ON THE ACIDITY CHARACTERISTICS OF DECABORANE(14) AND ITS BENZYL DERIVATIVES IN ORGANIC SOLVENT–WATER SYSTEMS

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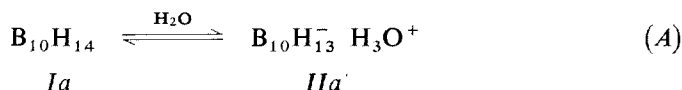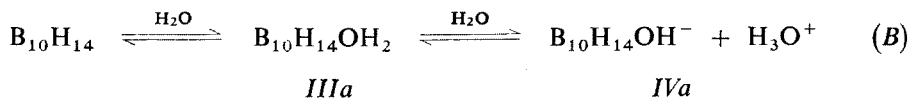*Czechoslovak Academy of Sciences, 250 68 Prague - Řež*

The paper describes the acidobasic behaviour of decaborane(14) and its 6-benzyl and 6,9-dibenzyl derivatives in six systems organic solvent–water in relation to concentration of water. Decaborane(14) behaved as a strong Lewis acid $B_{10}H_{14}OH_2$ in all cases. The 6-benzyl and especially the 6,9-dibenzyl derivatives moreover exhibited the Brönsted acidity, which was 2 to 3 orders of magnitude lower. The probable structures of the anions formed in the titrations and the course of the reaction are discussed.

The transfers of electronic effects through multicentred bonds in open boron skeletons have not yet been studied in detail. An insight into this problem can be obtained by studying the effects of various substituents in known positions on the acidity of a given borane. The best choice for this purpose seems to be decaborane(14) (*Ia*), which is readily accessible, sufficiently stable and can be alkyl-substituted and halogen-substituted in all the four possible positions, *i.e.* at position 1, 2, 5 and 6 (*I*).

Ia; $R^1 = R^2 = H$
Ib; $R^1 = CH_2C_6H_5$, $R^2 = H$
Ic; $R^1 = R^2 = CH_2C_6H_5$
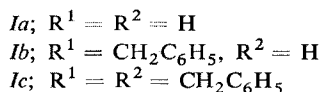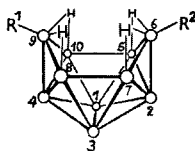
The acidity of decaborane(14) was first described by Guter and Schaeffer[1], who showed that in the presence of water the borane *Ia* behaved as a Brönsted acid (*A*) or a Lewis acid (*B*):

$$B_{10}H_{14} \xrightleftharpoons{\text{H}_2\text{O}} B_{10}H_{13}^- \ H_3O^+ \qquad (A)$$

Ia   *IIa*

$$B_{10}H_{14} \xrightleftharpoons{H_2O} \underset{IIIa}{B_{10}H_{14}OH_2} \xrightleftharpoons{H_2O} \underset{IVa}{B_{10}H_{14}OH^-} + H_3O^+ \qquad (B)$$

However, the kinetic study by these authors gives preference to neither type of acidity. The existence of the anions *IIa* and *IVa* has been demonstrated by Hawthorne and coworkers[2], but they did not investigate which type was responsible for the high acidity of decaborane(14). The problem has since been the subject of a number of papers (see[3] and the references therein), but the results show discrepancies both in the value of pK_a (2·8 to 11) and in views concerning the possibility of a second dissociation. In our previous paper[3] we reported a striking anomaly, *viz*, an increase in the acidity of decaborane(14) with a decrease in the content of water in the solvent. This anomaly was very strange, considering that oxalic acid, which in 20% aqueous ethanol was a stronger acid than the decaborane, exhibited the normal behaviour, *i.e.* decreasing acidity with decreasing concentration of water in the system.

An attempt to elucidate the above discrepancies is the subject of this paper.

