst Pd + Ag, I.

⊙, 21°C; **∅**, 40°C; **①**, 59°C; **●**, 77°C.

of table 3 shows that in five out of the six cases acceleration starts (as for palladium) when the ratio of the summed ethylene and hydrogen pressures to the acetylene pressure exceeds a value of about 7.5. The experimental error on these figures is about ± 1 due to the uncertainty in $-\Delta p_a$. It is concluded again that both hydrogen and ethylene are equally effective for securing the adsorption of the latter in the presence of acetylene.

Table 3.—The effect of added ethylene over catalyst Pd + Ag, III $P_{C_2H_2}$, 49.5 \pm 0.5 mm : temp. 21.0-21.5°C

$P_{C_2H_4}$ mm	$P_{\rm H2}\rm mm$	observed rate, mm/min	observed rate	$-\Delta p_a \mathrm{mm}$ ($\frac{P_{C_2H_4} + P_{H_2}}{at - \Delta pa}$
0	142.5	4.1	1.00	32	7.9
49.8	142.0	5.7	1.36	25	7.7
100.2	138.8	6.0	1.45	14	6.7
145.0	140.0	7.2	1.73	9	7.0
145.0	122.0	5.5	1.77	17	8.1
145.0	83.0	2.7	1.68	33	13.5

An experiment using 50 mm each of acetylene and ethylene was carried out and the products analyzed after a pressure fall of 25 mm; assuming the added ethylene had not started to react at this time, analysis showed a selectivity of 0.98. Added ethylene is therefore without effect on the initial selectivity.

DISCUSSION

THERMODYNAMIC AND MECHANISTIC FACTORS IN SELECTIVITY

The selective removal of acetylene from a gas mixture where the acetylene/ ethylene ratio is very low will only be achieved if either (i) the acetylene is very much more strongly adsorbed than the ethylene, or (ii) the catalyst is unable to cause the hydrogenation of ethylene. The ratio of the fractions of surface covered by the two unsaturated species, assuming no adsorption of hydrogen, is given in principle by the equation

$\theta_{\rm A}/\theta_{\rm E} = p_{\rm A}/p_{\rm E} \exp\left(-\delta\Delta G_a/RT\right),$

where p is the pressure in the gas phase and $\delta \Delta G_a$ is the difference between the free energies of adsorption of the two species under the relevant conditions; the subscripts A and E refer respectively to acetylene and ethylene. This equation embodies what might be termed the *thermodynamic factor* in selectivity. Now industrial experience shows that it is possible to attain selective removal of acetylene with an initial acetylene/ethylene ratio of about 10⁻⁴. If selectivity arose solely because of the stronger adsorption of acetylene, this would imply a most improbable value for $\delta \Delta G_a$, so it is therefore concluded that a palladium catalyst operating selectively under industrial conditions must be inactive for the hydrogenation of ethylene.

In the above system, it is largely immaterial whether the acetylene be converted to ethylene or to ethane, but in considering selectivity in the absence of a gross excess of ethylene this matter becomes highly relevant. The present work (confirming earlier findings) has shown that it is possible for acetylene to be converted to ethane without the intervention of gaseous ethylene. The reaction scheme may be formally written :

$$C_2H_2 + H_2 \rightarrow C_2H_4 \tag{A}$$

$$C_2H_2 + 2H_2 \rightarrow C_2H_6 \tag{B}$$

and hence the initial selectivity as determined for various catalysts in the present work depends simply on the ratio k_A/k_B . This may be termed the *mechanistic factor* in selectivity.

It is of interest to enquire how the direct formation of ethane may arise. The mechanism originally put forward by Sheridan ⁴ involved the initial formation of adsorbed vinyl radicals which can exist in two isomeric forms, viz.,

$$H_2C = CH \Rightarrow H_2C - CH.$$

The further addition of a hydrogen atom to the free radical form leads to chemisorbed ethylene which will have a definite chance of suffering hydrogenation to ethane rather than desorbing. The situation with the normal form of the vinyl radical is more complex. The addition of the second hydrogen atom to the carbon atom attached to the surface may be followed by the rupture of either carbonmetal bond (gaseous ethylene being formed) or the π -bond (leading again to chemisorbed ethylene). It is impossible to decide which is the more likely, and so the reaction scheme may be written



In this simplified scheme, the source of the hydrogen atoms in steps 1, 2 and 3 is not specified: they may be chemisorbed hydrogen atoms or they may come from other vinyl radicals. Steady-state treatment of this scheme gives the following equations for the rates of formation of ethylene and ethane:

$$\dot{P}_{C_2H_4} = [H] \left\{ k_1 f_n + \frac{k_4 B}{k_4 + k_5 P_{H_2}} \right\},\tag{1}$$

and

 $\dot{P}_{C_2H_6} = \frac{k_5 P_{H_2}[H]B}{k_4 + k_5 P_{H_2}},$ (2)

where

$$B = \{k_2 f_n + k_3 (1 - f_n)\},\$$

 f_n being the fraction of vinyl radicals in the normal form. The complete expression for the selectivity as a function of hydrogen pressure is therefore

$$S = \frac{P_{C_2H_4}}{\dot{P}_{C_2H_4} + \dot{P}_{C_2H_6}} = \frac{k_1 f_n (k_4 + k_5 P_{H_2}) + k_4 B}{k_1 f_n (k_4 + k_5 P_{H_2}) + k_4 B + k_5 P_{H_2} B}.$$
(3)

A fuller treatment would describe the concentrations of adsorbed intermediates in terms of the competitive adsorption of the reactants as chemisorbed acetylene and hydrogen atoms, and eqn. (1) and (2) should strictly contain such terms : they will, however, cancel in eqn. (3) and so the precise mode of formation of the vinyl radicals is not relevant to this discussion. Such a treatment would, however, account for negative orders in acetylene. Orders in hydrogen greater than unity have been noted before in similar systems,^{1, 2} and orders of 1.5 would result if steps 1, 2 and 3 were affected by molecular rather than atomic hydrogen.

