683. *The Role of Supports in Catalytic Hydrogenation. Part III.* The Energetics of Hydrogenation of Crotonic Acid with Platinum Catalysts and the Titration of their Adsorbed Hydrogen.*

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The apparent activation energies of hydrogenation of crotonic acid in aqueous solution have been determined between 0° and 40° for platinum black and for platinum supported on alumina, zirconia, and chromic oxide, under diffusion-free conditions. Hydrogen adsorbed by these catalysts in the liquid phase has been determined by a chemical dehydrogenation method. For the supported catalysts, the observed activation energies are higher than those for platinum black. A variation in the platinum : alumina ratio affected both the apparent activation energy and the volume of hydrogen adsorbed per gram of platinum. Although a strict logarithmic dependence of the activation energy on the frequency factor does not occur, the variation of the activation energy results in the disappearance of a promoter action of the supports at sufficiently low temperatures. There was no dependence of catalytic activity on the hydrogen content of these catalysts, as has been found by various authors in the case of Raney nickel, except that the adsorbed hydrogen per gram of supported platinum was always greater than that on platinum black.

THE distinction between supports (or carriers) and promoters in the literature is not always clear, because catalytic activities are not always referred to unit area. Furthermore there is an increasing amount of evidence which indicates that carriers can show a promoter action. Since there is no *a priori* difference between structural promotion and pure carrier action, ambiguity can be avoided by confining the term promoter action to those cases in which the specific activity of a two-or-more-component catalyst is greater than the sum of the specific activities of the separate components.

In any study of catalytic activity, it is desirable to measure as many parameters of the reaction rate as possible. For supported or promoted catalysts in particular, it is of interest to determine the extent of the separate contributions of the temperature-independent factor and of the activation energy to the total activity, so that it can be decided whether a support or promoter increases the activity by virtue of a decrease in the activation energy, by an increase in the frequency factor, or by both. Supported catalysts, identical with those discussed in Part II of this series, have been used to hydrogenate crotonic acid in aqueous solution at temperatures considerably below the inversion temperature, in the region in which the reaction is strictly of zero order with respect to the olefin concentration. The classical methods of determining rate-controlling steps have shown that the catalysts were employed under conditions in which mass-transfer did not control the reaction rates.

The independence of the hydrogenation rate on the concentration of crotonic acid can be attributed to a saturation of the catalyst surface with the olefin, and the first-order dependence on hydrogen pressure at pressures near atmospheric suggests that the reaction occurs through a Rideal–Eley type of mechanism. There are many variations of this mechanism, the simplest of which involves adsorption of the olefin and its collision with free hydrogen. Various reaction mechanisms can, however, result in a first-order dependence on the hydrogen pressure and a zero-order dependence on the olefin concentration;[1,2] and the precise mechanism cannot be deduced from the kinetics alone. If hydrogenation of crotonic acid occurs by a Rideal–Eley type of mechanism, the amount

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* Part II, *J.*, 1961, 5086.

[1] Laidler, " Catalysis." ed. Emmett, Reinhold Publ. Corp., New York, 1954, Vol. I, p. 156.

[2] Eley, *op. cit.*, 1955, Vol. III, p. 50.

of hydrogen adsorbed should not necessarily be parallel to the hydrogenation activity of the catalyst. Nevertheless, it was considered to be of interest to measure the absorptive capacity of the catalysts for hydrogen under conditions similar to those which prevail during the reaction. Numerous workers[3-5] have reported a correlation between the hydrogen content of Raney nickel and its activity for hydrogenation. The adsorption of hydrogen from the liquid phase on to supported platinum has been measured by Sokol'skii and Gil'debrand,[6] but catalytic activities were not determined.

EXPERIMENTAL

Catalysts and Reagents.—The supported catalysts consisted of platinum deposited on alumina-I, alumina-II, chromic oxide, and zirconia, and were identical with those used in Part II. *X*-Ray examination of alumina-I showed it to be α-alumina and that of alumina-II, γ-alumina; and this difference in crystal structure may, in part, account for their different efficacies as carriers. Platinum black was prepared by reduction of chloroplatinic acid solution with formic acid and sodium acetate. By this method, the tendency of the platinum to form a colloidal solution was avoided, and it was readily filtered by suction.

