

ON THE CHEMISTRY OF METAL HYDRIDES. VI.*
THE MECHANISM OF THE FORMATION
OF SODIUM HYDRIDE CATALYSED BY CARBON MONOXIDE

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The effect of concentration of carbon monoxide in hydrogen on the rate of the reaction of sodium with hydrogen has been investigated. The straight part of the conversion line for the reaction in the absence of CO was measured in relation to temperature and pressure, always in the region of independence on the mass transfer. The experimental data are interpreted in terms of two different mechanisms of the reaction, in the presence and in the absence of carbon monoxide. The marked dependence of the reaction rate on the amount of CO or sodium isobutylate suggests the idea that sodium isobutylate is the actual catalyst and carbon monoxide its precursor. The catalyst alters the mechanism of formation of sodium hydride, as well as the texture of this product. These conclusions are based on measuring the rate and course of the reaction of sodium with CO-free hydrogen in the presence of sodium isobutylate.

The preceding paper described the courses of the reaction of sodium with hydrogen in the absence and presence of carbon monoxide, which was found to alter the mechanism and rate of the reaction. The same effect has been brought about by products of the reaction of carbon monoxide with hydrogen and sodium, sodium isobutylate and sodium isobutyrate. The objective of this work was to elucidate the role of carbon monoxide and to reveal the mechanism differences between the catalysed and the non-catalysed reactions.

EXPERIMENTAL

The apparatus, chemicals and methods were described previously¹. X-ray analysis was performed in a Mikrometa apparatus with a copper anticathode.

The specific surface of sodium hydride was measured with Blain's apparatus modified by Mamula² for work in an inert atmosphere by Nelsen-Egertsen's method (the apparatus was made in the Research Institute of Electroceramics, Hradec Králové).

The chemical composition was investigated by measuring the volume of hydrogen released by hydrolysis of the hydride, and by titrating the sodium hydroxide formed by the hydrolysis. The calculations allow for the possible presence of metallic sodium in the product. Other analytical methods are described in the literature³.

* Part V: This Journal 38, 2845 (1973).

RESULTS

The non-catalysed reactions. We have demonstrated¹ that the reaction of hydrogen with sodium proceeds in three phases. The first is the induction period, when the reaction rate decreases. The length of the second phase increases with temperature, at the expense of the other two phases, and with pressure at the expense of the induction period. In a series of experiments, the purpose of which was to delineate the region of conditions where the mass transfer had no effect, it appeared that the first phase of the reaction depended on the efficiency of stirring much more than the other two. To account for this fact the following 4 experiments were carried out: keeping the rotation speed, pressure and temperature constant (120 rev./min, 100 g Na, 23 atm, 310°C), the number of stirring balls was varied (3, 6, 12 and 30). The experiments are illustrated in Fig. 1. Whereas the straight parts of the conversion lines have the same character (which demonstrates that the rate constant of the second phase was $0.0076 \text{ min}^{-1} \text{ atm}$) the first phase of the reaction was strongly dependent on stirring. With the increasing number of stirring balls the first phase was speeded up: in the use of 30 balls the induction period was very short, so that the reaction followed a linear course almost from its start. A similar dependence on stirring is observed in the absorption of gases in liquids. To corroborate our assumption that the first phase of the reaction is merely physical absorption of hydrogen in molten sodium we started the reaction at a given temperature and pressure and interrupted it at the end of the first phase (by stopping the rotation of the autoclave and turning off the heating). After the contents had cooled down the product was

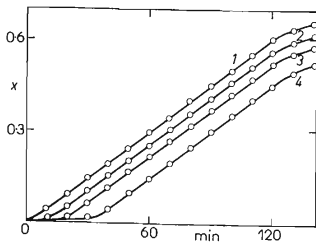


FIG. 1

The Dependence of the First Phase of a Non-catalysed Reaction on Stirring

Autoclave rotation 125 rev./min, 100 g of Na, 310°C, 23 atm; numbers of stirring balls: 1 30, 2 12, 3 6, 4 3.

