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RATE CONSTANTS FOR THE FORMATION OF TETRA-FLUOROBORIC ACID IN WATER-ETHANOL SOLVENT

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The reaction between boric acid and hydrofluoric acid yielding tetraflouroboric acid is the basis for the development of several spectrophotometric methods of analysis of trace quantities of boron (1-3). Menon (4) has recently demonstrated that the same reaction may be employed to develop a sensitive radioreagent method of boron analysis using HF labeled with 1.8 h ^{18}F as a radioreagent. However, the sensitivity depends not only on the specific activity of the radioreagent but also the HF-to-H_3BO_3 mole ratio in the reaction mixture and the time for the completion of the reaction. Wamser (5) has reported that the above reaction takes place in two steps as represented by the following equations:

$$H_3BO_3 + 3HF \longrightarrow HBF_3OH + 2H_2O \quad \text{(fast)} \quad \dots \quad (1)$$

$$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O \quad \text{(slow)} \quad \dots \quad (2)$$
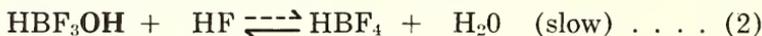
The rate constants for the slow reaction have been measured by Wamser at 25°C using water solutions of boric acid and hydrofluoric acid in stoichiometric amounts down to a conc. of 0.013 M of boric acid. It has also been reported that 0.001 M solution of boric acid requires about two months to come to equilibrium. However, Ducret (1) and others (2-3) have used a very large excess of HF to drive the reaction to equilibrium in a shorter time when only trace amount of boric acid is present in the sample. Since the success of the radioreagent method of analysis of boron depends on the HF-to-H_3BO_3 mole ratio in the reaction mixture as well as the reaction time better conditions for carrying out this reaction are desired. In this work the effect of ethanol on the rate of formation of HBF_4 at different temperatures and solvent composition was investigated.

Experimental

Reagents: Reagent grade boric acid, HF(40%), and ethanol (95%) were used. Stock solutions of boric acid ($\sim$ 0.1M) and hydrofluoric acid ($\sim$ .6 M) were prepared by mixing appropriate amounts of these reagents with deionized water and diluting to 500 ml. of the solution with more water. Both of these acids were standardized with standard sodium hydroxide using phenolpthalein as the indicator. In the case of boric acid about 0.5 g of mannitol was added towards the end of titration to detect the correct end point. From the standardized stock solutions working solutions of different concentrations were made. Only polypropylene wares were used to store the solutions and also to perform the experiments. Procedure: In a typical experi-

ment 50 ml of the boric acid solution was mixed with appropriate amount of 95% ethanol in a polypropylene bottle and kept in a thermostat at the desired temperature. The desired volume of hydrofluoric acid was mixed with enough water in a similar bottle so as to make the total volume 200 ml when the solutions are mixed. This was also kept in the same water bath. When the solutions reached thermal equilibrium, they were mixed and 5 ml of the reaction mixture was withdrawn at regular intervals and titrated immediately with standard sodium hydroxide using phenolpthalein as the indicator. About 0.5 g of mannitol was added to the titrating solution near the end of titration. From the volume of the titrant used for neutralization of the sample the conc. of HBF_4 formed at the time of withdrawal was computed. Treatment of the Data: Wamser (5) has shown that the reaction between HBF_3OH and HF is a second order reaction which determines the rate of overall reaction. The rate equation for a second order reaction when the initial concentrations of the reactants are identical is the following:

$$\frac{1}{C_0 - x} = k.t. + \frac{1}{C_0} \quad \text{.....................................} \quad (3)$$

where C_0 is the initial conc. of H_3BO_3 = initial conc. of HBF_3OH which is also the same as the initial conc. of HF, x is the conc. of HBF_4 at t= t and k the rate constant. It is obvious from this equation that the slope of a plot of $1/C_0$ — x versus t gives the value for the rate constant k.

