Chemistry

1965

SovietRxiv

Abstract

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Chemistry

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On the Reaction of Aqueous Solutions of Sodium Borohydride and Nickel Chloride

(Presented by Academician I. I. Chernyaev, July 3, 1964)

A. Stock had already noted that, in the reaction of alkaline solutions of boron hydrides, the so-called hypoborates, with nickel salts, black precipitates of a boride of composition Ni_2B are formed (^{1}). Precipitates of the same kind were subsequently obtained by a number of authors in the reaction of transition-metal salts with sodium borohydride. Schlesinger et al. (^{2}) confirmed for cobalt the composition of the boride Co_2B; Levy et al. (^{3}) showed that boride formation proceeds according to the equation

$$2Co^{2+} + 4BH_4^- + 6H_2O = Co_2B + 3HBO_2 + 12.5H_2.$$

In view of the fact that the precipitates obtained in the reaction of transition-metal salts with sodium borohydride are of practical importance both as catalysts for the decomposition of sodium borohydride and, to an even greater extent, as hydrogenation catalysts (^{4}), a large number of works have recently been devoted to the study of their composition and properties ($^{5-10}$). However, the question of the nature of these substances still remains insufficiently clear. The initially proposed assumption (^{1,2}) concerning the existence of borides is contradicted by the variable composition of these precipitates; the suggestion of a mechanical mixture of finely divided nickel and boron (^{9,10}) is not confirmed by the study of the ferromagnetic properties of the precipitates. The mechanism of formation and the individual stages of the reaction that determine the formation of the properties of boride catalysts remain unresolved.

We applied a method for studying complex reactions that consists in constructing composition–reaction-yield diagrams under continuous variation of the reacting substances (^{11}). The yield of the various reaction products in the solid, liquid, and gaseous phases, calculated with respect to both reagents, is plotted on a diagram as a function of the composition of the initial mixture. Such diagrams, as theoretical calculations based on the law of mass action and a number of experimental studies ($^{12-14}$) have shown, clearly indicate the direction of the principal reaction in the system and the occurrence of side reactions as the ratio of the initial components changes.

Fig. 1

Figure 1: Fig. 1

In this work, $0.1\,M$ aqueous solutions of chemically pure nickel chloride and ammonia-refined borohydride containing 99.5% $NaBH_4$ were used.

The reaction was carried out in an apparatus ensuring that the reaction, filtration, and washing of the solid phase were performed in a nitrogen atmosphere ([15]). The hydrogen evolved during the reaction was collected in a thermostatted gas burette. When a solution of nickel salt is added to a solution of sodium borohydride, a black precipitate forms and hydrogen is vigorously evolved; the temperature of the solution thereby rises by 5-6°.

After thorough washing successively with water, alcohol, and ether and drying in a stream of nitrogen, the solid precipitates were weighed and subjected to chemical analysis, as was the filtrate, for the content of nickel, boron, hydrogen, and chlorine.

The diagram of the dependence of hydrogen evolution on the ratio of the initial components (Fig. 1a) shows that only upon addition of small amounts of nickel chloride does the volume of evolved hydrogen approach the theoretical value. With an increase in the amount of nickel chloride added, the amount of hydrogen decreases and reaches a constant value, beginning from the ratio $NiCl_2 : NaBH_4 = 1 : 2$, amounting to 75% of the amount of hydrogen that could have been evolved upon complete hydrolysis of sodium borohydride in an acidic medium.

Fig. 1. Yield curves of the reaction products as a function of the ratio $NiCl_2 : NaBH_4$.
a—evolved hydrogen, in percent of the maximum possible; b, c—weight of the solid phase, referred to 1 g-mol of $NiCl_2$ and $NaBH_4$; g, d, e—Ni, B, and Cl transferred into the liquid phase

The weight of the precipitated solid sediment, referred to one mole of sodium borohydride (Fig. 1b), increases up to the ratio $NiCl_2 : NaBH_4 = 1 : 2$ and, with a further increase in this ratio, remains practically constant. The yield of solid precipitate per mole of nickel chloride reaches a maximum at the same ratio of the reacting components, $1 : 2$, and then begins to decrease.