EXPERIMENTAL

The potentiometric titration was described previously[3]; the titrant was again 0·05M tetramethylammonium hydroxide in carbonate-free water, a glass electrode and a calomel reference electrode being used. The UV spectra were measured with a double-beam spectrophotometer DK 1, Beckman, U.S.A., in pairs of 1 cm Suprasil Cells Hellma, German Federal Republic. The ^{11}B NMR spectra were measured at a frequency of 25 MHz with an apparatus developed at the Institute of Instrumental Technique (Ústav přístrojové techniky) Czechoslovak Academy of Sciences, Brno, and at 80 MHz with a prototype apparatus of the University of California, Los Angeles, U.S.A. Ascendent thin-layer chromatography of 75% ethanol solutions of decaborane, 6-benzyldecaborane and 6,9-dibenzyldecaborane was carried out on silica-gel-coated aluminium sheets (Silufol plates, Kavalier, Votice, ČSSR) with starch as binder.

The dissociation constants of decaborane(14) in ethanol–water systems were calculated from the equation[4]

$$A \sqrt{I} - \log \frac{B}{m_a - B} + pH = pK_a + CI. \qquad (1)$$

where

$$B = m_b + m_{H^+} - m_{OH^-}. \qquad (2)$$

A is the Debye–Hückel coefficient, I the ionic strength, m_a the analytical concentration of the acid, m_b the concentration of the added base and C a constant. The values of A for various ethanol–water systems were calculated from the equation[5]

$$A = -1·825 . 10^6 \left(\frac{\varrho_1}{\varkappa^3 . T^3} \right)^{1/2}, \qquad (3)$$

where ϱ_1 is density of the pure solvent and $\varkappa$ its dielectric constant. Into this equation we substituted the tabulated values[6,7] of ϱ_1 and $\varkappa$.

Since the measured values of pH did not exceed 4, the term m_{OH^-} in equation (B) was neglected. The titrated solutions of decaborane(14) were (2·5 to 25) . 10^{-3}M in mixtures ethanol–water. The ionic strength could not be kept constant by additions of an indifferent electrolyte, since spectral studies had shown that decaborane(14) reacts with indifferent electrolytes.

The left-hand side of equation (1) was plotted *vs* ionic strength. The value of pK_a was determined by extrapolating the linear part of this graph to zero ionic strength.

RESULTS AND DISCUSSION

Acidity of Decaborane(14) in Relation to Composition of the Solvent-Water System

The titrations in aqueous 2-methoxyethanol, ethanol, 1,2-dimethoxyethane, dioxan, tetrahydrofuran and acetonitrile, *i.e.* in solvents differing both in chemical nature and in physical properties (dielectric constant, dipole moment, formation of hydrogen bonds) have now revealed that decaborane(14) behaves as a relatively strong monohydric acid in all the systems, irrespective of the nature and properties of the individual solvents.

Although the number of solvents was greater than before[3], the $pH_{1/2}$ value of the decaborane decreased in all systems studied with the decreasing content of water; the decrease started from a certain point, characteristic of each solvent (Fig. 1). A similar character of curves observed with most diverse solvents had indicated that the increase in acidity with the decreasing concentration of water was not due to the nature of the solvent; by this behaviour decaborane(14) had markedly differed from moderately strong acids and resembled hydrochloric acid in the system ethanol–water[8]. This suggested that the acidity of decaborane(14) was probably
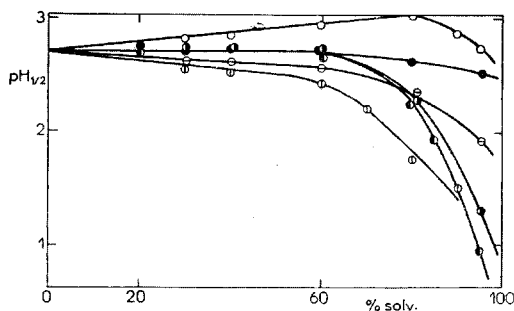

Fig. 1

$pH_{1/2}$ of 5 . 10^{-3}M $B_{10}H_{14}$ in Relation to Solvent Composition (% w/w)
○ Ethanol, ● acetonitrile, ◑ 1,2-dimethoxyethane, ◐ 2-methoxyethanol, ⊖ dioxan, ⊕ tetrahydrofuran.