Although the initial conc. C_0, of HBF_3OH and HF, in each reaction mixture, was known the conc., x, of HBF_4 formed at different times was computed indirectly. Since reaction (1) is fast, immediately after mixing H_3BO_3 and HF in the ratio 1:4 one would expect only two equivalents of the base for the complete neutralization of every equivalent of HBF_3OH and the remaining HF. However, Wamser (5) has shown that due to the rapid hydrolysis of $NaBF_3OH$ five equivalents of alkali are required for the titration of the total acidity in an aliquot of the reaction mixture. The acid-base titration, in this case, may be represented by the following reaction:

$$HBF_3OH + HF + 5 \ NaOH \longrightarrow 4 \ NaF + NaBO_2 + 4 \ H_2O \quad \text{.....} \quad (4)$$
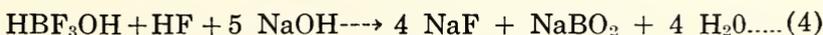
It can be shown that the conc., x, of HBF_4 formed at any time is related to the titer values and the initial conc. of the reactants by the following equation:

$$x = C_0 \left(\frac{5T_1 - T_2}{4T_1} \right) \quad \text{.............................} \quad (5)$$

where $5T_1$ is the titer value at t=0 and T_2 is the titer value at any other time t = t.

Results and Discussion

Table I lists the data from a typical experiment together with the computed values for x and $1/C_0$ — x. Figure 1 is a plot of $1/C_0$ — x versus time and the graph looks like a curve rather than a straight line. Nevertheless, the early part of the graph is linear and the slope of this portion of the graph is a measure of the rate constant. The curvature of the latter part of the graph results from the fact that the reverse reaction (hydrolysis of HBF_4) becomes significant as the time passes by and thus affects the rate of formation of HBF_4. The rate constants and the equilibrium yield for the formation of HBF_4 in water-ethanol mixture of two different compositions and at various temperatures have been measured. These results are summarized in Table II.

It can be seen from Table II that at any given temperature the rate constant for the formation of HBF_4 is much higher in water-ethanol solvent than in aqueous solution. Furthermore the rate constant can also be increased by raising the temperature. The equilibrium yield of HBF_4 formed using a water-ethanol mixture is significantly higher than that obtained using an aqueous solution, but the yield drops off with an increase in temperature. It appears, from this work, that the optimum conditions for the reaction to be carried out reasonably fast with the maximum yield of HBF_4 are the following: (1) the reaction mixture should contain about 64% ethanol, (2) the reaction be carried out at 40°C. The surprisingly better yield for the formation of HBF_4 in water-ethanol mixture indicates that the hydrolysis of HBF_4 is suppressed, to certain extent, by the presence of ethanol in the system.

Acknowledgement

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Table I

Typical Experimental Data and the Computed Values of the Conc. of HBF$_4$ formed at any time t

Time (t) (min)	Volume of NaOH (ml)	$x = C_0 \dfrac{5T - T_2}{4 T_1}$ *	$\dfrac{1}{C_0 - x}$
0.0	6.85 (5T$_1$)	0.0	75.0
7.25	6.00	0.0022	85.5
13.25	5.55	0.0033	94.3
19.00	5.10	0.0044	105.3
26.8	4.85	0.0051	113.6
34.9	4.45	0.0061	128.2
44.8	4.15	0.0068	140.8
55.4	4.00	0.0072	149.3
65.8	3.85	0.0076	158.7
77.0	3.70	0.0080	169.5
87.8	3.60	0.0082	175.4
103.7	3.45	0.0086	188.7
120.3	3.35	0.0089	200.0
infinite	2.90	0.010	256.4
infinite (equil.)	2.90	0.010	256.4

