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CHEMISTRY OF BORANES. XXII.*

THE ACIDITY OF BORANES

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The acidity of boranes was already observed more than ten years ago¹ but all relative data are rather scant and often mutually contradictory²⁻⁹. The dependence of their acidity on the type of solvent is an interesting feature. While in aqueous ethanol decaborane is a strong monoacid^{1,11}, in ether it is ten times less acid than phenol^{8,9}. It is not known certainly under which conditions it can function as a diacid⁹ and it is not clear which of the possible tautomeric anions $B_{10}H_{13}^-$ and under which conditions they apply¹¹. In addition to the monoanion structure Lipscomb also proposed the structure of the unknown dianion $B_{10}H_{12}^{2-}$ (ref.¹¹) which was recently identified¹².

Still less clear is the situation in the case of borane $n-B_{18}H_{22}$ ¹³. The structure of its monoanion $B_{18}H_{21}^-$ was also proposed by Lipscomb¹¹. Later on the existence of dianion $B_{18}H_{20}^{2-}$ (ref.¹³) was also proved.

In order to classify the controversies around higher boranes and the functionality of their anions we investigated the behaviour of decaborane and octadecaborane in some solvents miscible with water potentiometrically.

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EXPERIMENTAL

Apparatus and Chemicals

The apparatus for potentiometric titration was composed of a compensation laboratory pH-meter PHK 1 (Development Workshops, Czechoslovak Academy of Sciences), a high-resistance glass electrode SEV A (Laboratorní potřeby), a calomel electrode saturated SFI (Forschungsinstitut Meinsberg bei Waldheim), and a temperature controlled titration vessel.

Solvents. 2-Methoxyethanol was refluxed with calcium oxide and distilled. Fraction boiling between 124–125°C was collected. Ethanol was absolutised by boiling with sodium and diethyl phthalate and distilled. Acetonitrile was dried over calcium hydride and distilled. The product was spectrally pure (IR).

Titration solutions. An aqueous solution of 0.05M tetramethylammonium hydroxide was prepared by filtration of a 0.05 molar solution of the corresponding iodide through a column of a strongly basic anion exchanger Dowex 2 (in OH^- cycle) kept under nitrogen. An aqueous solution of 0.05M sodium hydroxide was prepared in a similar manner. Freshly prepared solutions were checked for the presence of carbonates by titration with 0.05M-HCl. Interfering quantities of carbonates make them apparent by a distinct deformation of the titration curve. Titration solutions were introduced into burettes and kept with the air excluded.

Measurements

All measurements were carried out at 25°C. The apparatus was calibrated before each titration with a 0.05M potassium acid phthalate in water (pH 4.008 at 25°C). Occasionally the calibration

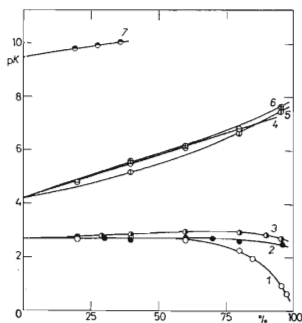


FIG. 1

Dependence of pK of Decaborane and Benzoic Acid in Organic Solvent-Water Systems on the Content of the Solvent

$\text{B}_{10}\text{H}_{14}$: 1 pK_1 in 2-methoxyethanol, 2 pK_1 in acetonitrile, 3 pK_1 in ethanol, 7 pK_{11} in acetonitrile; $\text{C}_6\text{H}_5\text{COOH}$: 4 pK in acetonitrile, 5 pK in 2-methoxyethanol, 6 pK in ethanol.

was controlled with a saturated solution of potassium acid tartrate (pH 3.57 at 25°C) and a phosphate buffer (pH 6.865 at 25°C). In order to decrease the sodium-ion error tetramethylammonium hydroxide was made use of in the majority of titrations. Only at a higher water content in the solvent (over 60%), when an insoluble tetramethylammonium salt was formed sodium hydroxide was used as titration agent. It was found that the course of the titration curve was identical in both cases. We did not apply the addition of neutral salts in order to secure a defined ionic strength, because from our spectral studies it follows that such salts can react competitively with decaborane.

Before each titration 10 ml of an approximately 0.005 molar solution of the investigated substance were measured, the pK value corresponded thus to the pH value after the consumption of 0.5 ml of the titration solution. The starting concentration of the solvents was chosen in such a way as to obtain the required concentration of the solvent after addition of 0.5 ml of the titration solution. For example, to attain a concentration of 80% of the solvent at a 50% neutralization, the chosen initial concentration was 84%.

The stirring of the titrated solution was carried out by a stream of nitrogen freed from all traces of carbon dioxide and saturated with the vapours of the corresponding solvents. This simultaneously prevented the access of air to the titrated solution.

