

KINETIC MODEL FOR THE HYDROGENATION OF SODIUM TO SODIUM HYDRIDE

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A kinetic model is proposed for the hydrogenation of sodium. The experimental data were correlated in the temperature range 270–340°C and at hydrogen pressures of 5–40 atm. Rate constants of this reaction were calculated and its activation energy was determined as 12.97 kcal/mol.

The simplest method of production of sodium hydride is its direct synthesis from elements at increased pressure and temperature. The related problems have been dealt with in detail in previous works¹⁻⁴. This work is aimed at elucidating the kinetics of this reaction performed in the absence of substances affecting the magnitude of the specific surface of resulting sodium hydride (carbon monoxide, sodium isobutylate, etc.)²⁻⁵, that means for the case if a sintered product results. The measurements were made at the hydrogen partial pressure of 5–40 atm and temperatures of 270–340°C.

EXPERIMENTAL

Processing. Measurements of the kinetics of the hydrogenation of melted sodium were performed in a rotating autoclave adjusted for experiments at constant pressure and temperature. The apparatus has been described in detail in the literature³. The temperature in the reaction space was maintained with an accuracy better than 1.5°C. For measuring the hydrogen pressure, an apparatus for inductive determination of pressure was used which made it possible to measure the pressure with an accuracy better than 0.2% of the total value; the temperature was measured with a Fe-Co thermocouple certified at the standard melting points of Sn and Zn. Purified sodium together with agitating bodies (6 steel spheres, 19 mm D.) was placed into the autoclave (100 mm D.), the rotating autoclave was evacuated (125 rev/min) and heated to the required temperature. Then hydrogen from a reservoir was fed into the autoclave reaction space through a pressure control valve which served simultaneously for maintaining a constant pressure in the reaction space. Decrease in the hydrogen pressure in the reservoir during the reaction was proportional to the amount of resulting NaH.

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Kinetic Model for the Hydrogenation of Sodium to Sodium Hydride

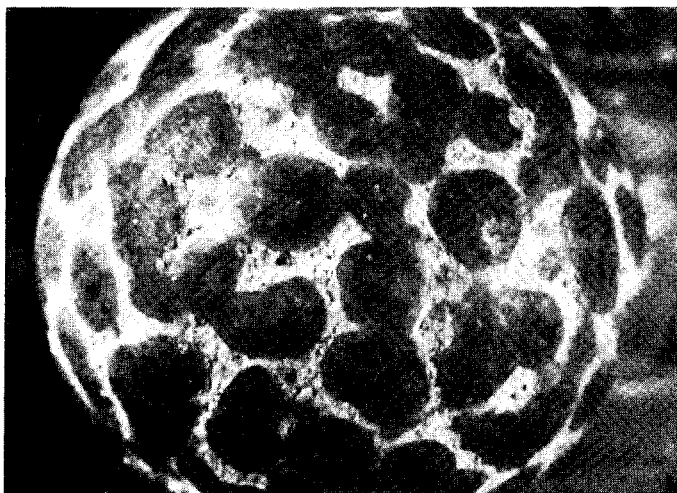


FIG. 1
Agitation Body Covered by Sodium Hydride

Materials used. Pure sodium (99.97% Na), a product of Fluka, was washed in hexane and dried in flowing dry nitrogen before use. Electrolytic hydrogen from pressure cylinders was employed after subsequent removal of oxygen on a Pd catalyst and water by freezing out at -80°C and drying on a nalsit 5 A molecular sieve. The content of oxygen or water in hydrogen was lower than 2 or 15 p.p.m, resp.

Analytical. The chemical composition of the product (content of sodium hydride and metallic sodium) was determined by measuring the volume of hydrogen evolved during the hydrolysis of the product and by titration of resulting sodium hydroxide. The method is described in detail in the literature⁶.

RESULTS AND DISCUSSION

At the given conditions, the sodium hydrogenation yields a sintered substance sticking firmly to the autoclave wall and to agitating bodies. This product contains 95–97% NaH, the rest is mainly metallic sodium; the product further contains small amounts of NaOH and Na_2O (1 wt.%). It is known from the literature⁷ that in the Na—NaH— H_2 system at temperatures below the melting point of NaH, the sodium liquid phase saturated with NaH is in equilibrium with a nonstoichiometric sodium hydride solid phase. These phases contain 0.04 and 98% NaH at the equilibrium hydrogen pressure and 300°C . It may be therefore assumed that the reaction product is a nonstoichiometric sodium hydride of the composition $\text{NaH}_{0.98}$. The further hydrogenation of this phase — after disappearance of the liquid phase — is controlled by the diffusion of hydrogen through a layer of this nonstoichiometric hydride; this diffusion is very slow^{8–12} and at our experimental conditions could not be practically measured at all.