higher than had been previously determined. The values of acidity given in Fig. 1 for different systems should be regarded as approximate only, since the determination of pK_a, as the pH at mid-neutralization, is based on simplifying assumptions. More accurate values of pK_a were therefore calculated from the general equation of the titration curve[9]. The results show that the best system for titration of decaborane(14) is aqueous ethanol, where the dependence of pK_a on composition of the system is almost linear in the range 20 to 60% of ethanol, and decomposition to by-products is minimum. The pK_a values of decaborane(14) in this system, calculated from equation (1), are given in Table I and Fig. 2. Extrapolation of the linear part of the graph to zero concentration of ethanol gave the pK_a value of decaborane (14) in water as 1·78.

TABLE I

pK_a Values of Decaborane(14) in Ethanol–Water Mixtures

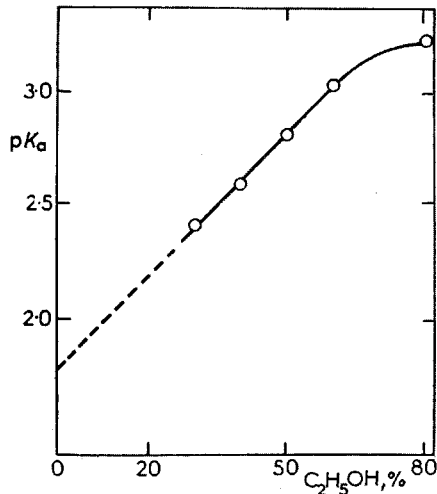| % C_2H_5OH	30	40	50	60	80
pK_a	2·41	2·58	2·81	3·02	3·21

FIG. 2

pK_a of $B_{10}H_{14}$ in Relation to Composition (% w/w) of C_2H_5OH–H_2O Systems

The Acidity Characteristics of Decaborane(14) *and Its 6-Benzyl and 6,9-Dibenzyl Derivatives in Aqueous Solvents*

The results of the titrations have failed to decide safely whether the high acidity is caused by release of protons from the borane *Ia* or from its water adduct *IIIa*.

The increasing acidity with a decreasing content of water in the medium suggests that the acidity of the free borane *Ia* exceeds that of the adduct *IIIa*, but it would also be expected that the adduct *IIIa* will behave as a rather strong acid, with pK_a not differing much from the values measured.

