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Abstract

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KINETICS OF THE HYDROLYSIS OF COORDINATION COMPOUNDS OF BORON FLUORIDE*

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We have found that the kinetics of hydrolysis of compounds $F_3B : Am$, where Am is an amine, depends not only quantitatively but also qualitatively on the nature of the amine.

The first analytically determinable stage of hydrolysis of the compounds studied is apparently irreversible and is described by the equation

$$F_3B : Am + H_2O = AmH^+ + BF_3OH^-. \quad (1)$$

In neutral and acidic media, reaction (1) is complicated by partial conversion of BF_3OH^- into BF_4^- (^{1}); in alkaline medium BF_3OH^- undergoes rapid final decomposition to borate and fluoride.

The decomposition of trifluoropyridineboron $F_3B : NC_5H_5$ in alkaline medium is a relatively rapid first-order reaction; hydrolysis in neutral or acidic medium proceeds at the same rate (^{2}). The hydrolysis of $F_3B : NC_5H_5$ is not accelerated by the presence of F^- ions accumulating in the alkaline solution as the complex decomposes.

An earlier attempt (^{3}) to study the kinetics of hydrolysis of $F_3B : NH_3$ did not yield quantitative data because of complications caused by the conversion of BF_3OH^- into BF_4^-. In the present work a new method was used to study the kinetics of hydrolysis of $F_3B : NH_3$, based on determining the concentration of $F_3B : NH_3$ remaining unhydrolyzed at a given time. The determination is based on the slowness of hydrolysis of $F_3B : NH_3$ in neutral or acidic solutions and its rapid decomposition in strongly alkaline medium; a cooled sample of the solution under study was neutralized to methyl orange in the presence of an excess of $CaCl_2$, then an excess of standardized alkali was added to the sample until an intense thymolphthalein color appeared, and after 10–15 min the excess alkali was back-titrated with acid to methyl orange. In this procedure the consumption of alkali corresponds to the equation

$$2F_3B : NH_3 + 3Ca^{2+} + 4OH^- + 2H_2O = 2NH_4^+ + 2H_3BO_3 + 3CaF_2 \downarrow. \quad (2)$$

The same method was also used in studying the kinetics of hydrolysis of $F_3B:NH_2CH_3$.

The rate of hydrolysis of $F_3B:NH_3$ and $F_3B:NH_2CH_3$ is low; hydrolysis proceeds according to a first-order equation and is neither catalyzed nor retarded by H^+ ions (in experiments in $\sim 0.25N$ HCl). In the presence of F^- ions, hydrolysis of both compounds is accelerated; at the same time the formation of BF_4^- is inhibited. The rate of hydrolysis in the presence of F^- ions is approximately proportional to their concentration; when the concentration of NaF remains constant during the experiment, hydrolysis proceeds as a first-order reaction; however, the rate constant thus determined, k_F, is the sum of two quantities:

$$k_F = k + k_2[\mathrm{F}], \tag{3}$$

where k is the rate constant of hydrolysis in water, and k_2 is the rate constant of the second-order process (in $\mathrm{mol}^{-1}\cdot\mathrm{l}\cdot\mathrm{min}^{-1}$). Acidification of the NaF solution to pH 5.2 did not eliminate the catalytic action of F^-.

* The experimental part was carried out jointly with S. L. Idel' s.

The temperature dependence of the rate constants k is well described by the usual relation

$$\lg k' = \lg(0.4343k) = A - \frac{B}{T}. \tag{4}$$

The quantitative characteristics of the hydrolysis kinetics of the substances studied are presented in Table 1, which also includes data for the hydrolysis of BF_4^- (a first-order reaction catalyzed by H^+ ions) (4), and the calculated values of the hydrolysis rate constants at 25°.

Table 1

Compound studied	Temperature range, °C	Coefficients of equation (4), A	Coefficients of equation (4), B	$0.4343\,k$ at 25°, min^{-1}	E, kcal	$\Delta S^{\neq}$, entropy units
BF_4^- (dilute solution)	20–80	7.11	3730	$3.98\cdot10^{-6}$	17.1	−34
BF_4^- (conc. solution)	20–80	7.554	3921.5	$2.52\cdot10^{-6}$	17.95	−32
$F_3B:NC_5H_5$	0–30	12.82	4448	$7.94\cdot10^{-3}$	20.3	−8.3

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$F_3B : NH_3$	25—80	14.70	5945	$5.75 \cdot 10^{-6}$	27.2	0.3
$F_3B : NH_2CH_3$	70—100	15.95	6845	$9.8 \cdot 10^{-8}$	31.3	6.0