The surface of this product (sintered sodium hydride), which developed on the autoclave wall and agitating bodies, is depicted on Fig. 1. It is obvious that solid sodium hydride grows from nucleation centres until it gradually fills up the whole space. Next we will assume that mass transfer from liquid sodium to the surface of the solid phase is the slowest reaction step during the formation of solid sodium hydride. The coefficient of mass transfer to the sphere surface in a stationary medium is inversely proportional to the sphere radius, whereas it does not depend on its radius if the sphere is bypassed by turbulent flow.

We have employed an empirical equation for the description of the growth rate of the solid phase in the form of hemispherical particles on the autoclave wall

$$dr/dt = k + D_{\text{ef}}/r . \quad (1)$$

This relation passes to relation (2) for small particles or to relation (3) for large particles:

$$dr/dt \approx D_{\text{ef}}/r , \quad (2)$$

$$dr/dt \approx k . \quad (3)$$

The volume of individual mutually overlapping nuclei of radius r is then given by Eqs (4)–(6) provided that centres of growing NaH hemispheres are regularly distributed on the autoclave wall and separated by distance d .

$$V_i = \frac{2}{3}\pi r^3, \quad \text{for } r \leq \frac{d}{2} \quad (4)$$

$$V_i = \frac{2}{3}\pi r^3 - 4V_1, \quad \text{for } \frac{d}{2} < r \leq d \frac{\sqrt{2}}{2} \quad (5)$$

$$V_i = \frac{2}{3}\pi r^3 - 2V_1 - 2V_2, \quad \text{for } r > d \frac{\sqrt{2}}{2} \quad (6)$$

$$V_1 = \frac{1}{8}\pi \left(r - \frac{d}{2}\right)^2 \left(2r + \frac{d}{2}\right). \quad (7)$$

The volume of body V_2 was calculated by numerical integration according to Simpson's formula. The shapes of bodies V_1 , V_2 and growing nuclei V_i are depicted on Figs 2 and 3. The total volume of resulting NaH is then given by Eq. (8)

$$V = AV_i/d^2. \quad (8)$$

The distance between reacting centres was determined experimentally as 0.2 cm by evaluating snapshots of the surface of sintered NaH (Fig. 1*). It is obvious that the total reaction area decreases as the liquid phase vanishes from the reacting mixture. Eq. (1) must be therefore written in the form

$$dr/dt = (k + D_{\text{ef}}/r) c_{\text{Na}}, \quad (9)$$

$$r = \int_0^t (k + D_{\text{ef}}/r) c_{\text{Na}} dt. \quad (10)$$

Factor c_{Na} is defined by Eqs (11) and (12):

$$c_{\text{Na}} = 1 \quad \text{for } (n_{\text{Na}} - a_{\text{Na}})/P > 0.002 \text{ mol/cm}^2, \quad (11)$$

$$c_{\text{Na}} = (5 \cdot 10^2/P) (n_{\text{Na}} - a_{\text{Na}}) \quad \text{for } (n_{\text{Na}} - a_{\text{Na}})/P \leq 0.002 \text{ mol/cm}^2. \quad (12)$$

It was found out experimentally that as long as the total amount of sodium per unit surface of NaH exceeds 2 mmol/cm², the reaction rate is independent of the amount

* See insert facing p. 3766.

of sodium which then covers the entire reaction surface. The degree of conversion of Na is given by Eq. (13):

$$x = V/V_m n_{\text{Na}} \quad (13)$$

By numerical solution of Eqs (4)–(6) and (10)–(13) on a GIER computer, the reaction degree of sodium was then calculated as a continuous function of time. Values of parameters k and D_{ef} were determined by minimizing the value of integral (14):

$$I = \int_0^n (x_{\text{te}} - x_{\text{tc}})^2 dt \quad (14)$$

Standard deviation σ was calculated by Eq. (15):

$$\sigma = \sqrt{[\sum(x_{\text{te}} - x_{\text{tc}})^2 / (n - 1)]} \quad (15)$$

The values of standard deviations of the experimental values from the calculated reaction course are given in Tables I and II. According to a statistical analysis, reaction courses which differ by $0.19 \cdot 10^{-6}$ mol/cm²s in their values of k may be distinguished with a 95% probability.

