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Abstract

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KINETICS OF THE HYDROLYSIS OF PYRIDINE SULFOTRIOXIDE

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As was shown by one of us (^{1}), the activation energies E of the hydrolysis, proceeding by the S_N1 mechanism, of coordination compounds of boron fluoride with amines, in which the solvent attacks the B—N bond, increase smoothly with decreasing pK of the basic dissociation of the amine; the point expressing the relation between the E of hydrolysis of BF_4^- and the pK of the F^- ion lies on the continuation of the same curve, although in BF_4^- it is the B—F bond that is hydrolyzed. The entropy of activation $\Delta S^\ddagger$ for hydrolysis of compounds of BF_3 with amines increases linearly with increasing E; the entropy of activation for hydrolysis of BF_4^- (^{2}) is extremely small, which is apparently caused by an increase in the ordering of the water structure occurring upon elongation of the bond

$$—B \ldots F^-$$

at the moment of formation of the transition state.

The data cited above confirm the existence of a dependence between the kinetics of hydrolysis of a coordination compound and the thermodynamic properties of the donor. It may be expected that, for a series of compounds of one and the same donor with different acceptors (Lewis acids), similar dependences also exist.

The extraordinary similarity of the hydrolysis kinetics of BF_4^- and SO_3F^- (^{3}) is connected both with the similarity of the structure of these ions and of the mechanism of their activation, and also, possibly, with the closeness of the strengths of BF_3 and SO_3 as Lewis acids.

If this is so, then one may expect a closeness of the kinetic characteristics of the hydrolysis of compounds of boron fluoride and sulfuric anhydride with tertiary amines; hydrolysis of the compounds with secondary or primary amines should differ more sharply, owing to the strong acid (proton) dissociation of the compounds of these amines with SO_3.

The kinetics of hydrolysis of $F_3B : Py$, where Py is pyridine, had previously been studied by one of us (^{4}). Concerning the rate of hydrolysis of $O_3S : Py$, there were only qualitative indications. Baumgarten (^{5}) indicated that this compound is relatively stable to the action of water up to 50°; according to A. P. Terent' ev and L. A. Kazitsyna (^{6}), pyridine sulfotrioxide is hydrolyzed by water "so slowly that it can be recrystallized from it."

Synthesis of pyridine sulfotrioxide. We used several modifications in comparison with the method described (^{6}). Into 75 ml of dichloroethane, stirred with a magnetic stirrer, 25 g of sulfuric anhydride was distilled. To the resulting solution, with external cooling by ice and stirring of the solution, a solution of 25 g of Py in 25 ml of dichloroethane was added dropwise. The precipitate $O_3S : Py$ was filtered off on a Nutsche filter, washed with dichloroethane, and freed from excess Py and dichloroethane by drawing dry air through it and subsequent keeping in a desiccator over concentrated sulfuric acid. The product was stored in sealed ampoules; the contents of an opened ampoule were immediately transferred to a weighing bottle placed in a desiccator.

In the synthesis, thoroughly purified and dried reagents were used; the apparatus was assembled with standard ground joints. Contact with atmospheric moisture

was allowed only during transfer of the substance to the weighing bottle and into the desiccator, and also during sealing in ampoules. However, owing to the rapid hydrolysis of $O_3S : Py$ according to the equation

$$O_3S : Py + H_2O = [PyH]HSO_4, \tag{1}$$

the substance obtained contained a considerable admixture of pyridine hydrosulfate.

The total content of SO_3 in the product was determined by precipitation as $BaSO_4$ after complete hydrolysis. The consumption of alkali for titration (in the presence of phenolphthalein) of the products of complete hydrolysis was also determined. Found, %: SO_3 48.43; 48.37; 48.39, on average 48.40; alkali consumption in meq/g: 12.17 and 12.18, on average 12.715.