Crotonic acid was distilled twice under reduced pressure, then recrystallised three times from distilled water. Its m. p. was 71—71·3°. The charge in the reaction vessel was 0·01 mole of crotonic acid and 12 c.c. of distilled water.

Kinetic Factors.—In a static system, as employed in this work, in which the mixing of hydrogen and the liquid is carried out by shaking, it is important to ensure that the reaction rate is independent of the rate of shaking. This was done by measuring the activity of several catalysts at different shaking rates. The activity of 2 g. of platinum on alumina-I at 30° became independent of the shaking speed when this exceeded 450 double strokes per minute, and that of the same weight of the other catalysts at speeds less than this. For all subsequent activity measurements, a shaking rate of 550 double strokes per minute was employed.

The first-order dependence of the reaction rate on the weight of catalyst is a necessary condition for the absence of mass-transfer effects. As the amount of the catalyst is increased, the reaction rate increases linearly at first, but subsequently becomes independent of the weight of the catalyst. Watt and Walling[7] represented this limiting value by an empirical formula: $k = Awp/(1 + Bw)$ in which w is the weight of catalyst, k the reaction rate, p is the hydrogen pressure, and A and B are constants. The activities of increasing amounts of platinum on alumina-I at 30° were found not to deviate from linearity until more than 1 g. was employed. Accordingly, the small amounts of catalysts which were subsequently used (0·05—0·25 g. of supported catalysts and 0·02 g. of platinum black) were well within the range of linear dependence of the activity on the weight of the catalyst.

The rates of hydrogenation of each catalyst were determined between 0° and 40°, the temperature being thermostatically controlled within $\pm 0{\cdot}2°$. It was necessary to correct these rates for the partial pressure of the solvent, since the rate at a given pressure is proportional to the partial pressure of hydrogen.[8] The validity of this correction has already been shown by Maxted and Moon.[9]

The Titration of Adsorbed Hydrogen.—The method of titrating adsorbed hydrogen was based on that used by Yamanaka, Taya, and Takagi,[4] in which potassium ferricyanide is reduced to ferrocyanide by chemisorbed hydrogen: $H + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} + H^+$.

Catalysts were shaken with 12 c.c. of distilled water for a standard time in an atmosphere of hydrogen. The hydrogen in the gas phase was displaced by bubbling nitrogen through the suspension of catalyst in water. After 20 min., 0·1 g. of potassium ferricyanide and 2 c.c. of N-sodium hydroxide were added, and the shaking was resumed for a further known time. The catalyst was filtered off by suction and washed several times, and the filtrate and washings were made up to 100 c.c. in a graduated flask. To 20 c.c. portions of this solution, contained

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[3] Beeck, Ritchie, and Wheeler, *J. Colloid Sci.*, 1948, **3**, 505.

[4] Yamanaka, Taya, and Takagi, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1958, **52**, 224.

[5] Kokes and Emmett, *J. Amer. Chem. Soc.*, 1960, **82**, 4497.

[6] Sokol'skii and Gil'debrand, *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, 609.

[7] Watt and Walling, *J. Phys. Chem.*, 1955, **59**, 7.

[8] Maxted, *J. Soc. Chem. Ind.*, 1921, **40**, 169T.

[9] Maxted and Moon, *J.*, 1935, 1190.

in a beaker, sufficient sulphuric acid was added to make the solution 2N with respect to the acid. This solution of ferrocyanide, in the presence of an excess of ferricyanide, was titrated potentiometrically with standard 0·01M-ceric ammonium sulphate. The latter, being of analytical reagent grade, was of sufficient purity for use as a primary standard. The potential of a bright platinum electrode was measured with respect to a saturated calomel electrode which made contact with the solution through an agar–potassium chloride salt bridge. The end-point was characterised by a rapid change in a potentiometer reading from ~0·5 to 1 volt.

