

955. *The Catalytic Hydrogenation of Unsaturated Hydrocarbons. Part III.* The Kinetics of the Hydrogenation of Acetylene over Various Types of Nickel Catalyst.*

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An expression of the form $-dp/dt = k_A P_{H_2} + k_B (P_{H_2} - P_{H_2}^0)$ describes the rate-dependence on hydrogen pressure over nickel-kieselguhr, regardless of the order of admission of the reactants to the reaction vessel. Results with three nickel powders also conform to this expression when hydrogen is admitted first; they are poisoned if acetylene is added first. Rates are generally independent of acetylene pressure. The results presented in Part I have been broadly confirmed: E_B lies between 15 and 29 kcal./mole, and E_A between 6 and 13 kcal./mole. The mean ratio E_B/E_A is 2.4 for supported catalysts and is somewhat lower for the powders.

In disagreement with earlier findings, $P_{H_2}^0$ has been found to be either independent of, or to increase only slightly with, increasing acetylene pressure; it normally decreases with increasing temperature. Possible reasons for the disagreement are discussed. Nickel-kieselguhr shows the highest activity, and of the powders that prepared by reduction of the oxide *in situ* is most efficient.

HYDROGENATION of acetylene has been little studied on nickel catalysts other than those of the pumice-supported type.^{1,2} Evaporated nickel films³ and nickel wires⁴ are both substantially poisoned by acetylene and are therefore not suitable forms to use. de Pauw and Jungers⁵ reported that nickel-kieselguhr failed to catalyse the reaction when acetylene was admitted first to the reaction vessel, but gave exceedingly fast rates when hydrogen was admitted first. We have failed to confirm these observations. With nickel powder, obtained by reduction of the nitrate, they failed to find constant activity even when hydrogen was admitted first, but they secured reproducible activity by reducing the powder between each run; our work has not confirmed the necessity for this.

In Part I¹ a complex rate expression was proposed to account for the results obtained over a nickel-pumice catalyst when the initial hydrogen : acetylene ratio was greater than about two. We now confirm this and extend the observations to examine whether this form of rate expression is shown by other types of nickel catalyst.

EXPERIMENTAL

Apparatus, purification, and procedure were essentially as described in Part I,¹ except that the catalyst invariably lay at the bottom of the reaction vessel. In later experiments the vessel was slightly modified to permit the reduction of the catalyst in a hydrogen steam.

Catalysts.—Nickel-pumice (containing about 10% of metal by weight) was prepared as before.¹ Nickel-kieselguhr was obtained unreduced from the British Petroleum Company; it was reduced in a slow stream of hydrogen at 450° for 12 hr. and contained 10% of metal by weight. Nickel powder prepared by the decomposition of nickel carbonyl was provided by the Mond Nickel Company. Two other types of nickel powder were prepared: (i) "AnalaR" nickel nitrate was calcined in a stream of oxygen at 250° for 8 hr. and the resulting oxide reduced in a stream of hydrogen at 300° for 10 hr. (ii) Basic nickel carbonate, precipitated from nickel nitrate solution by ammonium hydrogen carbonate, was dried at 105° and sintered at 400°. A portion of the resulting oxide was reduced in a slow stream of hydrogen in the reaction vessel at 500° for 24 hr.⁶

* Part II, *J.*, 1958, 4288.

¹ Bond, *J.*, 1958, 2705.

² Sheridan, *J.*, 1944, 373; 1945, 133.

³ Beeck, *Discuss. Faraday Soc.*, 1950, 8, 118; Wheeler, personal communication.

⁴ Farkas, Farkas, and Rideal, *Proc. Roy. Soc.*, 1934, A, 146, 630.

⁵ de Pauw and Jungers, *Bull. Soc. Chim. belges*, 1948, 57, 618.

⁶ Best and Russell, *J. Amer. Chem. Soc.*, 1954, 76, 838.

Samples not initially reduced in the reaction vessel were treated with hydrogen (*ca.* 100 mm.) *in situ* at 300° for $\frac{1}{2}$ hr. before use. The surface areas of the Mond Nickel powder and that prepared by method (ii) were determined after use by krypton adsorption at -196°.