The SO_3 content was 96.21%, and the alkali consumption was 96.89% of theoretical. This was due both to the content of an inert impurity (dichloroethane) and to the content of $[PyH]HSO_4$. As shown below, hydrolysis of dissolved $O_3S : Py$ at 0° proceeds relatively slowly; this made it possible to determine approximately the content of $[PyH]HSO_4$ in it: a weighed portion of the substance was introduced into ice water containing phenolphthalein and was immediately titrated with alkali to the first coloration of the vigorously shaken suspension. The alkali consumption was 2.44–2.46 meq/g of substance, which corresponds to a content of 21.7% $[PyH]HSO_4$, or 2.20% water bound according to equation (1); the content of inert impurity was therefore 1–1.5% (calculated by difference).

Kinetics of hydrolysis of dissolved pyridine sulfotrioxide. The rate of hydrolysis of pyridine sulfotrioxide according to equation (1) was studied by titrimetric determination of the time dependence of the alkali consumption for titration of $[PyH]HSO_4$ (in the presence of phenolphthalein). Because of the high rate of hydrolysis of $O_3S : Py$, taking samples of the solution for titration would have led to significant errors; therefore the method of successive titration of one and the same solution was used.

At 10-25° the reaction vessel was a double-walled flask closed with a ground-glass stopper, between the walls of which water from an ultrathermostat circulated. About 30 ml of water was introduced into the flask; after it had reached the temperature of the circulating water, a weighed portion of about 0.04 g of $O_3S : Py$, taken in a small weighing bottle, was thrown into the flask, and the flask was shaken vigorously for more rapid dissolution of the precipitate. After dissolution of the precipitate, 1 drop of a 1% alcoholic solution of phenolphthalein* was introduced into the flask, and the solution was periodically titrated with 0.10692 N NaOH from a 5-ml microburette; the moment of coloration of the solution was recorded with a stopwatch. In some experiments an excess of alkali (relative to the pyridine hydrosulfate present at that moment) was periodically added to the solution, and the intervals of time until decolorization of the indicator were measured. Titration with alkali (or introduction of its excess) was carried out as rapidly as possible in order to reduce absorption of CO_2 from the air.

The rate of hydrolysis of $O_3S : Py$, measured by both methods, proved to be the same; consequently, the rate of hydrolysis does not depend on the presence of H^+ or OH^- at moderate concentrations of these ions. The cleavage of $O_3S : Py$ to derivatives of glutaconic aldehyde by the action of concentrated cold alkali, noted by Baumgarten (^{5}), did not occur under the conditions we used. The relative content of pyridine sulfotrioxide in the solution at time ϑ is equal to

$$x = \frac{v_\infty - v}{v_\infty},$$

where v and v_∞ are the consumption of alkali at time ϑ and, respectively, after complete hydrolysis. The results of all experiments were well described by the equation

$$\lg \frac{x_0}{x} = 0.4343\, k\vartheta, \tag{2}$$

which is easily derived for first-order processes.

As is readily shown, x_θ (the value of x extrapolated to $k\vartheta = 0$) must be less than unity, since the initial substance contains pyridine hydrosulfate, which is instantaneously neutralized by alkali; x_0 may differ somewhat from the relative initial content of $O_3S : Py$ in the substance studied because of the difference in

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* A number of experiments showed that under these conditions the consumption of $O_3S : Py$ for sulfation of the alcohol was negligibly small; the indicator also did not react with pyridine sulfotrioxide.

the rates of heterogeneous hydrolysis (at the beginning of the experiment, before complete dissolution of the substance) and hydrolysis of the dissolved pyridine sulfotrioxide.

To study the rate of hydrolysis at 0°, a weighed portion of $O_3S:Py$ (0.07-0.09 g) was introduced into a flask surrounded by ice, with 60-70 ml of ice water and pieces of ice; the change in concentration of the solution due to melting of part of the ice does not affect the results of measuring the rate constant of a first-order reaction.