RESULTS AND DISCUSSION

The influence of temperature on the observed activity is a useful guide in the determination of the rate-controlling step, since the activation energies of diffusion processes are generally much smaller than those of adsorption or of reaction. The calculated activation energy for the transfer of hydrogen into water is reported to be 2·7 kcal. mole^{-1} on the basis of diffusion coefficients.[10] Since activation energies as low as this were not obtained, the activities were of first order with respect to the weight of the catalyst and independent of shaking rate, and transport of hydrogen across the gas–liquid boundary, or of products from the catalyst surface, cannot control the overall reaction rates.

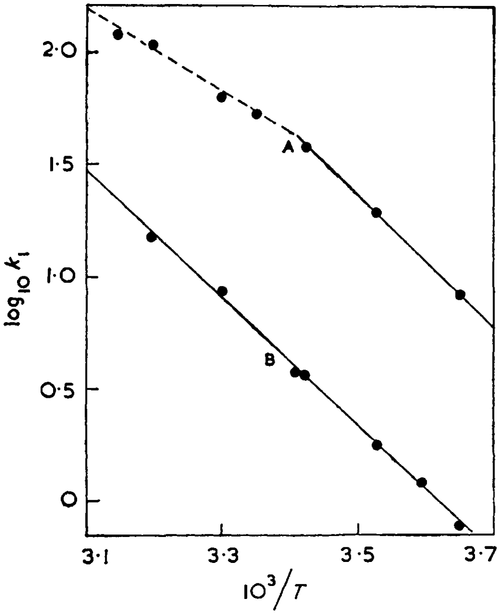

FIG. 1. The dependence of activity on temperature for 1·03% Pt/Al_2O_3-I: A, 1·20 g.; B, 0·120 g.

The quantitative effect of diffusion in lowering the true activation energy of gas reactions on solids has been adequately described by Weisz and Prater;[11] and the same principles apply to liquid-phase catalytic reactions. In the case of a porous catalyst, the apparent activation energy can be as much as one-half the real value if diffusion effects are large; and, in an Arrhenius plot, the gradient at high temperatures may change over to the true value at low temperatures, this being dependent on the relative rates of the chemical and of the diffusion processes.

The activity of 1·20 g. of platinum on alumina-I is shown as a function of the reciprocal temperature in Fig. 1. At low temperatures, the gradient corresponds to an apparent

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[10] Yao and Emmett, *J. Amer. Chem. Soc.*, 1959, **81**, 4125.

[11] Weisz and Prater, *Adv. Catalysis*, 1954, **6**, 143.

activation energy of 13·1 kcal. mole^{-1}, whereas, above 30°, there is a change of slope corresponding to ~9 kcal. mole^{-1}. When the amount of catalyst is reduced, this change in slope does not occur, the gradient corresponding to 13·1 kcal. over the whole temperature range. Accordingly, it is concluded that this apparent activation energy corresponds to that required by a chemical or an adsorption process.

Thus, in general, if a ten-fold decrease in the amount of catalyst did not alter the apparent activation energy, it was assumed that diffusion effects did not control the activities. Quantitative transference of platinum black to the reaction vessel was found to be inaccurate with amounts less than about 0·02 g., so the hydrogenation rate was substantially reduced by sintering the platinum at 300° and 400°. The activation energy did not change on sintering, as has been previously reported for the same reaction with acetic acid as the solvent.[9] The activities of 0·02 g. of platinum, not sintered and sintered at 300° and at 400° for 18 hr., were, respectively, 7·76, 3·88, and 0·89 c.c. per min at 20°.

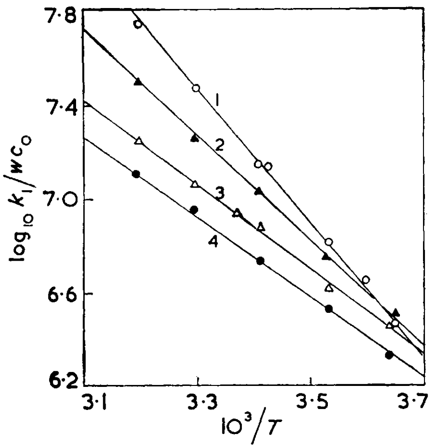

FIG. 2. Relative specific activity as a function of temperature for: (1) 1·03% Pt/Al_2O_3-I; (2) 0·625% Pt/Al_2O_3-I; (3) 11·1% Pt/Al_2O_3-I; (4) Pt black.