The apparent activation energy of the second-order process, E_2, calculated from the temperature dependence of k_2, for $F_3B : NH_3$ practically coincides with that found for hydrolysis; in the temperature interval studied (25—60°), $\lg k_2$ is 0.9 greater than $\lg k$. For $F_3B : NH_2CH_3$ the dependence of $\lg k_2$ on temperature is expressed by the equation

$$\lg k_2 = 13.64 - \frac{5600}{T}; \qquad E_2 = 25.6 \text{ kcal.} \tag{5}$$

The hydrolysis of $F_3B : NH_2CH_3$ is sharply accelerated in $NaHCO_3$ solutions saturated with carbon dioxide; hydrolysis is especially sharply accelerated if carbon dioxide is removed from the solution, which leads to an increase in the ratio of concentrations $[CO_3^{2-}]/[HCO_3^-]^2$; consequently, CO_3^{2-} ions catalyze hydrolysis more strongly than HCO_3^- ions.

According to our preliminary data, the hydrolysis of $F_3B : NH(CH_3)_2$ is catalyzed by F^- and OH^- ions and proceeds at almost the same rate as the hydrolysis of $F_3B : NH_2CH_3$. The rate of hydrolysis of $F_2B : NH_2C_6H_5$ could not be studied quantitatively, since the substance is poorly soluble in water; in NaOH solutions this substance decomposes very rapidly, and the rate of decomposition is apparently limited by the rate of its dissolution.

Discussion of results. Since the rate of hydrolysis of $F_3B : NC_5H_5$ and BF_4^- does not depend on the alkalinity of the solution, it is determined by the rate of solvolytic dissociation of the complexes; the high electronegativity of fluorine and the structure of the electron shell of boron give grounds for regarding these processes as nucleophilic substitutions S_N1. The same applies to the hydrolysis of complexes of BF_3 with NH_3 and with NH_2CH_3; they decompose rapidly in strongly alkaline medium, but the rate of their hydrolysis is not determined by OH^- ions arising from the dissociation of water—this is demonstrated by the fact that hydrolysis of the complexes is not retarded by the presence of HCl.

The acceleration of the hydrolysis of BF_3 complexes with NH_3 and with NH_2CH_3 in the presence of F^- ions is not the result of a reaction proceeding by the mechanism usually accepted for S_N2 processes (attack of the complexes by the F^- ion, which replaces the amine), since in that case decomposition of the complexes would be accompanied by the formation of equivalent amounts of BF_4^-, which contradicts experiment; moreover, replacement of the amine by F^-, or by the more nucleophilic OH^-, should occur more readily in the less stable complex of BF_3 with pyridine.

The catalytic action of F^- may be explained by the following hypothesis. Coordination of ammonia by boron fluoride, accompanied by withdraw-

the transfer of an electron pair from N to B, increases the acidic properties of the hydrogen of ammonia and its ability to form hydrogen bonds (manifested, for example, in the ability of $F_3B : NH_3$ to add ammonia molecules (^{5})). In this connection, in solution there exists a rapidly established equilibrium

$$F_3B : NH_3 + F^- \rightleftarrows F_3B : NH_3 \ldots F^- \tag{6}$$

The addition of a negative ion should weaken the $B \leftarrow N$ bond in the complex and facilitate its solvolytic dissociation; if this process also proceeds by an S_N1 mechanism, then the overall rate of hydrolysis of $F_3B : NH_3$ should be expressed by the equation

$$-\frac{dC}{dt} = kC + k_2 C[F^-] = k_F C, \tag{7}$$

where C is the concentration of $F_3B : NH_3$. Equation (3) follows from equation (7). The constant k_2 is the product of the rate constant for hydrolysis of $BF_3 : NH_3 \ldots F^-$ and the equilibrium constant for its formation; the apparent activation energy E_2 is, therefore, the sum of the activation energy and the enthalpy of formation of $F_3B : NH_3 \ldots F^-$ from $F_3B : NH_3$ and F^-.

The acceleration of the decomposition of $F_3B : NH_3$ and $F_3B : NH_2CH_3$ in the presence of HCO_3^-, CO_3^{2-}, and OH^- ions is apparently caused by analogous processes; direct rupture of the $B \leftarrow N$ bond as a result of attack on the complexes by these ions seems unlikely if, as was done above, their properties are compared with those of $F_3B : NC_5H_5$.

Under the proposed mechanism of hydrolysis of the complexes, the action of different anions should increase, as in the case of the S_N2 mechanism, in the order of increasing basic properties

$$(F^- < HCO_3^- < CO_3^{2-} < OH^-);$$

these anions should accelerate the hydrolysis also of compounds of BF_3 with other primary and secondary, but not tertiary, amines. This is consistent with the sharp qualitative difference between the kinetics of hydrolysis of BF_4^- or $F_3B : NC_5H_5$ and the hydrolysis of compounds of BF_3 with NH_3, NH_2CH_3, $NH(CH_3)_2$, and $NH_2C_6H_5$.