Since Lewis bases of most diverse types $(R_2S, R_3N, RCN, R_3P$ *etc.*) add to the B(6) or B(9) positions of decaborane(14) (ref.[10]), the addition of water would be expected to produce 6-$(H_2O)B_{10}H_{14}$. For this reason we compared the acidity characteristics of decaborane(14), 6-benzyldecaborane(14) (*Ib*), whose 9-position is freely accessible, and 6,9-dibenzyldecaborane(14) (*Ic*), where the addition of water at positions 6 and 9 is sterically hindered. With the two derivatives (*Ib, Ic*) the addition of water should further be retarded by the inductive effect of the alkyl (*cf*[11]). In titrating the boranes *Ia* − *Ic*, the acidity changes in aqueous ethanol with time (Fig. 3*a,b*) were in full accordance with this hypothesis. Hence it can be inferred that the high acidity of these compounds in the presence of water is due to the adduct *III*, whereas the acidity caused by dissociation of a proton from the boranes *Ia* to *Ic* is orders of magnitude lower. To the non-substituted borane (*Ia*) water added so rapidly that even in the titration of a fresh solution only one potential jump was observed, corresponding to neutralization of the acid *IIIa*; $(pK_a$ [80% C_2H_5OH] = 3·21, pK_a [50% C_2M_5OH] = 2·81). With the borane *Ib* the addition of water was already retarded; depending on the age of the solution there were observed two
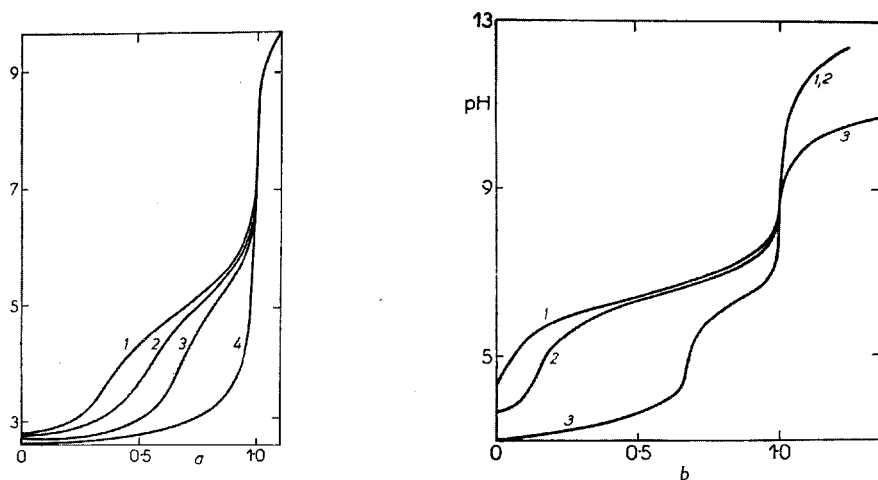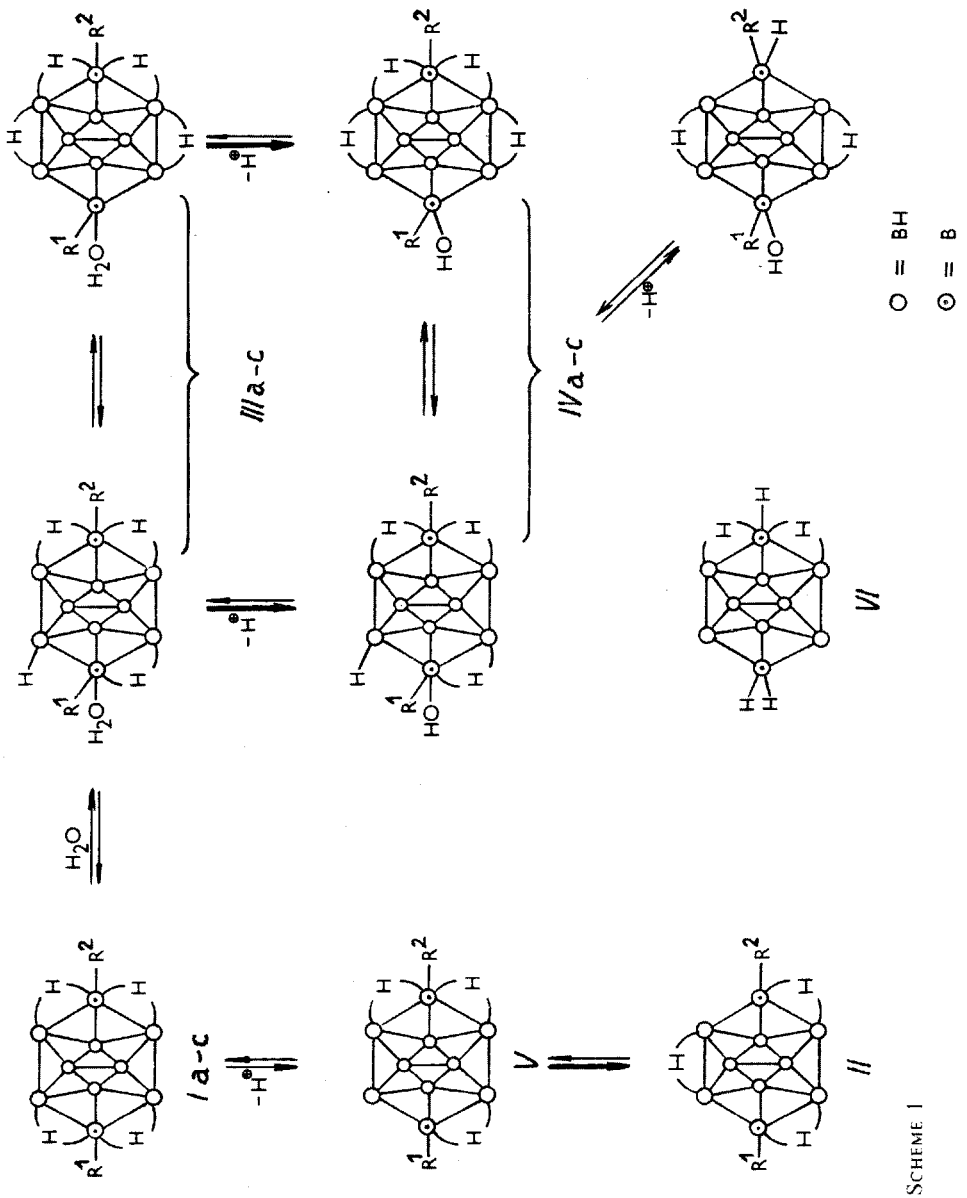