The decrease in selectivity with increasing temperature over platinum and the palladium + silver catalysts is thermodynamic rather than mechanistic in origin. Increasing temperature reduces the extent to which acetylene is more strongly

adsorbed than ethylene, and completely non-selective behaviour is found (for example, over catalyst Pd + Ag, I at $\sim 100^{\circ}$ C) when the two are adsorbed with approximately equal strengths.

RHODIUM, PALLADIUM AND PLATINUM

Over palladium, platinum and the palladium + silver catalysts, the selectivity is independent of hydrogen pressure when determined before the start of the acceleration in the rate (see fig. 1, 4 and 5). This requires k_4 in the above scheme to be zero, when the expression for the selectivity reduces to $k_1 f_n/(k_1 f_n + B)$: this accords with the expectation that for catalysts which hydrogenate ethylene very rapidly k_5/k_4 will be very large. Over rhodium, however, the initial selectivity clearly decreases with increasing hydrogen pressure and this is accommodated by giving k_4 a finite value. Eqn. (2) then predicts that the rate of ethane formation will be proportional to some fractional positive power of the hydrogen pressure, which is supported by the results given in fig. 1.

For the pure metals, initial selectivities fall in the order Pd > Rh > Pt: there is little difference between the values for the more and less active samples of the standard palladium catalyst. However, on the basis of the minimum ethylene/ acetylene ratios for entry of ethylene into the reactive layer, as deduced from values of $-\Delta p_a$, the order of selectivities controlled by the thermodynamic factor is Rh > Pt > Pd.

The effect of prolonged exposure of a sample of the palladium catalyst to hydrogen at room temperature following reduction was (i) to reduce its activity and (ii) to reduce to zero its ability to hydrogenate ethylene. This treatment has produced a selectively poisoned catalyst whose initial selectivity is, however, almost unaffected. The concept of a relation between the outstanding ability of palladium to absorb hydrogen and its ability to become a highly selective catalyst offers an explanation of these findings. The freshly reduced palladium sample is considered to have had insufficient time to absorb much hydrogen, while the second during its long exposure to hydrogen absorbed considerably more. Now it is known 5 that dissolved hydrogen reduces the activity of palladium for the parahydrogen conversion reaction, by reason of its donating electrons to the unfilled d-band of the palladium. The same effect is probably being observed here, but the problem as yet unresolved is the reason for the relatively much greater decrease in the catalyst's ability to reduce ethylene as against acetylene. There is abundant kinetic evidence that the latter is always in some degree more strongly adsorbed than the former. The theory is therefore advanced that when the *d*-band of the palladium is sufficiently filled, the chemisorption of the ethylene ceases to occur while the chemisorption of the more strongly held acetylene can still take place. It is further suggested that under operating conditions palladium is able to absorb enough hydrogen to bring about this state of affairs. Hydrogenation of ethylene cannot then occur, while acetylene can still be reduced to ethylene and ethane.

The order of activity of the metals per unit weight of catalyst is Pd (unpoisoned) > Pt > Rh: the high activity of palladium supports previous findings.^{6, 7} Apart from this, it is concluded that palladium in its unpoisoned state is not exceptionally different from rhodium and platinum in its behaviour in acetylene hydrogenation.

palladium + silver catalysts

The interpretation of the results obtained with these catalysts is rendered difficult by the uncertain nature of their physical state. They show high activities which, however, do not change regularly with increasing silver content, and initial selectivities which are distinctly higher than for pure palladium. This may be because a certain, but small, amount of solid solution formation has occurred, with a consequent reduction in the number of holes in the *d*-band, thus favouring

the desorption of the chemisorbed ethylene over its further reduction. The observation ⁸ that copper + Raney nickel catalysts show completely selective behaviour in the hydrogenation of octadecynes is further evidence of the relevance of this concept. A recent American patent ⁹ has claimed that supported palladium catalysts containing from 1 to 40 % of a group IB metal show a higher selectivity than pure palladium, in line with the observations recorded in this paper. It is not stated whether the metals are in solid solution or not.

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- ¹ Bond, in Catalysis, ed. P. H. Emmett (Reinhold, New York, 1955), 3, 109.
- ² Sheridan, J. Chem. Soc., 1945, 470.
- ³ Bond and Sheridan, Trans. Faraday Soc., 1952, 48, 651.
- ⁴ Sheridan, J. Chem. Soc., 1944, 373.
- ⁵ Couper and Eley, Faraday Soc. Discussions, 1950, 8, 172.
- ⁶ Sheridan and Reid, J. Chem. Soc., 1952, 2962.
- ⁷ Beeck, Faraday Soc. Discussions, 1950, 8, 118.
- ⁸ Elsner and Paul, J. Chem. Soc., 1953, 3156.
- ⁹ Frevel and Kressley, U.S. Patent 2,802,889 (to Dow Chemical Co.).