

ON THE CHEMISTRY OF METAL HYDRIDES. V.*

THE KINETICS OF THE FORMATION OF SODIUM HYDRIDE

V. PROCHÁZKA and M. NEDVĚD

*Institute of Inorganic Syntheses,
Czechoslovak Academy of Sciences, 250 68 Prague - Řež*

Received March 31st, 1972

An apparatus has been constructed for following the reaction of a batch of a molten metal with gases under constant pressure and temperature and under stirring. The apparatus was used to follow the rate of the reaction of sodium with hydrogen, $\text{Na} + \frac{1}{2} \text{H}_2 \rightarrow \text{NaH}$, at elevated temperatures and pressures, in the absence and in the presence of carbon monoxide. The region of conditions has been delimited under which the effect of mass transfer is eliminated. The courses of conversion in relation to time have been found different for the two types of reaction. The dependence of the rate constant on temperature and pressure for the reaction proceeding in the presence of carbon monoxide is described by semiempirical equations. The empirical relation for the reaction of pure hydrogen applies only to the straight-line part of the course of conversion.

The most feasible way of preparing sodium hydride is direct reaction of molten sodium with hydrogen under an elevated temperature and pressure. However, the product is often sintered and has a small specific surface. With an admixture of carbon monoxide in the hydrogen employed for the reaction the formed sodium hydride is a powder with a large specific surface¹⁻⁸, there being no differences in structure, chemical composition and appearance of particles between the powder form and the sintered form of the product. The specific surface is very different with the two forms, a few cm^2/g with the former and several m^2/g with the latter.

In order to ascertain whether carbon monoxide produces an active complex, or gives rise to a substance affecting the interfacial interactions (emulsifier), or to a catalyst we have investigated the rate of the formation of sodium hydride in the presence and absence of carbon monoxide. Our next communication will deal with the mechanism of action of this admixture.

EXPERIMENTAL

Chemicals. Technical-grade sodium, freed from the corroded surface and kerosene, was employed in all experiments; this sodium proved quite satisfactory since the reaction rate was the same as in the use of sodium that had been remolten and kept in an ampoule, or distilled. The hydrogen was of electrolytic origin; its purity conformed to the Czechoslovak norm (ČSN). Earlier experiments were carried out with technical-grade hydrogen, containing non-defined

* Part IV: This Journal 34, 813 (1969).

residual concentrations of carbon monoxide, carbon dioxide, nitrogen, methane and traces of ammonia and water. The quality of carbon monoxide complied with the Czechoslovak norm (ČSN); its concentration was 98%, the rest being made up by nitrogen and methane.

Apparatus (Fig. 1). The reaction of hydrogen with molten sodium proceeded at elevated temperatures and pressures in a rotating autoclave with inserted balls, ensuring efficient stirring. One hole in the lid of the autoclave was for the piping with a manometer and outlet valve, another hole, in the centre of the lid, was for the sensor of a thermocouple. The temperature in the autoclave could be read continuously and accurately since the mass of the sensor was negligible as against that of the autoclave, so that its temperature adaptability was very prompt. The pressure was read at intervals on stopping the rotation of the autoclave. The autoclave rotated horizontally in an oven, heated with a gas flame. The temperature was controlled pneuma-

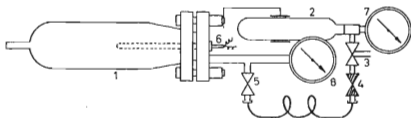


FIG. 1

The Apparatus

1 Autoclave, 2 pressure bottle, 3 valve, 4 pressure regulator, 5 autoclave valve, 6 thermocouple iron-constantan, 7 autoclave manometer, 8 pressure bottle manometer.

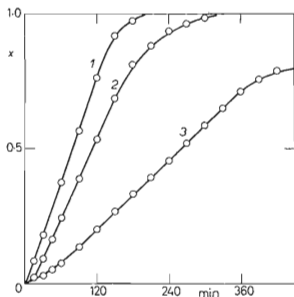


FIG. 2

Reaction Courses at a Pressure of 24 atm
in the Absence of CO

1 357°C, 2 300°C, 3 260°C.

