*Journal of Fluorine Chemistry*, 13 (1979) 465–471

Received: October 16, 1978

# EFFECT OF BORIC ACID ON TETRAFLUOROBORATE ION HYDROLYSIS IN SOLUTIONS OF TETRAFLUOROBORIC ACID

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## SUMMARY

The presence of boric acid in tetrafluoroboric acid solutions enhances the $BF_4^-$ ion hydrolysis. An increase of the boric acid content in a 32% $HBF_4$ solution from 0.1% to 3.8% is accompanied by a simultaneous increase of the degree of hydrolysis from 4.8% to 30.5%.

## INTRODUCTION

The $BF_4^-$ ion hydrolysis in acid medium is a stepwise process which can be described by following equation:

$$BF_4^- + nH_2O = \left[BF_{(4-n)}(OH)_n\right]^- + nHF, \qquad \text{where } 1 \leqslant n \leqslant 4$$

The presence of a variety of both single as well as complex ions in aqueous fluoroboric acid solutions render the latter a rather complex system that has been quite extensively investigated. When $HBF_4$ is obtained from $H_3BO_3$ and HF, the equilibrium position of the hydrolysis reaction is not only concentration and temperature dependent, but also depends on the $HF/H_3BO_3$ molar ratio in the starting mixture

(1,2,3). In basic media, the rate of the $BF_4^-$ ion hydrolysis is small and directly proportional to the $BF_4^-$ ion concentration (1,2,3). The equilibrium constants for the formation of $HBF_4$, $HBF_3OH$, and $HBF_2(OH)_2$ from $BF_3$ and $H_2O$ and from HF and $H_3BO_3$ have been determined and also the degree of the $BF_4^-$ hydrolysis in the $HBF_4$ solutions at room temperature (4,5). It has been pointed out (4,5) that the rate of the $HBF_4$ formation reaction is acid-dependent; however, no analytical expression has been proposed for the rate law that would also include the $H^+$ concentration (4,5). It has been found that in acid media the $BF_4^-$ ion hydrolysis reaction is first-order in $H^+$ and that it is consistent with the following expression:

$$v = k\left[H^+\right]\left[BF_4^-\right]$$

where v = the rate of the $BF_4^-$ ion hydrolysis reaction.

$H^+$ ions have been found (7) to catalyze the hydrolytic decomposition of complex fluorides. This was established for the following type of reaction:

$$\left[Co(NH_3)_5F\right]^{2+} + H_2O + H^+ = \left[Co(NH_3)_5H_2O\right]^{3+} + HF$$

$$PF_6^- + H^+ + 4H_2O = H_2PO_4 + 6HF$$

It is believed (7) that a wide range of complex fluorides can undergo acid hydrolysis (e.g. $AsF_5(OH)^-$, $BF_4^-$ and $AsF_6^-$), the process being accompanied by HF formation.

A further indication of the $H^+$ ion-catalyzed decomposition of the $BF_4^-$ ions is the fact that HF is the only fluorine containing product to be found in the system after the $HBF_4$ solutions have been boiled in the presence of HCl (8). The mechanism of the $BF_4^-$ ion hydrolysis, especially in acidic media is still not completely understood even though some of the relevant equilibrium constants have been determined (1) and the kinetics of the reaction in a 0.1105 M $HBF_4$ solution have been studied (4). The $BF_4^-$ hydrolysis has been investigated so far mostly for dilute $HBF_4$ solutions. The limited data available for the more concentrated $HBF_4$ solutions seem to suggest a low degree of the $BF_4^-$ hydrolysis: 5.5% in a 5.4 M $HBF_4$ solution (4), and less than 8% in a 2.5 M solution (1).

Reported in this work are our studies concerning determination of the hydrolysis degree in moderately concentrated $HBF_4$ solutions, ( 4M, or 31%), and also investigations of the effect of an excess of the starting reagents (HF or $H_3BO_3$) upon the equilibrium position of the hydrolysis reaction.

## EXPERIMENTAL

Concentrated $HBF_4$ solutions were prepared using stoichiometric amounts of the reactants, according to:

$$4HF + B(OH)_3 = HBF_4 + 3H_2O$$

Anhydrous boric acid and a 40% HF solution were utilized. In this manner, 4.35 to 4.5 M (31.5% - 32.8%) solutions were obtained. These $HBF_4$ solutions were stored in plastic containers and measurements were made at room temperature. The degree of hydrolysis was determined by three different methods: Ryss' procedure (9), Wamser's procedure (4) and a procedure proposed by us (10). All methods are based on the determination of: a/total acidity, b/content of the products created by hydrolytic decomposition of $BF_4^-$ ion, c/ free boric acid or hydrofluoric acid and d/content of boron in the solutions of $HBF_4$.

Results, obtained by different methods, were in good agreement. The degree of hydrolysis ranged between 4.6%-16%. The higher values for the degree of hydrolysis were found for the $HBF_4$ solutions containing an excess of the free boric acid.