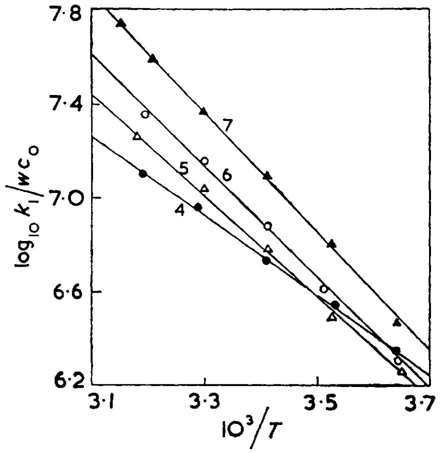

FIG. 3. Relative specific activity as a function of temperature for: (4) Pt black; (5) 0·826% Pt/Cr_2O_3; (6) 0·104% Pt/Al_2O_3-II; (7) 0·277% Pt/ZrO_2.

The rate of hydrogenation of crotonic acid at unit pressure, *i.e.*, the specific reaction rate, can be expressed by the relationship $k_1 = wSk_s$ in which w is the weight of platinum, S is its specific surface area, and k_s, the activity per unit area, is a characteristic of the catalyst surface. This activity constant is related to a frequency factor, A, and the apparent energy of activation, E_A, by the usual Arrhenius expression $k_s = A \exp(-E_A/\boldsymbol{R}T)$. Although absolute values of S are not known, they can be assumed to be proportional to the reciprocals of the poisoning coefficients per gram of platinum. These are given by the appropriate values of $c_0/0{\cdot}00625$ in Part II. The value of c_0 for the platinum black used in this work is $7{\cdot}2 \times 10^{-5}$ mole/g. Plots of log (k_1/wc_0) against $1/T$ are given in Fig. 2, for different ratios of platinum on alumina-I, and in Fig. 3, for the other supported catalysts containing the optimum ratio of platinum to support. The Arrhenius plots for platinum are included in both figures for comparison. The apparent activation energies obtained from the gradient of these lines are given in the Table.

If k is the true velocity constant, K_H the adsorption coefficient of hydrogen in the Langmuir adsorption isotherm, and p_H the partial pressure of hydrogen, the reaction rate is given by $v = kK_Hp_H$ and the true first order velocity constant $k_1 = kK_H$. It can readily be shown that, whenever the apparent first-order constant is given by the product of an adsorption equilibrium constant and the true velocity constant, the apparent activation energy is lower than the true activation energy by the value of the heat of adsorption of the hydrogen, irrespective of the reaction mechanism. Accordingly, the apparent activation energies in the Table should be corrected by the addition of 16—18 kcal./mole [12] in order to obtain the true values.

Another factor which can affect the observed activation energy, for a series of related catalysts, is a compensation effect between the activation energy and the frequency factor. Possible reasons for the compensation effect have been adequately described elsewhere.[13] The absence of a strict logarithmic relation between E_A and A is apparent from Figs. 2 and 3, since a necessary condition for this is that the Arrhenius plots should intersect in a common point, *i.e.*, a temperature exists at which all the reaction rates are equal. Nevertheless, it is evident that the relative activities at a given temperature do not depend only on the temperature-independent term, but also on the activation energy.

At temperatures above 15°, promoter action of the supports is involved, since the specific activities of the supported catalysts are greater than the corresponding activity of unsupported platinum. Owing to a compensation effect, the degree of this promoter action becomes smaller as the temperature decreases. At sufficiently low temperatures, the increase in the temperature-independent factor for the supported catalysts becomes inadequate to overcome the effect of a larger activation energy, and promotion does not occur. For platinum on chromic oxide and for platinum on alumina-II, these temperatures lie in the experimental region, being 15° and 3°, respectively.

