Polymerization by sodium dissolved in liquid ammonia, a new method for polymerization to give immediate and complete reaction at −75°, is described. Evidence is presented to show that these polymerizations proceed by an anionic chain mechanism.

URBANA, ILLINOIS RECEIVED APRIL 1, 1948

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Effect of Ratio of Catalyst and Other Factors upon the Rate of Hydrogenation

BY HOMER ADKINS AND HARRY R. BILLICA[1]

The rate of a catalytic hydrogenation is particularly dependent upon the temperature, pressure of hydrogen and the amount and ratio of catalyst to hydrogen acceptor. The rate and even the possibility[2] of hydrogenation of α-amino and hydroxy esters over Raney nickel to the corresponding amino alcohols or glycols is so much influenced by these factors that a rather extensive study of the hydrogenation of ethyl piperidinoacetate and ethyl lactate to 2-piperidino-1-ethanol and 1,2-propanediol has been made. Some of the more significant results are recorded in Figs. 1–4 inclusive.

The rate of reaction of the esters was followed by recording the drop in pressure as the hydrogenations proceeded. The times recorded in the figures are for hydrogenations 75% complete, since these values could be more accurately observed than those for complete reaction. The relative effect of the variables is much the same irrespective of whether the comparison is based upon hydrogenations 50, 75 or 100% complete.

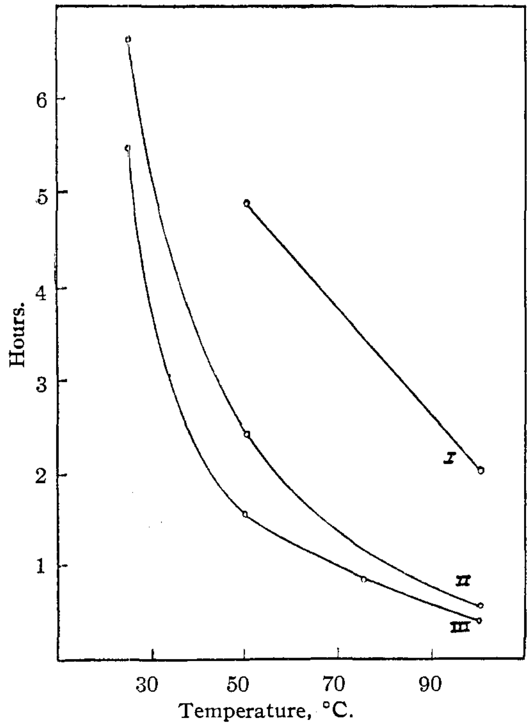

Fig. 1.—Effect of temperature in the hydrogenation of esters at 5000 p. s. i. with 15 g. of W-6 Raney nickel in 35 ml. of ethanol: I, 10 g. of ethyl lactate; II, 10 g. of ethyl lactate and 1.0 ml. of triethylamine: III, 10 g. of ethyl piperidinoacetate.

The effect of variations of temperature, pressure and amount of catalyst is quite similar for ethyl piperidinoacetate and ethyl lactate if the latter contains a little triethylamine. However, the slopes of the lines marked I in Figs. 1, 2 and 3 for pure ethyl lactate are quite different from the curves marked II, which are for the corresponding reaction mixtures containing triethylamine.

The rate of hydrogenation increased rather rapidly with temperature (Fig. 1) but the increase

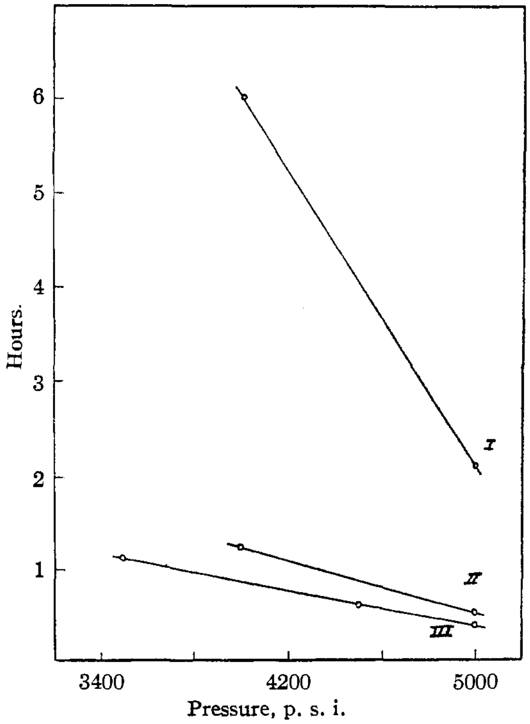

Fig. 2.—Effect of pressure of hydrogen on the hydrogenation of esters at 100° with 15 g. of W-6 Raney nickel in 35 ml. of ethanol: I, 10 g. of ethyl lactate; II, 10 g. of ethyl lactate and 1.0 ml. of triethylamine; III, 10 g. of ethyl piperidinoacetate.

---

[1] Monsanto Chemical Co. Fellow in 1946 and 1947.

[2] Adkins and Billica, THIS JOURNAL, 70, 3121 (1948).