This fact was confirmed in a series of experiments in which the change in the $BF_4^-$ hydrolysis was monitored following the addition of an excess of HF or of boric acid into a concentrated $HBF_4$ solution. Thus in one case the $HBF_4$ concentration was 31.5%, that of the free boric acid 1.4%, and the degree of hydrolysis 16.2%. When small amounts of hydrofluoric acid were added, the free boric acid content fell to 0.9%, and the degree of hydrolysis to 9.35%. Next, hydrofluoric acid was added to the same solution: all of the free boric acid reacted leaving behind a small excess of the free HF, and the degree of hydrolysis fell to 5.4%. Subsequent addition of 2.5% boric acid into the same solution caused an increase of the degree of hydrolysis from 5.4% to 26.0%. Similar experiments, conducted with another series of solutions, clearly showed that with the concentrated $HBF_4$ solutions even a small excess of boric acid leads to a significant shift of equilibrium towards hydrolysis and thus an increase of the $BF_4^-$ ion hydrolysis.

The highest degree of hydrolysis (30.5%) was established in a solution containing 3.84% of the free boric acid (the latter is close to the concentration of the concentration of the saturated $H_3BO_3$ solution). The lowest value of the $BF_4^-$ hydrolysis degree (4.6%) was found in a solution that has a 2.0% excess of HF. The above results are set out graphically in Fig.1.

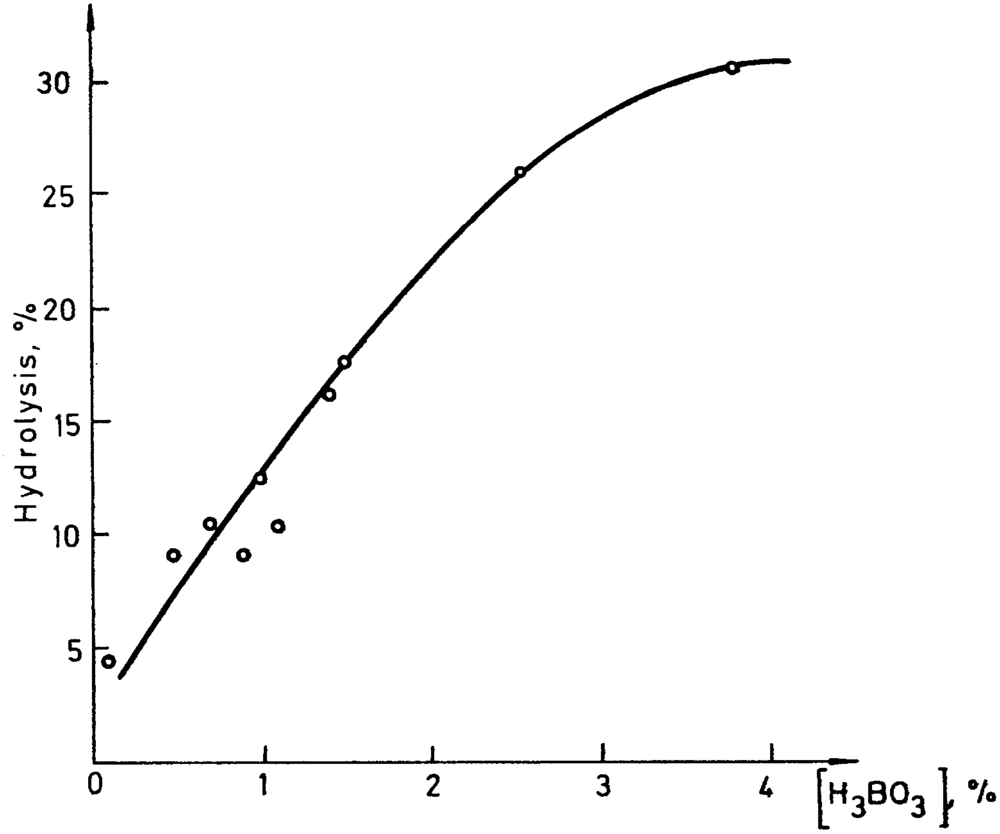

Fig.1. Dependence of the $BF_4^-$ ion hydrolysis degree on the boric acid excess (in 32% $HBF_4$ solutions).

## DISCUSSION

It appears that boric acid does affect the hydrolysis of the $BF_4^-$ ion in concentrated $HBF_4$ solutions. As already known (11), the increase in the boric acid concentration is accompanied by an increase in the acidity of the solution due to the formetion of oligomeric anions, the latter being described as follows:

$$3B(OH)_3 = B_3O_3(OH)_4^- + H^+ + 2H_2O$$

We believe the process shown in the above equation also takes place in the $HBF_4$ solutions that contain an excess of boric acid: the $H^+$ ions that so become available then accelerate the hydrolysis of the $BF_4^-$ ions.

The $H^+$ ion-catalyzed hydrolytic decomposition of the $BF_4^-$ ion can be illustrated by the following equation:

$$BF_4^- + nH_2O \xrightarrow{H^+} [BF_{(4-n)}(OH)_n]^- + nHF$$

where $1 \leqslant n \leqslant 4$. An excess in $H^+$ ions will shift the reaction toward formation of the weakly dissociated HF owing to the fact that $H^+$ is a good acceptor of $F^-$ ions. The $OH^-$ groups replace the $F^-$ ions as ligands, thus yielding the hydroxofluoroborate anions. The net result is that the relative amount of the $BF_{(4-n)}(OH)_n^-$ anions is increased: in other words, the $BF_4^-$ ion hydrolysis degree increases.

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