The pK value was determined by reading the corresponding pH value from the titration curve when the acid was half neutralised. The accuracy of the measurement of pH was determined by statistical treatment of the measured values in 80% 2-methoxyethanol. The corresponding value for decaborane was $pK_1 = 2.25 \pm 0.01$, and for octadecaborane $pK_1 = 2.18 \pm 0.01$.

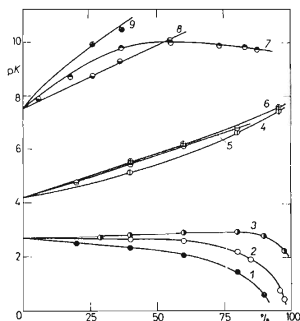


FIG. 2

Dependence of pK of Octadecaborane and Benzoic Acid in Organic Solvent-Water System on the Content of the Solvent

$B_{18}H_{22}$: 1 pK₁ in acetonitrile, 2 pK₁ in 2-methoxyethanol, 3 pK₁ in ethanol, 7 pK₁₁ in acetonitrile, 8 pK₁₁ in 2-methoxyethanol, 9 pK₁₁ in ethanol; C_6H_5COOH : 4 pK in 2-methoxyethanol, 5 pK in acetonitrile, 6 pK in ethanol.

RESULTS

The results of our measurements are presented in Figs 1–3. From Fig. 1 and 2 it is evident that the organic acids, represented here by benzoic acid, behave in a different manner from both boranes studied. While the dissociation of organic acids to the first degree is strongly suppressed¹⁴ in non-aqueous solvents, both boranes behaved in just the opposite manner.

This fact alone shows that in addition to the commonly considered effect of solvents another factor also plays a role. That this is complex can be deduced from the fact that the acidity of decaborane increases in the following sequence of solvents: ethanol < acetonitrile < 2-methoxyethanol (Fig. 1), while in the case of n-octadecaborane the acidity augments in the sequence: ethanol < 2-methoxyethanol < acetonitrile.

During the titration of decaborane in acetonitrile we observed two potential increase steps — the first one at approx. the consumption of 0.8 equivalents, and the second at 1.0 equivalent of the base (Fig. 3).

The first step (pK 2.5) is due in our opinion to the titration of decaborane itself, while the second (pK approx. 8.0) is due to the titration of the reaction product of decaborane with acetonitrile. With the increasing water content the amount of less acid substance decreases and in the presence of 40% of water both steps coalesce.

The determination of the dissociation constants of decaborane and octadecaborane in pure water could not be performed directly due to the insolubility of boranes in this medium. From the course of pK changes of both boranes in three solvents containing various amounts of water the value pK_1 2.70 for decaborane, (Fig. 1), could be obtained by extrapolation. In our opinion this value is far closer to the actual value than the value pK 4.464 given in an inaccessible research report (ref.⁹, p. 262). In a similar manner the values pK_I 2.68 and pK_{II} 7.5 can be estimated for octadecaborane. The second value is in good agreement with that from the literature¹³.

The unusual behaviour of both boranes was also observed during the determination of the dissociation constant to the second degree. When organic acids are transferred from an aqueous

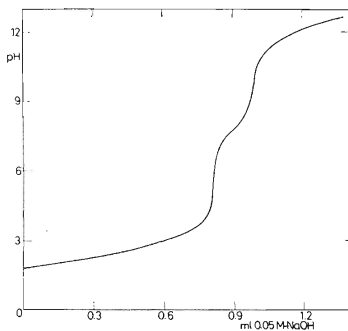


FIG. 3

Titration Curve of Decaborane in Acetonitrile

to non-aqueous medium their pK_1 and pK_2 values increase but their difference does not change appreciably. In contrast to this, when octadecaborane is transferred into a less aqueous medium the $pK_{11} - pK_1$ difference steadily increases. In solvents with a low content of water the pK_{11} value is already so high¹¹ that it practically cannot be measured.

From Bjerrum's equation¹⁵ it follows that the dissociation to the second degree is the easier the higher is the dielectric constant of the medium. In accordance with this we found that in acetonitrile with a high content of water the second potential step in the titration of decaborane is found in the region of 2.0 equivalents of the base (Fig. 1). Hence, in a medium with high dielectric constant decaborane can behave as a diacid. When the difference $pK_{11} - pK_1$ attains approximately the value 7, which for decaborane was found in a 20% aqueous acetonitrile, it can be calculated from Bjerrum's equation that the product $r.D = 38$ (for r expressed in Å). As all molecules present ($B_{10}H_{14}$, H_2O , CH_3CN) possess a high dielectric constant ($D > 20$) the distance of negative charges is less than 2 Å which corresponds roughly to the length of the B-B bond. In view of the fact that the presence of a complete charge on boron atoms next to the hydrogen bonds is excluded, the only possible explanation consists in the view that the charge is readily transported *via* the bonds between boron atoms.

The explanation of complex problems concerning the causes of the acidity of higher boranes and their manifestation under various conditions is the subject of our further studies.

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