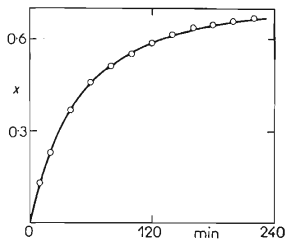


FIG. 2

The Course of a Reaction Catalysed by Sodium Isobutylate

290°C, 36 atm, CO-free hydrogen.

taken out of the autoclave and examined by X-ray analysis. In an analogous experiment the reaction was discontinued at the end of the second phase and the product was submitted to X-ray analysis. The diffraction patterns showed that the product of the first phase contained no sodium hydride. This demonstrates physical absorption of hydrogen in liquid sodium. In chemical analysis of the product the amount of the hydrolytic hydrogen exceeded that corresponding to pure sodium, which again proved the presence of hydrogen in the solidified sodium. The product of the second phase contained both sodium and sodium hydride, in practically equal amounts (diffraction pattern and chemical analysis). According to some authors⁴, sodium hydride and sodium are mutually soluble to a certain extent. This view and the results of our experiments allow us to arrive at the following conclusions: The first phase is physical absorption of hydrogen in sodium. The rate of this process increases with increasing temperature, pressure and efficiency of stirring. The second phase is the actual reaction of sodium with hydrogen, proceeding at a constant rate and producing sodium hydride. There co-exist two physical phases, *viz.* a liquid solution of sodium hydride in sodium and a solid solution of sodium in sodium hydride. As the reaction advances the mass ratio of the co-existing phases changes in favour of the latter, and the concentrations of sodium hydride increase in either. In the third stage of the reaction the liquid phase (the solution of sodium hydride in sodium) is no longer present and the solid solution of sodium in sodium hydride undergoes hydrogenation. The dissolving of the remaining sodium hydride in sodium may cause the decrease in reaction rate in the final stage.

The catalysed reaction. Four experiments were carried out under identical conditions (315°C, 26 atm, 120 rev./min, 100 g of Na, 6 stirring balls in a rotation autoclave), except that different concentrations of carbon monoxide in hydrogen were employed, *viz.* 0.25%, 0.75%, 1.5% and 3%. The reactions with 3% and 1.5% of CO in H₂ were formally of second order with respect to hydrogen. They only differed

TABLE I

Reaction Rate and Specific Surface of NaH in Relation to Concentration of CO at 315°C to 25 atm

CO in H ₂ , %	k , min ⁻¹ atm	Specific surface m ² /g
3	0.0075	4.9
1.5	0.019	3.1
0.75	0.090	1.8
0.25	other mechanism	order of cm ² /g

in rate; the reaction with 3% of CO un H₂ was slower. At the 0.75% concentration of CO the reaction was of second order with respect to sodium for the first 40 min, the rate constant being 0.09 min⁻¹, but later the plot of conversion *vs* time was linear, as in the non-catalysed reactions. With 0.25% of CO in H₂ the reaction proceeded as in the complete absence of the catalyst; the specific surface of the formed sodium hydride was immeasurably small. With the decreasing concentration of CO in hydrogen the specific surface of the product decreased. This dependence is well apparent from Table I: in the concentration range measured an increase in the content of CO slowed down the reaction and the specific surface of the reaction product was greater. The dependence of the reaction rate on the content of the catalyst indicates that the effect of carbon monoxide has a chemical nature. The reaction rate is a complex function of concentration of carbon monoxide, which under the given reaction conditions operates as precursor of the catalysts. We were unable to reveal the character of this function since the phase diagram for the system sodium—catalyst—hydrogen is not known.

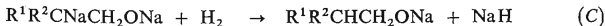
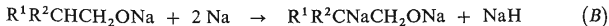
After the reaction of hydrogen containing 1.5% of CO the concentration of CO in the residual gas was 0.045 to 0.05%, so that over 97% of the carbon monoxide had been utilized for the formation of the catalyst. This catalyst is a reaction product of carbon monoxide with hydrogen and sodium, as was proved by measuring the reaction of sodium with CO-free hydrogen in the presence of sodium isobutylate (1.5% w/w). The course of the reaction is shown in Fig. 2 (100 g of Na, 6 stirring balls, 125 rev./min, 290°C, 36 atm). The reaction was again formally of second order with respect to sodium, the rate constant being 0.0099 min⁻¹. Unlike carbon monoxide, sodium isobutylate keeps its catalytic effect even in the presence of Raney nickel, which observation was described by Landa and coworkers⁵.

DISCUSSION

In the presence of the catalyst the process is more complex than the simple reaction



The facts that catalysts act chemically and that the individual reactions are of second order with respect to sodium and of first order to hydrogen support the reaction scheme propounded by Procházka⁶:



The reaction of the catalyst with sodium occurs first. By the action of hydrogen the catalyst is then regenerated and sodium hydride is formed. In our subsequent work we

will try to corroborate this mechanism chemically by deuteration and methylation of the postulated intermediate.

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