Fig. 1. Dependence of the activation energy of hydrolysis of BF_3 complexes on the pK of the basic dissociation of the addend. Addends: 1 –F^-, 2 –NC_5H_5, 3 –NH_3, 4 –NH_2CH_3.

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Another possible explanation leads to analogous conclusions: an increase in the pH of the solution by F^-, HCO_3^-, etc. ions promotes the dissociation of $F_3B:NH_3$ into H^+ and $F_3B:NH_2^-$, which also hydrolyzes faster than the neutral complex; when studying the rate of hydrolysis in water, the rapid drop in the pH of the solution suppresses the dissociation of $F_3B:NH_3$ and excludes its influence on the rate of hydrolysis.

Figure 1 shows that the activation energy E of hydrolysis of boron fluoride complexes increases regularly with strengthening of the basic properties of the addends; there is a relationship between the thermodynamic properties of the addend and of the transition state. The hydrolysis of BF_4^- is slow, despite the relatively low value of E, owing to the very small activation entropy, $\Delta S^\ddagger$. It is known (^{6}) that, in a number of cases, changes in $\Delta S^\ddagger$ for a series of analogous reactions are proportional to changes in the standard entropies of equilibrium processes, ΔS^0. It might have seemed that the difference in ΔS^0 for the dissociation of BF_4^- and $F_3B:NH_3$ in the gas phase is large, since F^- has no rotational entropy. However, the influence of changes in the symmetry numbers and changes in the number of vibrational degrees of freedom reduce this difference; estimates based on the application of the equations of statistical thermodynamics show—

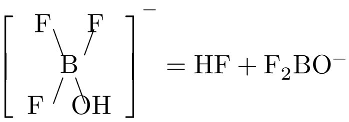
Approximate calculations have shown that this difference does not exceed a few entropy units.

Consequently, even if there is proportionality between $\Delta S^\neq$ and ΔS^0, the latter quantity depends substantially on the solvation effect; the influence of solvation on $\Delta S^\neq$ is also confirmed by the fact that hydrolysis of BF_4^- in an aqueous-alcoholic medium (^{7}) proceeds more slowly than in water, owing to a decrease in $\Delta S^\neq$. Ordering of the structure of water by the field of the ion leads to a decrease in entropy; the action of the small F^- is more pronounced than that of the large BF_4^-. The influence of solvation on ΔS^0 for the dissociation of BF_3 complexes with amines should be smaller.

Sometimes, for a series of analogous reactions, proportionality of activation energies and entropies is observed (^{8}). Indeed, for $F_3B:\mathrm{Am}$ there is the relation (see Table 1) $\Delta S^\neq = 1.325E - 35.4$, but this equation is not applicable to the kinetics of hydrolysis of BF_4^-.

The H^+ ion catalyzes the hydrolysis of BF_4^-, SO_3F^-, PF_6^-, and, probably, other fluoro-complex anions as a result of outer-sphere association, caused by attraction of the ionic charges, which facilitates cleavage of HF. For neutral $F_3B : Am$ molecules this mechanism is excluded; addition of H^+ to an unshared electron pair of one of the fluorine atoms of the complex does not occur to such an extent as to affect the kinetics of hydrolysis.

The rapid decomposition of BF_3OH^- in alkaline medium is apparently connected with intramolecular proton transfer and successive processes of HF cleavage and water addition:



$$= HF + F_2BO^-$$

$$F_2BO^- + H_2O = [F_2B(OH)_2]^- = HF + FB(OH)O^- \qquad \text{etc.}$$

The rapid decomposition by alkali of other boron fluoro-complexes is explained similarly, for example, $K_2[B_3O_3F_4OH]$ or $Na_3[B_3O_3F_6]$ (1) (in this case there is a mobile equilibrium between $B_3O_3F_6^{3-}$ and BOF_2^- or $F_2B(OH)_2^-$). The same mechanism also explains the rapid decomposition of hydroxyfluoro complexes of a number of other elements, for example $[AsF_5OH]^-$ (9).

The high rate of hydrolysis of BF_3 compounds with ethers, alcohols, etc., is connected with the weakness of the basic properties of the adducts.

The kinetics of hydrolysis of fluoro-complexes of most other elements has not been studied, and assumptions about the mechanism of their hydrolysis cannot be quantitatively substantiated. It is possible that the slow hydrolysis of coordinatively saturated PF_6^- and AsF_6^- proceeds by the S_N1 type, and that, as in the case of BF_4^-, the values of $\Delta S^{\neq}$ are sharply negative; the values of E for these compounds, thermodynamically unstable in aqueous solutions, are unlikely to be large. The rapid hydrolysis of hexafluoro complexes of transition metals (VF_6^-, NbF_6^-) may be connected with addition of water molecules (at the free *d*-levels of the metal atoms) and cleavage of HF as a result of intramolecular proton transfer.

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