RESULTS

Nickel-Pumice Catalysts.—Experiments were carried out on samples drawn from two preparations; batch I, from which the samples used in Part I were drawn, gave samples B (0.51 g.) and B* (1.00 g.; identical with B of Part I), and batch II, a fresh preparation, gave samples D (0.21 g.), E (0.50 g.), and F (0.50 g.). Preliminary observations on B differed from some of those in Part I: thus for example while a rate expression of the form

$$-(dp/dt)_0 = k_A P_{H_2} + k_B (P_{H_2} - P_{H_2}^0) \quad . \quad . \quad . \quad (1)$$

was still found when acetylene was admitted before hydrogen, pressure-time curves with initial hydrogen pressures greater than $P_{H_2}^0$ were not invariably of the linear (Type I) form. Instead they showed two linear parts (a Type IIA curve) with the point of intersection, $-\Delta P_\alpha$, increasing from about $2/3 P_{C_2H_2}$ to $P_{C_2H_2}$ (where $P_{C_2H_2}$ is the initial acetylene pressure) with increasing initial hydrogen : acetylene ratio between 2 and 6 at 100°. Type III curves were still, however, obtained below $P_{H_2}^0$. In addition, the sample from batch I no longer showed the previously-found proportionality between $P_{H_2}^0$ and $P_{C_2H_2}$, and instead the former was broadly independent of the latter. For these reasons a second batch of catalyst was prepared but samples from this batch also showed behaviour not conforming with earlier work.

Since in all cases type IIA curves were found with initial hydrogen pressures greater than $P_{H_2}^0$, the general rate expressions are

$$-dp/dt = k_A P_{H_2} + k_\alpha (P_{H_2} - P_{H_2}^0) \quad . \quad . \quad . \quad (2)$$

$$\text{and } -dp/dt = k_A P_{H_2} + k_\beta (P_{H_2} - P_{H_2}^0) \quad . \quad . \quad . \quad (3)$$

where $k_A + k_\alpha$ is the slope of the line obtained on plotting R_α against initial hydrogen pressure, and $k_A + k_\beta$ is the slope obtained when R_β is so plotted. The results will therefore be described in terms of the temperature- and acetylene pressure-dependence of the first-order rate constants k_A , k_α , and k_β and of $P_{H_2}^0$. Table I shows the activation energies, E_i , and the logarithms

TABLE I. *Activation energies (kcal./mole) and pre-exponential factors for nickel-pumice.*

Sample	B	B*	Part I	D	E	F
Temp. range	100—115°	53—83°	86—110°	115—160°	85—130°	111—135°
E_A	9.6	10.5	10.3	9.2	8.2	6.4
E_α	24.2	21.2	23.8	22.0	18.2	16.0
E_β	—	—	—	22.8	19.0	—
ΔE_α	15.0	10.5	13.5	12.8	10.5	10.1
ΔE_β	—	—	—	14.6	12.3	—
$\log_{10} A_A$	4.0	5.2	5.3	3.3	2.9	2.1
$\log_{10} A_\alpha$	12.2	12.1	12.5	10.3	8.7	7.3
$\log_{10} A_\beta$	—	—	—	9.5	10.7	—
$\log_{10} \Delta A_\alpha$	8.7	6.7	7.8	6.9	6.0	5.4
$\log_{10} \Delta A_\beta$	—	—	—	8.6	6.8	—

of the pre-exponential factors, A_i [expressed as $\text{min.}^{-1} (\text{g. of metal})^{-1}$], obtained from the corresponding k_i 's by the Arrhenius equation, while other quantities are related as

$$\log_{10} (k_\alpha/k_A) = \log_{10} \Delta A_\alpha - \Delta E_\alpha/2.3 RT; \quad \log_{10} (k_\beta/k_A) = \log_{10} \Delta A_\beta - \Delta E_\beta/2.3 RT$$

The initial acetylene pressure was 30 mm. in all series where it was not purposely varied. The sample B* gave type I curves above $P_{H_2}^0$ and values for E_β , etc., are not therefore quoted in the table. Values of E_β etc., for samples B and F are too inaccurate to quote. Mean values and standard deviations for E_A , E_α , and E_α/E_A are respectively 9.0 ± 1.2 ($\pm 13\%$), 20.9 ± 2.5 ($\pm 12\%$), and 2.34 ± 0.15 ($\pm 6.5\%$); the quotient E_α/E_A is thus much less variable than either activation energy separately. A convincing "compensation effect" of the form $\log_{10} A_i = 0.55 E_i$ holds for all samples except B*.