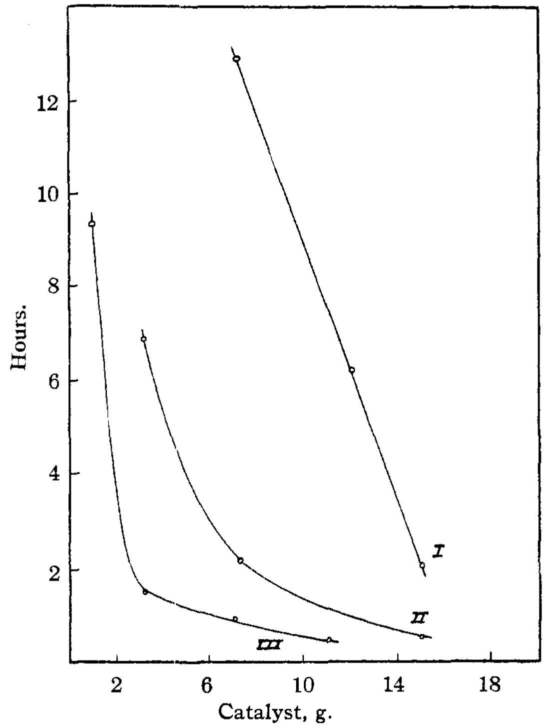

Fig. 3.—Effect at 100° of amount of catalyst on the hydrogenation of esters at 5000 p. s. i. in 35 ml. of ethanol: I, 10 g. of ethyl lactate; II, 10 g. of ethyl lactate and 1.0 ml. of triethylamine; III, 10 g. of ethyl piperidinoacetate.

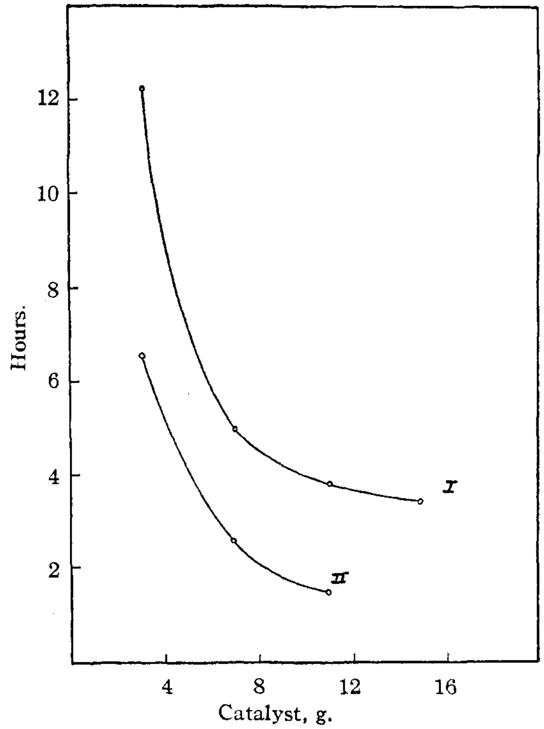

Fig. 4.—Effect at 50° of amount of catalyst on the hydrogenation of esters at 5000 p. s. i. in 35 ml. of ethanol: I, 10 g. of ethyl lactate and 1.0 ml. of triethylamine; II, 10 g. of ethyl piperidinoacetate.

was only about 12-fold at 100° as compared with 25°, or 4-fold as compared with 50°. The effect of increase in pressure was quite marked, for example, the rate doubled with an increase from 4000 to 5000 p.s.i. In contrast with these results it may be noted that the rate of hydrogenation of ethyl acetoacetate with a little triethylamine at 25° was not proportionally affected, by a change in pressure from 25 to 1000 to 4000 p.s.i., as the time of hydrogenation only decreased from thirty-four to twenty to ten minutes.

The ratio of catalyst to ester is perhaps the most critical factor in hydrogenating α-amino and α-hydroxy esters over Raney nickel. Even with the most active catalysts it was impractical to carry out this type of hydrogenation using the conventional 1 to 5% as much catalyst as compound to be hydrogenated. Even with 10% as much catalyst as ester the reaction was slow with ethyl piperidinoacetate and impractical with ethyl lactate even at 100°. With 70% as much catalyst as compound the hydrogenation was more rapid at 50° than with 20 to 30% catalyst at 100°. The really rapid reactions were obtained when the amount of catalyst was equal to or greater than the amount of compound hydrogenated.

Activity of catalyst, purity of reactants, temperature of reaction, pressure of hydrogen, and ratio of catalyst to hydrogen acceptor are interdependent variables, so that, within certain limits, deficiency in one factor may be compensated for by an increase in one or more of the others. However, it is unwise to attempt to supplement marked deficiencies in other factors by excesses in temperature and duration of reaction. This is particularly true in the use of the W-3 to W-7 Raney nickel for these catalysts[3,4] may cause a rather violent reaction at temperatures above about 100°, when in alcohol under pressures of the order of 5000 p.s.i. of hydrogen.