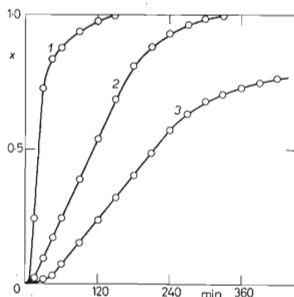


FIG. 3

Reaction Courses at 300°C in the Absence
of CO

1 49 atm, 2 24 atm, 3 14 atm.

tically with an accuracy of $\pm 0.5^\circ\text{C}$. The pressure in the autoclave was kept constant with the aid of a pressure regulator, fixed to a stock pressure-bottle. Hydrogen was brought in from the pressure regulator through a capillary and the piping on the lid of the autoclave. The pressure-bottle was clamped in a holder, fixed to the lid with bolts.

Procedure. The autoclave was charged with sodium and the stirring balls and evacuated. The pressure bottle with hydrogen was inserted into the holder, and the rotating system was brought to the selected temperature. When this temperature had been attained the rotation was stopped and hydrogen was introduced *via* the pressure regulator up to a chosen pressure. This pressure was checked on the manometer of the autoclave M_1 . The rotation was then resumed and the reaction started. Its course was followed by reading, on manometer M_2 , the pressure decrease of hydrogen in the bottle. In the experiments conducted in the presence of carbon monoxide the pressure bottle first contained 10% (v/v) CO in H_2 . When the autoclave had attained a given temperature its rotation was stopped and the gaseous mixture was introduced in a quantity corresponding to 1.5% of the amount of hydrogen needed for the complete reaction. The remaining carbon monoxide was then let out from the stock vessel, which was then replenished with pure hydrogen to a selected pressure. The rotation of the autoclave was resumed and the reaction was followed as described above.

Efficiency of stirring. The reaction of hydrogen with sodium is a heterogeneous process, giving rise to a third, solid phase, *viz.* sodium hydride. To study the kinetics of such a reaction it was necessary to eliminate the effect of mass transport on the reaction rate. Preliminary experiments were conducted under the conditions employed in the manufacture of sodium hydride: 400 atm, 300°C , 125 rev./min. Two experiments with pure hydrogen, one in the absence of stirring balls and the other with 6 balls in the autoclave, showed that the stirring was an important factor. To eliminate the effect of stirring a series of experiments was carried out at the same temperature, pressure, revolving speed of the autoclave and quality of sodium (310°C , 23 atm, 125 rev./min, 100 g of Na), but with different numbers of stirring balls, from 3 to 30. The results of the reactions, in the absence or presence of CO, were no longer different if the number of stirring balls was 20 or higher at a revolving speed of at least 10 rev./min. These data delineate the region of mechanical conditions where the reaction was no longer dependent on stirring, *i.e.* the region where the transport of mass did not affect the reaction rate.

RESULTS AND DISCUSSION

The reaction was followed by measuring the decrease in pressure of the hydrogen in the stock vessel. Employing the compressibility factor, the consumption of hydrogen was calculated in relation to time. As the system was heterogeneous it was impossible to express the reaction rate as a change of concentration in relation to time. We evaluated the degree of conversion as a function of time. The degree of conversion, x , is here defined by the ratio of the number of gramatoms of the reacted sodium to the number of gramatoms originally present. The reaction rate is defined as $r = dx/dt$.

Hydrogenation in the absence of carbon monoxide was carried out at a pressure of 24 atm and temperatures 260, 300 and 370°C , and at pressures 14 and 49 atm and 300°C (Figs 2 and 3). The plot of conversion *vs* time reveals that the reaction proceeds in 3 stages. The first has a small reaction rate, depending on the degree

of conversion. The second is the most extensive one and has a higher, constant rate. In the third stage the drop of the reaction rate takes an exponential course. The constant reaction rate of the second, extensive stage can be described by the equation

$$r = kX_{\text{Na}}^{\alpha} P_{\text{H}_2}^{\beta} \quad (1)$$

Since the pressure of hydrogen in the reaction space was constant, the quantity $P_{\text{H}_2}^{\beta}$ can be included in the constant, so that