Time dependences of the reaction degree at equal reaction conditions and different amounts of sodium are plotted on Fig. 4 (Table I); it is obvious that the reaction proceeds more slowly at higher amounts of sodium used. Therefrom it is evident that the dependence of the reaction course on the reaction conditions cannot be expressed by a function of the reaction degree as it is usual for solid phase heterogeneous reactions. On the other hand, the calculations of the reaction rate according to Eqs (4)–(6) and (10)–(13) yielded practically identical values for the rate constant (Table I). The computed value of D_{ef} is $6 \cdot 10^{-5}$ mol/cm s and it should correspond to the

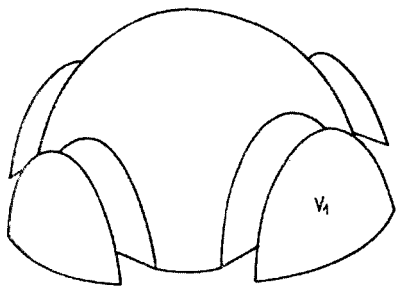


FIG. 2

Growing NaH Centres for $d/2 < r \leq d\sqrt{2}/2$

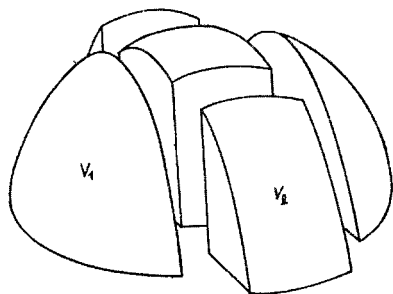


FIG. 3

Growing NaH Centres for $r > d\sqrt{2}/2$

diffusivity of NaH in sodium at the given temperature. As this quantity has not been measured so far, it cannot be even checked whether its order is of correct magnitude.

Reaction courses of the sodium hydrogenation plotted on Figs 5 and 6 differ by addition of 15% of pulverized and preliminarily prepared sodium hydride into the reaction mixture — this reaction is depicted on Fig. 5. As it is obvious from the $x - t$ and $dx/dt - t$ dependences, this addition affects considerably the initial reaction stage, which is characterized by increase in the reaction rate. The addition of pulverized NaH results in achieving the maximal reaction rate at the beginning of the reaction. A substantial acceleration of the initial reaction stage, *i.e.* origination and growth of nuclei of the sodium hydride solid phase brought about by the addition of the reaction product, might be suggested as a possible explanation of this effect.

Time dependences of the reaction degree computed with minimal values of quantity I are plotted on Fig. 7. The syntheses were performed at equal pressures and sodium amounts and at different temperatures. Good agreement between our experimental data and theoretical model is evident from this figure.

TABLE I

Effect of the Amount of Sodium on the Kinetics of the Sodium Hydride Formation

Temperature °C	H ₂ , atm	Na, g	$k \cdot 10^6$ mol/cm ² s	σ %
294	39.7	50	3.029	3.94
300	40.0	100	3.095	6.16

TABLE II

Correlation of the Experimental Data and Calculation of the Rate Constants for the Sodium Hydrogenation

Temperature °C	H ₂ , atm	Na, g	$k \cdot 10^6$ mol/cm ² s	σ %
294.0	39.7	50	3.029	3.94
316.9	39.5	50	4.638	6.51
322.9	39.2	50	5.212	3.76
329.6	39.5	50	6.606	2.38
332.6	39.7	50	5.832	2.02
332.66	5.4	50	2.649	1.67
332.5	9.5	50	3.027	3.69

Table II contains results of calculations of the rate constants (quantity k from Eq. (11)) and deviations of the model employed calculated according to Eq. (15) from the experimental data. Within the reaction conditions, our model conforms well to the experimental reactions course.

The temperature dependence of rate constant k may be expressed by the Arrhenius equation. The computed value of the activation energy of 12.97 ± 1.65 kcal/mol is in the range of activation energies reported in the literature for sodium hydrogenations performed at intensive agitation (10–13 kcal/mol)^{3,13,14}. This is a substantially lower value than in the case of diffusion in the solid phase (e.g.¹¹ 23.3 kcal/mol).

The assumption that the reaction rate-determining step during the sodium hydrogenation is the formation of a nonstoichiometric product (permeation of NaH through the liquid–solid interface) and therefrom derived equations describe well the kinetics of the NaH formation. The idea known from the literature¹⁴ and stating that the reaction rate is determined by the area of liquid sodium which is in contact with the gaseous phase, can only hardly explain the existence of the region in which the reaction rate increases at the beginning of the reaction and which is moreover affected by addition of the reaction product. Although a final decision on the mechanism of any reaction cannot be based only on results of kinetic measurements, the

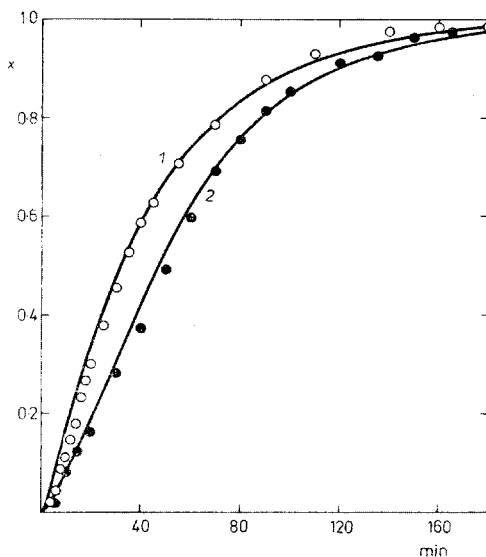


FIG. 4

Dependence of the Sodium Hydrogenation on the Amount of Sodium Employed
1 50 g, 2 100 g.