The W-6 Raney nickel catalyst used in these studies is alkaline in reaction, as in fact are all Raney nickel catalysts. If the W-6 catalyst is shaken with distilled water, the water will then show, with a glass electrode, a *p*H of 9 ± 0.3. The less alkaline catalysts are less active; *e.g.*, in one comparison the time of hydrogenation of ethyl lactate was five and one-half hours for the standard catalyst, seven and one-half hours for a double washed catalyst, ten to eleven hours when 0.5 g. of acetic acid or carbon dioxide was added to the reaction mixture and twenty-eight hours for a catalyst washed with water saturated with carbon dioxide.

The addition of a small amount of triethylamine to ethyl lactate decreased the time required for the hydrogenation of the ester from five and one-half to two hours. In fact the W-6 Raney nickel prepared and used under triethylamine was

---

(3) Adkins and Pavlic, THIS JOURNAL, **69**, 3039 (1947).

(4) Adkins and Billica, *ibid.*, **70**, 695 (1948). Please note well the warning on p. 697.

slightly more active against ethyl lactate than when prepared under ethanol without the addition of any amine. The effectiveness of triethylamine in increasing the rate of hydrogenation of ethyl lactate is brought out by a comparison of the curves marked I and II in Figs. 1, 2 and 3.

The addition of triethylamine is also very effective in increasing the rate of hydrogenation of ketones and aldehydes.[5] For example, the hydrogenation of acetone required seventy-two minutes in water, thirty-five minutes in alcohol, eighteen minutes in alcohol containing 2% triethylamine and eight minutes in triethylamine free of ethanol. The length of the intervals required for the hydrogenation of benzophenone (six and fifteen minutes), *n*-hexaldehyde (sixty and one hundred and thirty-nine minutes), benzaldehyde (twenty-five and sixty minutes), and acetophenone (fifteen and twenty-eight minutes) were about one-half as long when triethylamine was added to the reaction mixture as when the hydrogenation was made in ethanol. The hydrogenations referred to above in this paragraph were all made at 25–30° under a pressure of about 4000 p.s.i. of hydrogen with 10 g. of compound and 2 g. of W-6 Raney nickel except in the case of acetone where 10 g. of the catalyst was used.

In contrast with the beneficial effect of triethylamine on the hydrogenation of aldehydes, ketones and α-keto- and hydroxy esters, is its retarding effect upon the hydrogenation of a benzenoid nucleus. For example, 6.1 g. of 2-phenylethanol in ethanol was completely converted within four and one-half hours to 2-cyclohexylethanol under 5000 p.s.i. of hydrogen at 50° over 10 g. of W-6 Raney nickel. The length of the hydrogenation was increased to five and one-half hours when the reaction mixture contained 2% triethylamine, to nine hours when 15% triethylamine was used and to twenty hours in pure triethylamine. As might be expected the addition of triethylamine to an amino ester was without effect.

The general trends and conclusions drawn from the data summarized in Figs. 1 to 4 inclusive, have been substantiated by other less extensive and systematic studies. For example, 1-amino-1-carbethoxycyclohexane was completely hydrogenated in forty-five minutes over the W-5 Raney nickel at 100° while six and one-half hours was required at 50°. 5-Carbethoxy-2-pyrrolidone over the W-6 Raney nickel was hydrogenated after thirty hours to the extent of 72%, while the reaction was practically complete after fourteen hours at 75° or seven hours at 100°. An increase in pressure from 3000 to 5000 p.s.i. increased the hydrogenation of the same ester over the W-5 catalyst from 72% in seventy hours to 95% in thirty hours. An increase in the amount of catalyst from 7 to 11 to 15 g. of W-5 catalyst with 10 g. of 5-carbethoxy-2-pyrrolidone decreased the time for complete hydrogenation from twenty-two to fourteen to seven hours.

The procedures for the preparation of catalysts W-5 and W-6 differ in that in the washing of W-6 the catalyst wash is kept under a pressure of hydrogen about 0.5 above that of the atmosphere. The W-5 catalyst was prepared by a procedure differing little from that used by Pavlic[3] for the W-4 catalyst. No precise or extensive comparisons of these catalysts have been made as they were the result of the evolution of a procedure. In one comparison ethyl piperidinoacetate was hydrogenated in 1.7 hours over W-6 while 3.9 hours was required with W-5. Ethyl α-amino-α-methyl-isocaproate required 0.8 hour with W-6 and 3.5 hours with W-5. The hydrogenations of ethyl lactate and diethyl tartrate went about 20% faster over W-6 than over W-5. With diethyl malate and ethyl mandelate the time of the hydrogenations were reduced from 48 to 14 and from 5 to 1.25 hours, respectively, by using W-6 instead of W-5. These and other comparisons of a less quantitative nature indicate the W-6 catalyst to be significantly more effective than the W-5 or W-4 catalysts for many reactions.

Summary

Some of the effects of variation in ratio of catalyst, pressure of hydrogen, temperature and alkalinity of reaction medium, upon the rate of hydrogenation of α-amino and α-hydroxy esters and of aldehydes and ketones over Raney nickel catalysts are reported.

MADISON, WISCONSIN RECEIVED FEBRUARY 17, 1948

---

[5] The beneficial effect of a little sodium hydroxide upon the hydrogenation of ketones was noted by Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935).