FIG. 3

Titration Curves of *a* 6-$C_6H_5CH_2B_{10}H_{13}$ in 50% C_2H_5OH and *b* 6,9-$(C_6H_5—CH_2)_2B_{10}H_{12}$ in 80% C_2H_5OH

a Titration after 20 min (*1*), 40 min (*2*), 1 h (*3*) 4 h (*4*). *b* Titration after 20 min (*1*), 1 h (*2*), 20 h (*3*).

Scheme 1

potential jumps (Fig. 3a), of which the first corresponded to neutralization of a Lewis acid $(pK_a [50\% C_2H_5OH] = 2·71)$ and the other to neutralization of a Brönsted acid $(pK_a [50\% C_2H_5OH] = 5·05)$. The addition of water to the compound Ic was very markedly impeded by a strong steric hindrance; the potential jump associated with neutralization of the weaker, $i.e.$ the Brönsted acid was considerable $(pK_a [80\% C_2H_5OH] = 6·49)$ and only very slowly decreased with age of the solution in favour of the stronger, $i.e.$ the Lewis acid $(pK_a \sim 3)$, Fig. 3b.

The view that more acidic species belong to type III rather than I is consistent with measurements of the UV spectra of boranes $Ia-Ic$ in 80% ethanol; the absorption band at 335 nm, corresponding to the anion type $B_{10}H_{13}^- (II)$, had its longest existence in the borane Ic. With the borane Ib it disappeared within an hour, and in the case of decaborane(14) it practically did not appear. As the content of anion II decreased, the band at 249 nm, previously assigned[2,12] to the anion type $B_{10}H_{14}OH^-$, became more intense.

The same conclusions are drawn from the time-change study of aqueous–ethanolic solutions of boranes $Ia-c$ by thin-layer chromatography; this has confirmed that these boranes react with water and produce a polar, reducing substance. Reaction (B) has a reversible character, since after an addition of hydrochloric acid more than 30% of the free borane I was recovered from an aqueous–ethanolic solution that had been proved free of this borane by thin-layer chromatography.

The Probable Structure of the Anions $B_{10}H_{13}^-$, $B_{10}H_{14}OH^-$ and of the Dianion

The possibility that the changes in pK_a and $pH_{1/2}$ with the decreasing content of water in the solvent were due to shifts of equilibrium between the two assumed forms[13], V and VI, of the anion $B_{10}H_{13}^-$ had been studied by ^{11}B -NMR and shown to be improbable, for the anion $B_{10}H_{13}^-$ in very different solvents (diethyl ether, methylene chloride, acetonitrile) exhibited only small changes in the character of the ^{11}B-NMR spectrum[14]. The observed changes can be attributed to the solvent effects rather than to the position changes of the B—H—B bridges which had been shown to be very important for chemical shifts of some B atoms in $nido$-boranes[15]. The measured spectra (Fig. 4) are in a mediocre agreement with the structural form V, at complete variance with the form VI, but in good accordance with structure II (Scheme 1), propounded by Siedel and coworkers[16] on the basis of a similar study.