Table 1

Conditions and results of studying the kinetics of hydrolysis of pyridine sulfotrioxide

No. of experiments	°C	Duration of experiment, min	Number of measured points	$2 + \lg x_0$	$0.4343k$, min^{-1}	$\eta \cdot 10^3$
1	0.0	126.8	6	1.8665	$2.41 \cdot 10^{-3}$	2.8
2	0.0	137.2	8	1.8526	$2.42 \cdot 10^{-3}$	1.8
3	10.0	128.2	8	1.8721	$7.31 \cdot 10^{-3}$	7.7
4	10.0	127.3	8	1.8716	$8.06 \cdot 10^{-3}$	9.2
5*	10.0	146.2	8	1.8689	$7.74 \cdot 10^{-3}$	7.7
6	14.9	61.1	[[unclear: number of measured points]]	1.8711	$1.33 \cdot 10^{-2}$	3.8
7	14.9	74.7	6	1.8010	$1.30 \cdot 10^{-2}$	11.2
8*	14.9	75.4	7	1.7766	$1.26 \cdot 10^{-2}$	2.0
9	15.1	64.2	8	1.8112	$1.40 \cdot 10^{-2}$	9.0
10	25.0	34.3	8	1.8437	$4.06 \cdot 10^{-2}$	12.7
11	25.0	18.4	8	1.7871	$4.12 \cdot 10^{-2}$	9.0

Table 1 gives the experimental conditions and the values of $\lg x_0$ and $0.4343\,k$

(in min^{-1}) calculated by the method of averages; to characterize the scatter of points, Table 1 also gives the mean errors in determining $\lg x$,

$$\eta = \frac{\Sigma|\Delta|}{n},$$

where Δ is the discrepancy between the value of $\lg x$ found for the time ϑ and that calculated from equation (2) for the same ϑ, and n is the number of measurements in one experiment. The maximum value of η corresponds to an error in determining $\lg x$ (or in reading the time) of $\sim 3\%$.

Asterisks mark the experiments (Nos. 5 and 8) in which the hydrolysis of pyridine sulfotrioxide proceeded in an alkaline medium. The higher values of $\lg x_0$ in experiments 1-6 are explained by the fact that they were carried out with a sample of pyridine sulfotrioxide from a freshly opened ampoule; in all cases, $\lg x_0$ decreased with increasing storage time of pyridine sulfotrioxide in a desiccator, in a closed box.

From the values of k averaged for each temperature, except 0°, the following equation, describing the dependence of the rate constant (in min^{-1}) on temperature, was derived by the least-squares method:

$$\lg(0.4343\, k) = -\frac{4088.4}{T} + 12.3215. \tag{3}$$

The discrepancies between the values found and those calculated from equation (3) for $\lg(0.4343\, k)$ are given below:

Temp., °C	$\lg(0.4343k)$ found	$\lg(0.4343k)$ calculated	$\Delta \cdot 10^3$
~ 0	$\bar{3}.3856$	$\bar{3}.3543$	31.3
10.0	$\bar{3}.8856$	$\bar{3}.8817$	4.8
14.9	$\bar{2}.1139$	$\bar{2}.1286$	−14.9
15.1	$\bar{2}.1461$	$\bar{2}.1384$	7.7
25.0	$\bar{2}.6117$	$\bar{2}.6094$	2.3

The value $0.4343\, k$ at $\sim 0°$, not used in calculating the coefficients of equation (3), corresponds to that calculated for +0.57°.

It follows from equation (3) that the experimental activation energy of the hydrolysis of pyridine sulfotrioxide is $E = 18.7$ kcal/mole, and the entropy of activation is $\Delta S^{\neq} = -10.6$ entropy units. For the hydrolysis of $F_3B : Py$, close values were found(4): $E = 20.3$ and $\Delta S^{\neq} = -8.3$. Thus, the similarity we proposed in the kinetics of hydrolysis of both coordination compounds is confirmed. At 25° $O_3S : Py$ is hydrolyzed 5.2 times faster than $F_3B : Py$.

The results of the study show that the hydrolysis of pyridine sulfotrioxide proceeds considerably faster than could have been judged from qualitative data(5,6). At 50° the value of $\lg(0.4343\,k)$ should be equal to $\bar{1}.670$, i.e., the half-life of dissolved $O_3S : Py$ is only 1.5 min.; obviously, recrystallization of pyridine sulfotrioxide from hot water is impossible.

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