Table 1

Composition of the solid phase as a function of change in the ratio $NiCl_2 : NaBH_4$

$NiCl_2 : NaBH_4$	Ni content in precipitate, g	B content in precipitate, g	Ni : B in precipitate
0.25	0.0821	0.0070	2.01
0.50	0.1383	0.0113	2.07
1.00	0.1454	0.017	1.67
2.00	0.1552	0.0135	2.13

Pyrophoric precipitates are completely decomposed by nitric acid, but when dissolved in hydrochloric acid (1 : 1) and sulfuric acid (1 : 4), only nickel passes into solution; part of the boron dissolves with difficulty even on heating in a mixture of hydrogen peroxide with sulfuric acid. At different ratios of the $NiCl_2$ and $NaBH_4$ taken, the ratio of nickel to boron in the precipitate is held fairly steadily at 2 : 1 (Table 1), while the sum of nickel and boron constitutes 96–98% of the weight of the entire precipitate.

Chemical analysis of the filtrates shows that, beginning with the ratio $NiCl_2 : NaBH_4 = 1 : 2$, all the nickel passes into the precipitate. Boron, however, introduced with sodium borohydride, is not completely bound in the precipitate; the greater part of it enters the filtrate: after the ratio $NiCl_2 : NaBH_4 = 1 : 2$, the boron content in the filtrate remains constant and amounts to about 67% of all the boron participating in the reaction.

Chlorine and sodium, according to chemical analysis, are entirely in the filtrate, and the curves of change in their concentrations are antibatic to one another.

When comparing the curves for the hydrogen yield (Fig. 1a), the amount of solid precipitate (Figs. 1b and c), and the content of boron and nickel in solution (Figs. 1d and e), one may note characteristic breaks in them at the point with the ratio of the initial components $NiCl_2 : NaBH_4 = 1 : 2$. With a further increase in this ratio, both the volume of evolved hydrogen and the amount of precipitate formed, as well as the boron concentration in the filtrate and, consequently, its weight amount in the precipitate, remain constant. As the ratio $NiCl_2 : NaBH_4$ increases from 0 to 0.5, the amount of evolved hydrogen decreases from 100 to 75% (calculated for all the hydride hydrogen of sodium borohydride); at the same time the amount of boron in the filtrate and the amount of precipitated sediment decrease.

All these regularities are in agreement with the proposed reaction according to the overall equation:

$$4NaBH_4 + 2NiCl_2 + 9H_2O \longrightarrow Ni_2B + 3H_3BO_3 + 4NaCl + 12.5H_2. \quad (1)$$

The nature of hydrogen evolution in the interval of the ratio $NiCl_2 : NaBH_4 = 0.5$ can be understood if one takes into account the catalytic action of the precipitates on the hydrolysis reaction according to the equation

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2. \qquad (2)$$

The results obtained reliably establish that the first stage of the reaction, expressed as a whole by equation (1), is the interaction

$$NiCl_2 + 2NaBH_4 \longrightarrow Ni(BH_4)_2 + 2NaCl. \qquad (3)$$

At the same time, an unquestionable conclusion from the analysis of both the solid precipitates and the filtrates is the assertion that only one quarter of the boron entering into reaction (3) is retained in the solid phase, and three quarters pass into solution. The composition of the solid phase corresponds to the ratio of the components in the compound Ni_2B—the most stable compound in the Ni—B system [16]. The most interesting questions—the nature of the intermediate stages on the path of conversion of the proposed compound $Ni(BH_4)_2$ into a precipitate with a ratio of components corresponding to the compound Ni_2B, as well as the chemical nature of this precipitate, which may be a mixture of metallic nickel and boron—apparently cannot be resolved within the framework of studying the reaction only in aqueous solutions.

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Received
2 VII 1964

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