The probable structure of the anion $B_{10}H_{14}OH^-$ follows from analysis of changes in the ^{11}B-NMR spectrum of a 2·5M solution of Ia in 60% 1,2-dimethoxyethane, where we observed a rapid decrease in Ia in favour of a new compound, whose signals were in the range $10-30$ p.p.m. (related to $BF_3O(C_2H_5)_2$), $i.e.$ in the spectral range of the ion[17] $B_{10}H_{15}^-$. Hence we deduce that the character of the ion $B_{10}H_{14}OH^-$ is close to that of the ion $B_{10}H_{15}^-$ with a hydrogen atom at B(6) replaced by a hydroxyl group. The narrow spectral range in p.p.m. units suggests a fast H-tautomerism[15]

in the anion *IV*. This H-tautomerism is the probable cause of the greater stability of the ion $B_{10}H_{14}OH^-$ compared to the ion $B_{10}H_{13}^-$, for in our ^{11}B-NMR study the pre-formed anion *II* in aqueous 1,2-dimethoxyethane got rapidly converted into $B_{10}H_{14}OH^-$.

Unlike $B_{10}H_{14}$, its analogue 5,6-$C_2B_8H_{12}$ (*VII*) behaved exclusively as a Brönsted acid of $pK_a = 6\cdot18$ in 50% ethanol[18] (*cf.* $pK_a = 5\cdot05$ for $B_{10}H_{14}$). The presence of the stronger acid, *i.e.* the Lewis acid, was not observed, the probable reason being the impossibility of its stabilization by H-tautomerism (analogous to the equilibrium *III* ⇌ *IV*), which cannot occur in the skeleton of this carborane.

In titrating decaborane(14) in some solvents (tetrahydrofuran, 1,2-dimethoxyethane, acetonitrile) containing over 60% of water a potential jump indicating
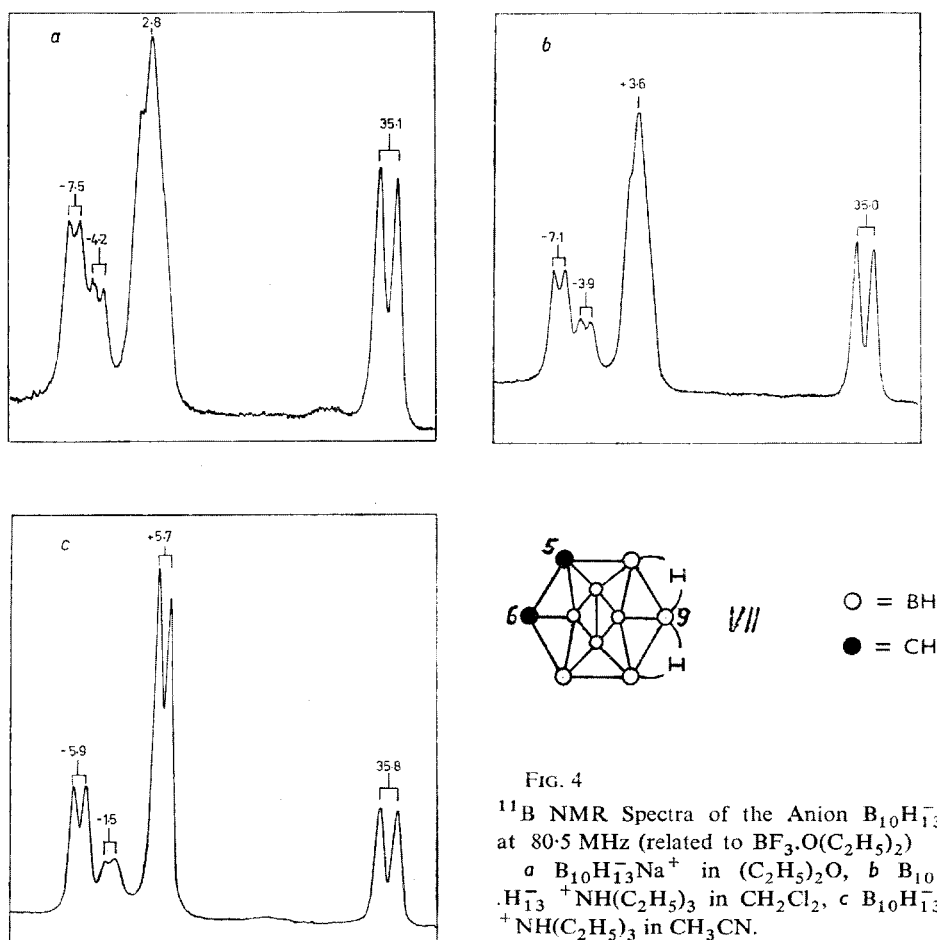

