

CATALYSTS OF THE REACTION OF SODIUM WITH HYDROGEN PRODUCING SODIUM HYDRIDE WITH A LARGE SPECIFIC SURFACE*

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Catalysts have been found for direct synthesis of sodium hydride from the elements, at an elevated temperature and pressure, giving rise to sodium hydride with a large specific surface (10^4 to 10^5 cm²/g). The general formulae of these catalysts are given and the applicability of the catalysts reported previously is discussed.

Attempts at finding good catalysts for the synthesis of sodium hydride have been given much effort. Reaction of liquid sodium with hydrogen at an elevated temperature and pressure is generally not quantitative, the product being a sintered, little reactive substance, contaminated with the unreacted sodium¹. As has been found², certain compounds added to sodium in an amount of about 1% (w/w) give rise to sodium hydride of a large specific surface and the course of the reaction agrees with stoichiometry. Landa and coworkers³ observed that this effect of some of these compounds is inhibited by an admixture of Raney nickel. Procházka reported⁴ that in the course of the hydrogenation some of the active compounds disappeared from the reaction mixture; careful analysis of the formed sodium hydride revealed the presence of stable active compounds, *viz* sodium isobutoxide and sodium isobutyrate.

The objective of this work was to determine the general formulae of compounds that catalyse the reaction of sodium with hydrogen, are stable under the conditions of the reaction and give rise to sodium hydride with a large specific surface.

The active compounds either produce catalysts under the conditions of the reaction or are stable catalysts themselves and remain chemically unchanged in the product. Compounds liberating carbon monoxide under the conditions of the reaction are very numerous. Landa and coworkers³ reported that the effect of carbon monoxide was suppressed by an addition of Raney nickel. We have found that the addition of Raney nickel to sodium does not interfere with the effect of the active compounds that are stable under the conditions of the reaction (catalysts). This observation showed us how to differentiate stable active admixtures from precursors. From the previous work³ it is known that sodium isobutoxide and sodium isobutyrate are stable under the conditions of the synthesis of sodium hydride and occasion the formation of sodium hydride having a large specific surface. Therefore, we have studied the effect of various organic compounds the molecules of which have a tertiary carbon atom, primary alkyl group or a carboxyl group.

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EXPERIMENTAL

Chemicals. Electrolytic hydrogen from a pressure bottle was employed. Sodium was a pure-grade Fluka chemical. Prior to use the oxidized surface was cut off, the metal was washed with hexane and dried in a jet of an inert gas. The investigated catalysts, of different origin, were distilled before use and checked for purity by measuring the refractive indices and by gas chromatography.

Procedure. Sodium hydride was synthesized in a 2.5-l rotary autoclave⁵. The temperature and pressure were maintained with a precision of $\pm 3^\circ\text{C}$ and ± 1 at. Under a jet of argon the autoclave was charged with sodium, six stirring steel balls (\varnothing 19 mm) and the catalyst to be investigated. The revolving autoclave was brought to the desired temperature, then hydrogen was introduced into the reaction space of the autoclave ($t = 300^\circ\text{C}$, $p = 42$ at) from the pressure bottle via a pressure-reducing valve. After the reaction had ended the autoclave was allowed to cool down to ambient temperature and sodium hydride was transferred under argon into a ground-glass bottle. The product was then investigated for its specific surface and analysed chemically.

Hydrogen, released by hydrolysis, was determined volumetrically and the formed sodium hydroxide was determined by titration⁶. The content of NaH in the product ranged between 90 and 96%.

The specific surface of sodium hydride was determined by the method of heat-induced desorption. Mangel's apparatus⁷ for determining the specific surface of a powder being employed. The mixture of nitrogen and hydrogen used for the determination contained 14% of N_2 .