The activation energy for 11·1% platinum–alumina-I approaches that for unsupported platinum. This is not unexpected, since electron micrographs of these catalysts have shown that, at such a high concentration of platinum, a considerable proportion of the catalyst is not associated with any particular particle of the support, but is dispersed among the support in a colloidal form. When the platinum/support ratio is decreased to 1·03%—the optimum ratio—all the platinum is deposited on the surface of the support. At a lower concentration, both the activity and the activation energy decrease.

The standard time allowed for the saturation of the catalysts with hydrogen was 30 min., although preliminary experiments showed that the adsorption of hydrogen was virtually complete after only 15 min. The reduction of ferricyanide took longer than this. Titres obtained with platinum black, after 10, 45, and 960 min., were, respectively, 9·15, 10·55, and 10·53 c.c. of hydrogen per gram. A similar variation of the hydrogen titre with time was found for the supported catalysts. Accordingly, the standard time allowed for the reduction was 90 min.

The supports were subjected to the same pre-treatment as the catalysts during their preparation, except that an equivalent amount of hydrochloric acid was used in place of chloroplatinic acid. Experiments with these and with the supported catalysts were not so reproducible as with platinum black; nevertheless, values did not differ from the mean of five experiments with one catalyst by more than 2%. The results obtained are given in the annexed Table, in which the volumes of hydrogen adsorbed per gram of platinum obtained from the second, third, and fourth columns are compared with the activities of the catalysts at 20°.

Catalyst	Pt (wt. %)	Total titre of H_2/g. of catalyst (c.c.)	H_2 adsorbed/g. of support (c.c.)	H_2 adsorbed/g. of Pt (c.c.)	Activity at 20°/g. of Pt (c.c./min.)	E_A (kcal./mole)
Pt	—	10·5	—	10·5	392	7·8
Pt/Al_2O_3-I	11·1	3·96	0·00410	35·6	1420	8·2
	1·03	0·886	,,	85·6	3160	13·1
	0·625	0·293	,,	46·2	2140	10·3
Pt/Al_2O_3-II ...	0·104	0·111	0·00746	99·6	1360	10·9
Pt/Cr_2O_3	0·826	0·944	0·637	37·8	1500	9·9
Pt/ZrO_2	0·277	1·201	0·0245	42·5	1810	11·6

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[12] Maxted and Hassid, *J.*, 1931, 3313; Maidanovski and Bruns, *Acta physicochim., U.R.S.S.*, 1938, **9**, 927; Kwan, *Adv. Catalysis*, 1954, **6**, 67; Chon, Fisher, and Aston, *J. Amer. Chem. Soc.*, 1960, **82**, 1055.

[13] Constable, *Proc. Roy. Soc.*, 1925, *A*, **108**, 355; Cremer, *Adv. Catalysis*, 1955, **7**, 75; Kemball, *Proc. Roy. Soc.*, 1953, *A*, **217**, 376.

The supported catalysts adsorb greater volumes of hydrogen per gram of platinum than do those which are adsorbed by platinum black. The volumes of hydrogen adsorbed by platinum on alumina do not approach the very high values, of the order of 600 c.c./g., which have been reported by Sok'olskii and Gil'debrand.[6] This can be attributed to the different kinds of alumina and the different method of preparation of the catalyst. The alumina gel used by the above workers completely adsorbed chloroplatinic acid in the concentration range 0·17—1·79% of platinum, and their catalysts were prepared by reduction with hydrogen.

For platinum on these different supports, there is no simple correlation between the volume of hydrogen adsorbed and the activity; indeed, platinum on alumina-II is less active than platinum on alumina-I, although it adsorbs a larger volume of hydrogen per gram of platinum. For platinum on alumina-I, however, in which only the ratio of platinum to support was varied, there is a qualitative correspondence between the hydrogen adsorbed and the catalytic activity, in that a maximum in the activity is associated with the greatest specific adsorption of hydrogen.

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