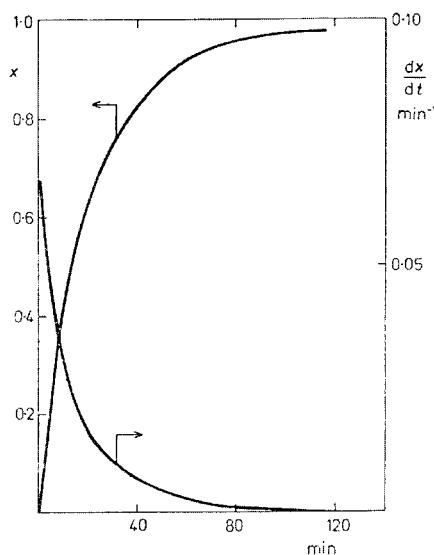


FIG. 5

Sodium Hydrogenation at 300°C and 40 atm H_2 with Addition of 15% NaH into the Reaction Mixture at the Beginning

equations employed offer a possibility to describe the reaction course mathematically and explain simultaneously the texture of the product.

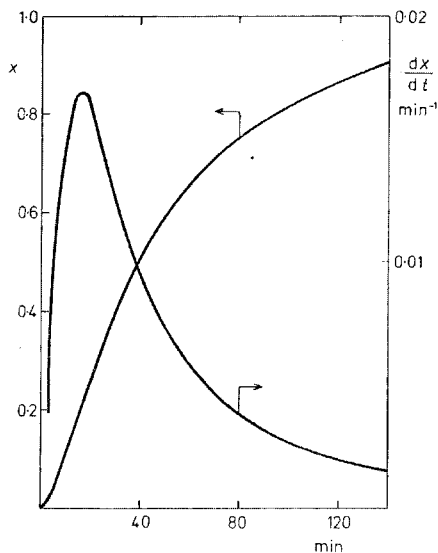


FIG. 6

Sodium Hydrogenation at 300°C and 40 atm H_2

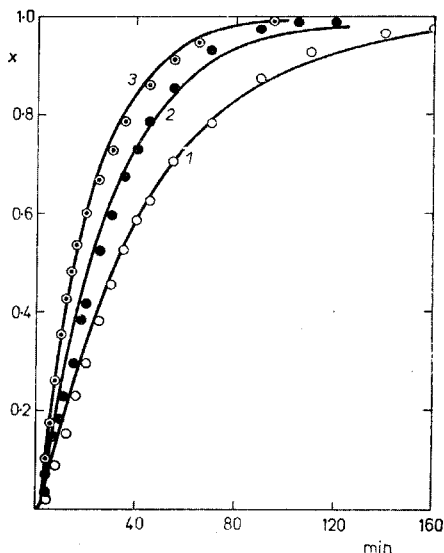


FIG. 7

Temperature Dependence of the Hydrogenation

1 294°C, 2 316°C, 3 322°C.

It is well-known that as long as sodium hydrogenation is performed in the apparatus used in our work and without agitating bodies, the reaction practically ceases to proceed at the reaction degree $x = 0.3$ and the reaction products are sodium beads covered by sodium hydride, a further hydrogenation of which is limited by slow diffusional processes in the sodium hydride layer on the surface of these beads. It is therefore obvious that the kinetics of hydrogenation of melted sodium is strongly affected by experimental arrangement and mechanical effects. We have described a model which is valid for an arrangement with intensive agitation but its validity at other conditions can be diminished considerably. Any description of this process should be based on a definition of the contact area between resulting sodium hydride and melted sodium saturated with dissolved NaH.

LIST OF SYMBOLS

a_{Na}	amount of reacted sodium (mol)
c_{Na}	parameter from Eq. (11)
d	distance between reacting centres of NaH (cm)
D_{ef}	parameter from Eq. (12) (mol/cm s)
I	quantity defined in Eq. (16)
k	rate constant of the reaction (mol/cm ² s)
P	area on which the sodium hydrogenation proceeds (cm ²)
n_{Na}	amount of sodium employed (mol)
r	radius of particles of resulting NaH (cm)
t	reaction time (s)
V_i	volume of individual NaH reacting centres (cm ³)
V_1, V_2	volume of bodies according to Figs 2 and 3 (cm ³)
V_m	molar volume of NaH (cm ³ /mol)
V	total volume of resulting NaH (cm ³)
x	reaction degree
x_{te}	experimentally found reaction degree in time t
x_{tc}	calculated reaction degree in time t
σ	standard deviation (Eq. (17))

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