FIG. 4

^{11}B NMR Spectra of the Anion $B_{10}H_{13}^-$ at 80·5 MHz (related to $BF_3.O(C_2H_5)_2$)
  a $B_{10}H_{13}^-Na^+$ in $(C_2H_5)_2O$, *b* $B_{10}.H_{13}^-$ $^+NH(C_2H_5)_3$ in CH_2Cl_2, *c* $B_{10}H_{13}^-$ $^+NH(C_2H_5)_3$ in CH_3CN.

dissociation of the univalent anion to the second degree appeared on the titration curve at the consumption of two equivalents. In all probability it was conversion of the ion $B_{10}H_{14}OH^-$ into the previously described[19] ion $B_{10}H_{13}OH^{2-}$.

The significant difference between the Brönsted acidity and the Lewis acidity observed with 6-benzyldecaborane can also be assumed to exist in decaborane(14). The possible co-existence of the two types of acid and the anomalous sensitivity to the content of water in the solvent may account for the discordant pK_a values reported for decaborane(14). This demonstrates that comparison of acidities of substituted decaboranes, to reveal the transfer of electronic effects along a borane skeleton, will only be possible in absolutely water-free solvents, since mere traces of moisture give rise to the strongly acidic form, which precludes determination of the Brönsted acidity.

REFERENCES

 1. Guter G. A., Schaeffer G. W.: J. Amer. Chem. Soc. *78*, 3546 (1956).
 2. Hawthorne M. F., Pitochelli A. R., Strahm R. D., Miller J. J.: J. Amer. Chem. Soc. *82*, 1825 (1960).
 3. Heřmánek S., Plotová H.: This Journal *36*, 1639 (1971).
 4. Dvořák J., Koryta J., Boháčková V.: *Elektrochemie*, p. 193. Academia, Prague 1966.
 5. Hála E., Reiser A.: *Fysikální chemie* 2, p. 300. Academia, Prague 1966.
 6. *Fysikálně chemické tabulky*. Published by SNTL, Prague 1953.
 7. King E. J.: *Acid–Base Equilibria*. Pergamon Press, Oxford 1965.
 8. Bates R. G.: *Determination of* pH, p. 211. Willey, New York 1965.
 9. Kučera Z., Kimla A.: Sb. Vys. Šk. Chemicko-Technol. Praze, *H4*, 177 (1969).
10. Muetterties E. L.: *The Chemistry of Boron and its Compounds*, p. 274. Wiley, New York 1967.
11. Holzmann R. T.: *Production of the Boranes and Related Research*, p. 286. Academic Press, New York 1967.
12. Schaeffer G. W., Burns J. J., Klingen T. J., Martincheck L. A., Rozett R. W.: Abstract of Papers, 135th Meeting Am. Chem. Soc. Boston, Mass., April 5—10, 1959.
13. Lipscomb W. N.: *Boron Hydrides*, p. 224. Benjamin, New York 1963.
14. Heřmánek S., Wiersema R. J., Hawthorne M. F.: Unpublished results.
15. Heřmánek S., Plešek J.: Z. Anorg. Allg. Chem. *409*, 115 (1974).
16. Siedle A. R., Bodner G. M., Todd L. J.: J. Inorg. Nucl. Chem. *33*, 3671 (1971).
17. Rietz R. R., Siedle A. R., Schaeffer R. O., Todd L. J.: Inorg. Chem. *12*, 2100 (1973).
18. Plešek J., Heřmánek S.: Chem. Ind. (London) *1971*, 1267.
19. Benjamin L. E., Stafiej S. F., Takacs E.: J. Amer. Chem. Soc. *85*, 2674 (1963).