RESULTS AND DISCUSSION

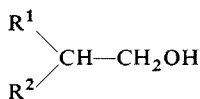
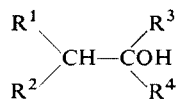
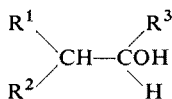
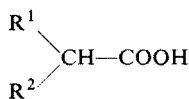
The reaction of carbon monoxide with sodium and hydrogen produced a number of compounds. Out of these, sodium isobutoxide and sodium isobutyrate catalysed the formation of sodium hydride with a large specific surface. The catalytic effect was not inhibited by Raney nickel, and under the reaction conditions (270–320°C, hydrogen pressure 1–100 at) these catalysts were stable. Sodium hydride was also synthesized using admixtures of compounds formed by the reaction of sodium hydride with carbon monoxide⁴ and/or in the presence of compounds reported^{8–16} to catalyse the reaction of sodium with hydrogen. The results show that some admixtures occasioning the formation of large-surface sodium hydride (pivalic acid, methyl and ethyl formates, methyl oxalate, abietic acid) are inhibited by Raney nickel, which catalytically removes carbon monoxide from the reaction mixture and gives rise to products having no effect on the synthesis of sodium hydride. By contrast, compounds capable of releasing carbon monoxide under the conditions of the synthesis (abietic acid) are not real catalysts. The other compounds have no effect. Some authors use technical mixtures in which carbon monoxide may be present (acetylene obtained by cracking natural gas)⁸; also recommended as catalysts are substances capable of protecting carbon monoxide from the catalytic conversion into inactive compounds (mercury)⁹. Our results are at variance with the view¹ that sodium hydride can only be prepared by hydrogenation of sodium finely dispersed in an inert medium (oil, hexane *etc.*).

Consequently, the only stable active compounds, isolated from the reaction product

of carbon monoxide and sodium hydride, are isobutyric acid and isobutyl alcohol, or their sodium salts.

Further we have studied the effects of alcohols and carboxylic acids on the synthesis of NaH. The results showed again that isobutyric acid and isobutyl alcohol were the only catalysts giving rise to sodium hydride with a large specific surface. In catalysts of this type (alcohols and carboxylic acids) the hydroxyl-binding carbon atom or the carboxyl group is adjacent to an isopropyl group. In view of this fact we also studied the effects of other alcohols and carboxylic acids on the synthesis of sodium hydride. This study has revealed that a prerequisite for a catalyst to effect the formation of sodium hydride with a large specific surface is the neighbourhood of a tertiary carbon upon the group COOH, CH₂OH, CHR¹OH or CR¹R²OH. Where the tertiary carbon was separated from one of these groups, *e.g.* by a methylene group (isopentyl alcohol), the compound had no effect. With the active compounds the specific surface of NaH ranged between 0.52 and 10.5 m²/g, the amount of a catalyst being 0.3–0.5 g/100 g Na.

On the basis of these findings we propound general formulae of the catalysts giving rise to sodium hydride with a large specific surface (formulae *I, II, III, IV*). The symbols R¹, R², R³ and R⁴ denote alkyl groups, possibly replaced by a cycloalkylidene radical (cyclohexanemethanol, 2-methyl-1-hexanol *etc.*).

*I**II**III**IV*

To verify the validity of our conclusions we synthesized sodium hydride with the use of a number of alcohols and carboxylic acids conforming to formulae *I* to *IV*, and with the use of some of their inactive isomers. The following series of catalysts were studied: R₂CH · COOH (R : CH₃, C₂H₅, n-C₃H₇, C₆H₅), R₂CH · CH₂OH (R : CH₃, C₂H₅, n-C₃H₇, C₆H₅), R(CH₃)CH · CH₂OH (R : CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, CH(CH₃)₂), (CH₃)₂CH · CHR · OH (R : CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, CH(CH₃)₂), (CH₃)₂CH · CR₂ · OH (R : CH₃).

All admixtures corresponding to formulae *I* to *IV* were effective, unless the substituents R¹ and R² were aromatic (diphenylethanol, 2,2-diphenylacetic acid, 2-phenylpropionic acid and 2-phenyl-1-propanol showed no effect). Also inactive were all isomers that were inconsistent with these formulae (*n*-alcohols *etc.*).

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