With samples B and B*, $P_{H_2}^\circ$ was roughly independent of temperature, the mean values being respectively 62 and 98 mm.; for sample D it was 75, 69, 66, and 65 mm. at 115°, 130°, 145°, and 160°; for E it was 80, 74, 63, and 57 mm. at 85°, 100°, 115°, and 130°, respectively. In all cases the initial acetylene pressure was 30 mm.

For sample F the behaviour was irregular; when the dependence of the parameters on initial acetylene pressure, $P_{C_2H_2}$, was studied over it the results were complicated by a continuously increasing activity. At 120° and 135°, however, $P_{H_2}^\circ$ was approximately independent of $P_{C_2H_2}$ between 15 and 90 mm., the mean value for eight series of experiments being 83 ± 10 mm. The quotient k_α/k_A was independent of $P_{C_2H_2}$ at each temperature.

Over sample F between 90° and 120°, type IIA curves were obtained when hydrogen was admitted before the acetylene, whereas type IIB curves were previously¹ obtained under these conditions; however the same rate expressions still describe the results. The ratio k_α/k_β was independent of temperature and the mean value, 1.20, agrees well with those quoted in Table 4 of Part I (1.15—1.22). The activation energies E_α and E_β (not determined previously since the activities were not comparable) are respectively 14.5 and 14.1 kcal./mole, much larger than the value of E_α (6.4 kcal./mole) found when the reverse order of addition was employed.

Nickel-Kieselguhr Catalyst.—Four samples of the nickel-kieselguhr catalyst had the following weights: A, 0.29 g.; B, 0.10 g.; C, 0.12 g.; D, 0.14 g. The rate expressions (2) and (3) applied under all conditions, acetylene being admitted before the hydrogen; pressure-time curves were invariably of type IIA above $P_{H_2}^\circ$ and of type III below it. $-\Delta p_\alpha$ was essentially independent of both initial hydrogen pressure and temperature. The temperature-dependence of the first-order rate constants is given in Table 2, the fixed initial acetylene pressure being 30 mm.;

TABLE 2. *Activation energies (kcal./mole) and pre-exponential factors for nickel-kieselguhr.*

Sample	E_A	E_α	ΔE_α	$\log_{10} A_A$	$\log_{10} A_\alpha$	$\log_{10} \Delta A_\alpha$
A	12.8	27.4	17.3	6.8	16.4	10.4
B	12.1	28.8	16.9	6.3	16.3	10.0
D	9.2	25.6	18.7	4.7	15.2	11.3
Mean	11.4 ± 1.4	27.3 ± 1.1	17.6 ± 0.7	—	—	—

sample C was used at only one temperature. Variations of k_β with temperature followed closely those of the k_α , so no values for E_β , etc., are quoted. The "compensation effect" is described by the equation $\log_{10} A_i = 1.0 + 0.65 E_i$, and the mean value of E_α/E_A is 2.40 ± 0.27 .

Values of k_A and k_α were independent of the fixed initial acetylene pressure used. For example, in series of experiments carried out over sample D at 60° with fixed initial acetylene pressures of 15, 30, 60, and 90 mm., the resulting mean values of k_A and k_α were respectively $(3.45 \pm 0.25) \times 10^{-2} \text{ min.}^{-1}$ and $(8.92 \pm 0.09) \times 10^{-2} \text{ min.}^{-1}$. That the reaction is strictly of zero order in acetylene was confirmed by series of initial-rate measurements made at 60° and 80° with a fixed initial hydrogen pressure of 60 mm. and acetylene pressures varying between 10 and 120 mm. Rates were always independent of the variable pressure provided $P_{H_2}/P_{C_2H_2}$ exceeded 0.5. The various samples of this catalyst behaved much more consistently than did those of nickel-pumice. For example, the mean values of the acetylene pressure-independent quotient k_α/k_A at 60° were respectively 1.12, 1.00, 1.09, and 1.07 for the four samples.

The dependence of $P_{H_2}^\circ$ on acetylene pressure is described by the equation (4). Values of

$$\log_{10} (P_{H_2}^\circ/P_{C_2H_2}) = \log_{10} k - x \log P_{C_2H_2} \quad . \quad . \quad . \quad (4)$$

$\log k$ and x (within error the same for all samples and dependent only on temperature) were respectively 1.58 and 0.73 at 60°, 1.45 and 0.69 at 70°, and 1.31 and 0.65 at 80°.