$$r = k'X_{\text{Na}}^{\alpha} \quad (2)$$

As in the considered (linear) range the reaction rate is constant the reaction is formally of zero order with respect to sodium. The calculated rate constants for the linear parts of hydrogenation are listed in Table I. The effective energy of the reaction for a pressure of 23 atm was calculated from the Arrhenius equation as 13 kcal/mol. The value of the pre-exponential factor was 425. The dependence of the rate constant on pressure can be expressed by an empirical formula $k [\text{min}^{-1}] = 5.8310^{-4} P_{\text{H}_2}^{1.02}$ (P in atm). The exponent 1.02 was obtained by the least-square method. In view of the experimental error the exponent can be set equal to 1, so that

$$r = kP_{\text{H}_2} \quad (3)$$

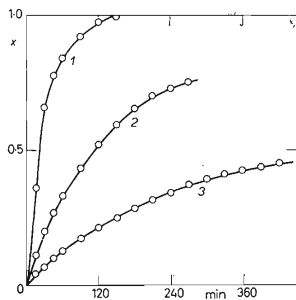


FIG. 4
Reaction Courses at 300°C in the Presence of CO
1 49 atm, 2 24 atm, 3 14 atm.

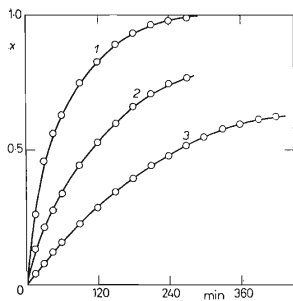


FIG. 5
Reaction Courses at a Pressure of 24 atm in the Presence of CO
1 375°C, 2 300°C, 3 260°C.

TABLE I
Rate Constants for the Linear Part of the Reaction in the Absence of CO

atm	°C	$k \cdot 10^2 \text{ min}^{-1}$	at
49	300	0.947	2.6
24	300	0.446	1.13
14	300	0.208	0.39
24	375	1.68	10.4
24	260	0.272	0.25

Hydrogenation in the presence of carbon monoxide was conducted at a pressure of 24 atm and temperatures 260, 300 and 375°C, and at pressures 14 and 49 atm at 300°C (Figs 4 and 5). The dependence of the degree of conversion upon time is clearly an exponential function. The reaction rate monotonously decreases as the reaction advances. The integral method has shown that the reaction is formally of second order with respect to sodium (the term reaction should be understood as the sum of the individual processes producing the powder of sodium hydride). The rate constants are given in Table I. The effective activation energy was calculated from the Arrhenius equation (22 kcal/mol). The exponential pressure for a pressure of 24 atm was $2.65 \cdot 10^6$. The rate constant in relation to pressure is $k [\text{min}^{-1}] = 0.000324P_{\text{H}_2}^{1.13}$. In view of the experimental error the exponent in this equation can also be regarded as approximately 1. It is seen that the presence of carbon monoxide affects the kinetics of the reaction of hydrogen with sodium. A precise physico-chemical interpretation of the results cannot as yet be advanced. This will be the subject of our subsequent communication, which will substantiate chemically the mechanisms propounded.

REFERENCES

1. Landa S., Petrů F., Vít J., Procházka V., Mostecký J.: Czechoslov. Pat. 86 722.
2. Landa S., Petrů F., Vít J., Procházka V., Mostecký J.: Sborník prací Vysoké školy chemicko-technologické, Prague 1957, 495.
3. Landa S., Petrů F., Vít J., Procházka V., Mostecký J.: Chem. listy 52, 1357 (1958).
4. Procházka V.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1965.
5. Landa S., Lébl B., Mostecký J., Procházka V., Stuchlík J., Vít J.: Czechoslov. Pat. Appl. 2267, — 67 (1967).
6. Vít J., Procházka V., Stuchlík J., Karel M.: Unpublished results.
7. Macek J., Tančev A.: Unpublished results.
8. Ullrych J.: Unpublished results.

Translated by J. Salák.