Table II

Rate Constants and Yield for the Formation of HBF$_4$ in Water-ethanol Mixture

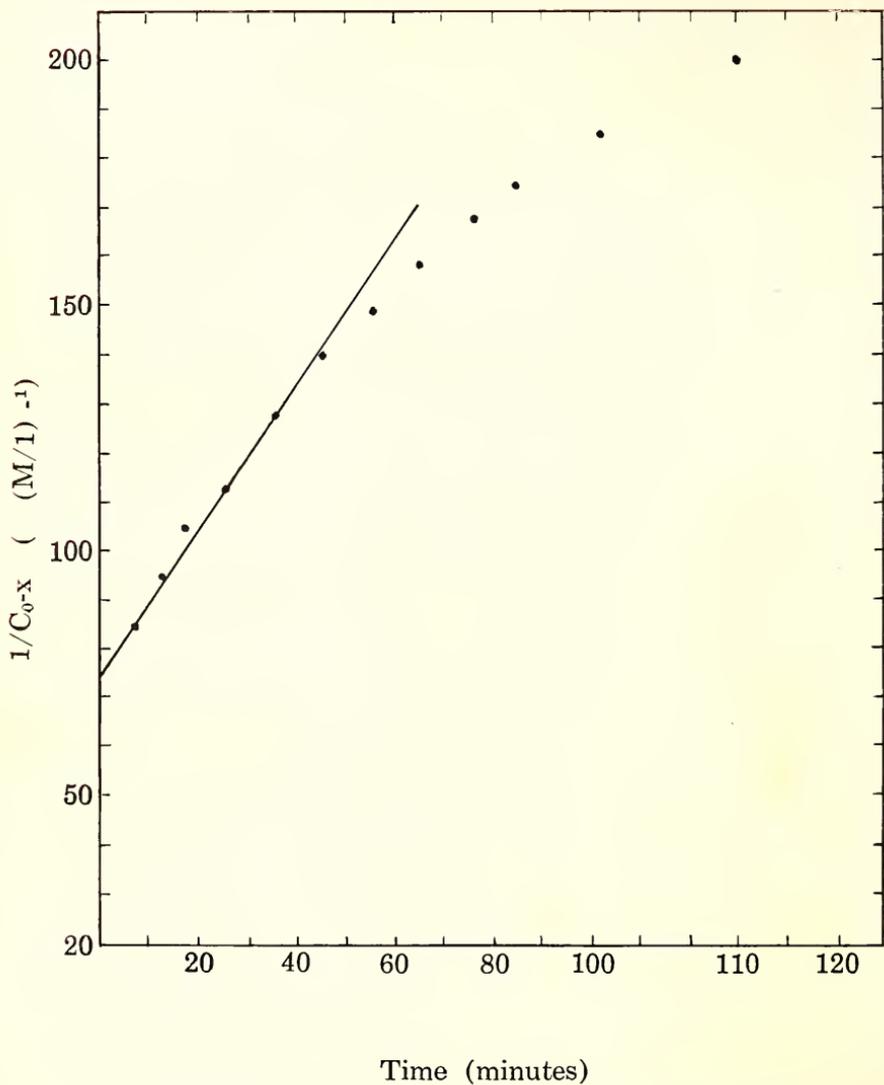| Temp. t^{0}C	Solvent Composition (% alcohol)	H$_3$BO$_3$ (mole/l)	HF (mole/l)	Rate Constant k(min^{-1} (m/l^{-1})	Yield of HBF$_4$ (Percent)
60	0.0	0.0134	0.0536	1.00	50.8
60	47.5	0.0134	0.0536	4.75	58.5
60	64.3	0.0134	0.0536	4.95	62.2
40	47.5	0.0134	0.0536	1.50	72.1
40	64.3	0.0134	0.0536	3.30	74.3
30	47.5	0.0134	0.0536	0.566	65.8

* $C_0 = 0.0134$ M

Time (minutes)

Figure 1. Plot of the reciprocal of the conc. of H_3BO_3
as a function of time

Rate constant, k = slope = 1.50 $(M/l).^{-1}$

min^{-1}