One series of experiments was performed over sample D at 80°, hydrogen being admitted first; type IIA curves were obtained at all hydrogen pressures, and the rate expression (2) was valid. Its parameters had the values: $P_{H_2}^\circ$, 50 mm.; k_A , $9.2 \times 10^{-2} \text{ min.}^{-1}$; k_α , $42.0 \times 10^{-2} \text{ min.}^{-1}$. Reversal of the order of addition therefore reduces $P_{H_2}^\circ$ (71 to 50 mm.) and approximately doubles both k_A and k_α , leaving their ratio unaffected.

Nickel Powder Catalysts.—The characteristics of the samples were as follows: Samples A (0.220 g.) and B (0.215 g.) were produced by reduction of the oxide from the nitrate, C (0.240 g.)

was produced by reduction of the oxide from the basic carbonate and had a surface area of 0.41 m.²/g., and D (0.165 g.) was from the Mond Nickel Co. and had a surface area of 1.48 m.²/g. Prior addition of acetylene to sample A at 150° led to rapid poisoning, which however was counteracted by a short reduction at 300°. In all subsequent experiments with the powders, hydrogen was admitted before acetylene, and no poisoning then occurred. Type III curves were always obtained with hydrogen pressures less than $P_{H_2}^0$; at higher pressures, type IIA curves were obtained with samples A and B, and type I curves with C and D.

Activation energies and pre-exponential factors obtained from series of experiments in which the initial acetylene pressure was 30 mm. are given in Table 3; the subscript (α , B) indicates that the quoted activation energies, etc., are values of E_α for samples A and B [where the rate expressions (2) and (3) hold], and are values of E_B for C and D [where the appropriate rate expression is equation (1)]. No values are quoted for E_β , etc., since the variations of k_β with temperature were not sufficiently regular. The "compensation effect" equation is $\log_{10} A_i = 0.40 + 0.48E_i$.

TABLE 3. Activation energies (kcal./mole) and pre-exponential factors for nickel powders.

Sample ...	Temp. range	E_A (kcal./mole)	$E_{(\alpha, B)}$ (kcal./mole)	$\Delta E_{(\alpha, B)}$ (kcal./mole)	$\log_{10} A_A$	$\log_{10} A_{(\alpha, B)}$	$\log_{10} \Delta A_{(\alpha, B)}$
A	107—150°	11.4	18.3	8.6	5.5	9.2	4.7
B	124—150°	6.4	16.0	9.1	3.0	8.2	5.2
C	73—150°	8.2	15.1	7.3	5.0	8.3	4.4
D	88—126°	9.2	15.6	5.5	4.8	8.0	3.0

The effect of variation in acetylene pressure was examined only with sample B, on which experiments at 124°, 140°, and 150° with fixed initial acetylene pressures of 15, 30, 60, and 90 mm. showed that k_A and k_α were both independent of it. At the same temperatures, and with a fixed initial hydrogen pressure (60 mm.), initial rates were accurately independent of acetylene pressure within the range 10—120 mm. Samples A and B gave reasonably consistent values of k_α/k_A : values at 124°, 140°, and 150° were respectively 0.85 and 0.87; 1.42 and 1.24; and 1.88 and 1.79. Equation (4) again describes the dependence of $P_{H_2}^0$ on $P_{C_2H_2}$; over sample B, α was 0.75 (independent of temperature) while at 124°, 140°, and 150° the values of $\log k$ were respectively 1.64, 1.58, and 1.50. Over sample A, $P_{H_2}^0$ declined smoothly with increasing temperature (107—150°) from 90 to 50 mm., and a similar decline from 170 to 125 mm. was observed with sample D in the range 90—126°. The last values are abnormally high. With sample C, $P_{H_2}^0$ was not dependent on temperature (73—114°) and had a mean value of 101 ± 10 mm.

DISCUSSION

This more extensive study of the kinetics of hydrogenation of acetylene over nickel catalysts has revealed a very complex pattern of results. There is no apparent consistency between the types of pressure-time curve found for supported nickel catalysts and the experimental conditions. Whereas previously¹ type I curves resulted on prior admission of acetylene to nickel-pumice, type IIA curves are now found with samples drawn from the same and from a new batch: the age of the catalyst is not therefore the sole variable. On re-examining a previously used sample (B*), the previous behaviour was found. Following prior admission of hydrogen to nickel-pumice, curves of type I,² type IIB,¹ and type IIA (present work) have been found. The observations may be summarised as follows. (i) Reasonably fresh nickel-pumice may yield, on prior admission of acetylene, curves of either type I or IIA, and on prior admission of hydrogen one of three types: the precise conditions of preparation and reduction may be decisive. (ii) On prolonged storage, nickel-pumice will yield type IIA curves (whereas type I curves were originally given), unless the sample had been used soon after its preparation.

