FORMATION OF MOLECULAR HYDROGEN FROM A PROTON AND THE HYDRIDE-MOBILE HYDROGEN OF A C–H BOND

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Abstract

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FORMATION OF MOLECULAR HYDROGEN FROM A PROTON AND THE HYDRIDE-MOBILE HYDROGEN OF A C–H BOND

The formation of molecular hydrogen from a proton and hydride-mobile hydrogen is well known for hydrides of alkali and alkaline-earth metals, and for boron, aluminum, and tin hydrides under the action of protonic acids. However, attempts to obtain hydrogen from a proton and hydrogen bonded to carbon have had little success, even in those cases where a carbonium ion is formed as a result of the reaction, i.e., where hydride ion is split off from carbon.

Nenitzescu and co-workers (*1*) succeeded in isolating small amounts of hydrogen (0.02–0.2%) when hydrocarbons were treated with protonated water of aluminum chloride.

It might have been expected that, under the action of a sufficiently strong acid on such a donor of hydride ions as cycloheptatriene, molecular hydrogen would be evolved. We observed that when cycloheptatriene is added to trifluoroacetic acid, heating occurs, a white precipitate and tropylium salt are formed, but hydrogen is not evolved. Analysis of the reaction product agrees with the supposition that hydrogen is consumed in the hydrogenation of the double bonds of cycloheptatriene or of its polymer. The possibility of hydrogenation of a double bond under the experimental conditions is also indicated by the fact that, when methylcyclohexene is added to the initial mixture, it is hydrogenated to methylcyclohexane.

Harmon and co-workers (*2*) showed that, under the action of boron tribromide on cycloheptatriene, tropylium tetrabromoborate is formed in good yield; however, the fate of the hydride ion split off from the cycloheptatriene molecule remained unknown.

When the product of the reaction of cycloheptatriene with BBr_3 was treated with water, we succeeded in isolating molecular hydrogen in a yield of 12%, calculated on the cycloheptatriene that had entered into the reaction. To increase the yield of hydrogen, the reaction was carried out in cyclohexane. The precipitate of tropylium salt was separated, and water was added to the filtrate. Hydrogen was formed in a yield of up to 40%.

The evolution of hydrogen indicates direct cleavage of hydride ion from cycloheptatriene and confirms Harmon' s proposal concerning disproportionation of the anion $[HBBr_3]^-$ according to the scheme:

$$\text{cycloheptatriene} + BBr_3 \longrightarrow \text{tropylium}^+ [BBr_3H]^-$$

$$\text{tropylium}^+ [BBr_3H]^- + BBr_3 \longrightarrow \text{tropylium}^+ [BBr_4]^- + BBr_2H$$

Hydrogen is formed in the reaction of BBr_2H with water

$$BBr_2H + 3HOH \rightarrow H_3BO_3 + 2HBr + H_2.$$

The role of BBr_3 consists in the transfer of the hydride ion from the cycloheptatriene molecule to the proton of water.

Experimental Part

Boron tribromide was prepared according to the procedure(3) and purified by double distillation under dry argon. B.p. 90–91°. Chromatographic analysis of cycloheptatriene, obtained by reduction of tropylium bromide with $LiAlH_4$, showed no impurities. Cyclohexane was distilled and stored over P_2O_5. All experiments were carried out in a chamber with dry argon. Hydrogen was determined chromatographically. The chromatograph was an KhT-63 with an EPP-17 recorder. Column—steel; internal diameter 4 mm; length 6 m; packing —5 Å molecular sieves; detector—G-20 katharometer. Carrier gas—nitrogen*.

1. **Reaction of cycloheptatriene with** CF_3COOH**.** To 5.40 g of CF_3COOH, 0.23 g of cycloheptatriene was added. The solution becomes turbid, and a precipitate forms. After 20 min the mixture was poured into water and the precipitate was filtered off. 0.16 g of a white substance was obtained. The filtrate was neutralized with soda and thoroughly extracted with ether. By precipitation with H_2PtCl_6, 0.185 g of tropylium chloroplatinate was obtained (25% of the theoretical amount). The white precipitate does not melt and decomposes above 350°. Analysis: C 82.8%; H 8.4%; F 5.8%, which corresponds to the formula $C_{69}H_{84}F_3O_2$. Considering the CF_3COOH elements as terminal groups, we obtain the formula $C_{67}H_{83}$ for the hydrocarbon chain. If the polymer consisted of cycloheptatriene molecules, then for 67 carbon atoms there would be 76.5 hydrogen atoms. Analysis of the substance shows that part of the double bonds in the hydrocarbon chain has been hydrogenated.
2. **Reaction of cycloheptatriene with** BBr_3**.** To 0.981 g of cycloheptatriene, 15 g of BBr_3 was added. A vigorous reaction occurs with heating, and a white precipitate forms, which darkens on storage. After one day the mixture was decomposed with water. The gas formed was passed

through alkali and collected in a gas burette. The increase in volume was 15 ml, calculated to normal conditions. After addition of water, the mixture was neutralized with soda, extracted with ether, and the tropylium content was determined by precipitation with H_2PtCl_6. 1.60 g of chloroplatinate precipitate was obtained. The hydrogen yield, calculated on the cycloheptatriene that entered into reaction, is 12%.

3. **Reaction of cycloheptatriene with** BBr_3 **in cyclohexane.** To a solution of 0.540 g of cycloheptatriene in 10 ml of cyclohexane, 3.75 g of BBr_3 in 10 ml of cyclohexane was added. A white precipitate formed, the amount of which slowly increased. After a week the precipitate was filtered off, washed with 3 × 10 ml of cyclohexane, and dried in vacuum. The yield of tropylium tetrabromoborate was 1.38 g (55.6%). Water was added to the filtrate, and the gas was collected in a burette, absorbing HBr with alkali. The increase in volume, calculated to normal conditions, was 26 ml. The hydrogen yield, calculated on the cycloheptatriene that entered into the reaction, was 35%. In another experiment the hydrogen yield was 40%.

As a result of the investigation it has been shown that molecular hydrogen can be obtained from a proton and the hydridically mobile hydrogen of cycloheptatriene if boron tribromide is used as the hydrogen carrier.

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* The gas analysis was carried out by R. V. Kudryavtsev. We take this opportunity to express our deep gratitude to him.

Note: Figure translations are in progress. See original paper for figures.

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