However, it is possible for initial rates determined from different types of pressure-time curve to conform to similar rate expressions. Thus, nickel-pumice being used, a rate expression of the form of equation 1 is obtained regardless of whether the curves are of

type I¹ or IIA (present work), provided only acetylene is admitted first, while the equation

$$-(dp/dt)_0 = k_\alpha P_H. \quad \dots \quad (5)$$

holds over a wide range of conditions when hydrogen is added first, regardless of the form of the pressure-time curve form (refs. 1 and 2 and this work). It is therefore concluded that the form of the rate expression is more fundamental than the form of the pressure-time curves. Possible effects of the order of addition on the mechanism were discussed in Part I, and that differing mechanisms do operate (depending on the addition order) is confirmed by the finding that for nickel-pumice (sample F) E_A is 6.4 kcal./mole while E_α is 14.5 kcal./mole. The α - and the β -part of the type IIA curves found in this work are not kinetically independent, for the activation energies E_α and E_β (where the latter could be accurately estimated) are not significantly different.

Nickel-kieselguhr and the powders differ from nickel-pumice in that they show the complex rate expression even when hydrogen is admitted first. Mean values of E_A and especially of E_α vary considerably between the various catalyst types, but it is perhaps significant that the mean values of E_α/E_A are practically identical for the two supported catalysts (2.34 and 2.40); this ratio is somewhat lower (*ca.* 1.9) for the powders.

It is evident from the differing temperature ranges in which the various samples were studied that there exist substantial differences in activity per unit weight of metal. Because of the "compensation effect," activities at an arbitrary temperature are a better guide than pre-exponential factors, and Table 4 gives the approximate mean values of

TABLE 4. *Approximate mean values of rate constants (min.⁻¹ g.⁻¹) k_A and $k_{(\alpha, B)}$ at 100°.*

Sample	Ni-pumice	Ni-kieselguhr	Powders A & B	Powder C	Powder D
$10^3 k_A$	47	600	1.0	24	9.0
$10^3 k_{(\alpha, B)}$	21	7700	4.0	28	9.5

k_A and $k_{(\alpha, B)}$ at 100° (results for sample B* of nickel-pumice are not included). Since the relative activities will vary with temperature, it is not the precise values, but only their orders of magnitude, which are significant. Nickel-kieselguhr is much more active than nickel-pumice, which may be due to a large difference in crystallite size. Amongst the powders, C is by far the most active, and this may be because it was never exposed to air after reduction. The batch from which samples A and B were taken may have been slightly pyrophoric after reduction, and so have been sintered when first exposed to air, with consequent loss of area and subsequent activity. The *specific* activities of samples C and D are more disparate than the activities quoted above, the specific rate constants for C being both about ten times greater than for D. The specific area of C (0.41 m.²/g.), determined after use, may be much less than when in use, again because of sintering on exposure to air. The high activity of nickel-kieselguhr is accompanied by consistently high activation energies. The ready poisoning of unsupported nickel by acetylene has been confirmed.

$P_{H_2}^\circ$ generally decreases with increasing temperature. In Part II it was suggested that the second mechanism (whose rate constants are k_B or k_α and k_β) was initiated by molecularly adsorbed hydrogen. $P_{H_2}^\circ$ was previously¹ found to be proportional to $P_{C_2H_2}$, and a possible mechanism invoking competition between physically adsorbed acetylene and molecularly adsorbed hydrogen for the surface above the primary chemisorbed layer was discussed. This behaviour has however not been repeated, and $P_{H_2}^\circ$ now appears to be either approximately independent of $P_{C_2H_2}$ (nickel-pumice F and powder C) or proportional to about $(P_{C_2H_2})^{0.3}$ (nickel-kieselguhr and powders A, B, and D). A possible interpretation is that here incremental acetylene pressures are respectively ineffective and only weakly (and progressively less) effective in inhibiting molecular hydrogen adsorption. $P_{H_2}^\circ$ decreases with rising temperature, except, significantly, in those cases where it is

also broadly independent of acetylene pressure. In the other cases, the explanation may be that with rising temperature the physically adsorbed acetylene is desorbed, thus reducing the minimum hydrogen pressure required to give molecular adsorption.

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