KINETICS OF THE ALKALINE HYDROLYSIS OF ALKOXYFLUOROBORATE ANIONS

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The kinetics of the alkaline hydrolysis of BF_3OR^- anions ($R = C_2H_5$, C_3H_7) have been investigated. It has been shown that the reaction mechanism includes the solvolytic dissociation of a B–F bond and that the processes resulting in the replacement of the first fluoride ion act as the rate-limiting step. The influence of the electron-donor ability of the substituents on the rate of processes has been studied, and the reactivity of alkoxyfluoroborates has been compared with the data from quantum-chemical calculations of the distribution of the electron density in the anions in the framework of Dewar's MNDO method with complete optimization of the structural parameters.

It was previously shown that the hydrolysis of fluoroborate complexes, which takes place according to a dissociative mechanism, is strongly influenced by the introduction of substituents which have a positive inductive effect into the inner sphere [1, 2]. For example, the replacement of one fluoride ion in BF_4^- by an electron-donor OCH_3^- ion (the basicity indicators are $pK_{F^-} = 3.2$, $pK_{OCH_3^-} = 15.1$ [3]) results in weakening of the B-F bonds and an increase in the role of hydrolysis by four orders of magnitude. The increase in rate is caused mainly by the decrease in the activation energy (61.0 ± 0.7 kJ/mole as opposed to 74.8 ± 0.8 kJ/mole for BF_4^-), as well as a certain increase in the entropy of activation $\Delta S^{\neq}$ (−93.0 ± 2.0 J/mole·deg for $BF_3OCH_3^-$ and −134.0 ± 2.0 J/mole·deg for BF_4^- [1, 4, 5]). In the present work we studied the kinetics of the alkaline hydrolysis of BF_3OR^- ($R = C_2H_5$, C_3H_7) and compared the reactivity of the alkoxyfluoroborates with the results of the quantum-chemical calculations of the distribution of the electron density in anions in the framework of Dewar's MNDO method [6] with complete optimization of the structure parameters.

EXPERIMENTAL

There is no information in the literture on the synthesis and isolation of salts containing $BF_3OC_2H_5^-$ or $BF_3OC_3H_7^-$ anions in the literature; the ethoxytrifluoroborate ion was detected by ^{19}F NMR in systems containing BF_3 and ethanol in [7, 8]. We obtained $KBF_3OC_2H_5$ and $KBF_3OC_3H_7$ by reacting the corresponding alkoxides with boron trifluoride etherate in absolute alcohols at 308 K and identified them by means of ^{19}F NMR. The products formed were contaminated by tetrafluoroborate ions, which were removed by recrystallization, after which the content of the main substance was equal to ∿95%. It should be noted that the admixture of tetrafluoroborate ions does not have any effect on the kinetic results due to the enormous difference between the rates of hydrolysis of BF_4^- and BF_3OR^-. The kinetics of the hydrolysis process were studied conductometrically with the use of an R 5021 ac bridge, according to the method described in [1, 2]. The calculations of the observed rate constants and activation parameters were carried out by the methods of mathematical statistics (the least-squares method, Neumann's method of confidence intervals, and Grubbs' evaluation of random measurements [9]) on an ES-1050 computer at p = 0.95.

RESULTS AND DISCUSSION

The kinetic curves of the alkaline hydrolysis of $KBF_3OC_2H_5$ constructed in the coordinates of a first-order reaction are presented in Fig. 1. As in the case of $BF_3OCH_3^-$, the process takes place according to a dissociative mechainism, and the rate-limiting step is the elimination of the first fluoride ion. The temperature dependence of the rate is conveyed by the

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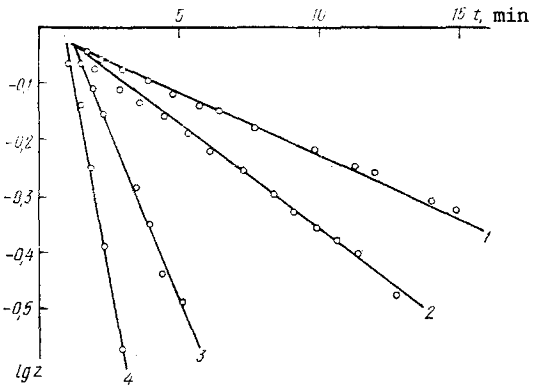

Fig. 1

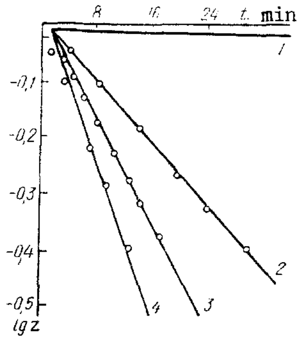

Fig. 2

Fig. 1. Kinetics of the alkaline hydrolysis of $BF_3OC_2H_5^-$ at various temperatures: 1) 273 K; 2) 283 K; 3) 293 K; 4) 303 K; z is the fraction of the undissociated substance.

Fig. 2. Aklaline hydrolysis of alkoxyfluoroborate anions at 273 K: 1) BF_4^-; 2) $BF_3OCH_3^-$; 3) $BF_3OC_2H_5^-$; 4) $BF_3OC_3H_7^-$.

TABLE 1. Basicity of Substituents, Values of $\Delta S^{\neq}$, and Rates of Replacement of Fluoride in BF_3L^-

Anion	$-\Delta S^{\neq}$, J/mole·deg	pK (of substituent)	$\Delta\varepsilon$, eV	K, min^{-1} (at 273 K)
BF_4^-	144±2	3,2	18,36	$6{,}44\cdot10^{-7}$
$BF_3OCH_3^-$	94±2	15,1	14,21	0,029±0,001
$BF_3OC_2H_5^-$	119±2	15.9	13.50	0,051±0,002
$BF_3OC_3H_7^-$	—	16,1	12.82	0,073±0,002

Arrhenius equation

$$\lg K(\mathrm{min}^{-1}) = (10{,}15 \pm 0{,}1) - (3195 \pm 35)/T;$$

The energy and entropy of activation are: $E = 52.7 \pm 1.5$ kJ/mole, $\Delta S^{\neq} = -119.0 \pm 2.0$ J/mole·deg. The comparison of the rates of replacement of the fluoride ions in the isostructural tetrahedral anions of the type BF_3L^-, where L = F, OCH_3, OC_2H_5, and OC_3H_7 is shown in Fig. 2. An increase in the electron donor ability of the substituent results in labilization of the compounds, which is most probably caused by the weakening of the B–F bond. The influence of the substituents on the rate of the monomolecular elimination of a fluoride anion was qualitatively evaluated with the use of perturbation theory as applied to reactivity [10]. The interaction with the solvent evidently results in an increase in the electron density on the negatively charged fluorine atom, i.e., in an increase in its effective electronegativity, which is usually simulated by the appearance of a negative value of the contribution $\Delta\alpha$ (the change in the effective electronegativity of the boron atom) to the corresponding (negative) diagonal elements of the Hamiltonian used in the quantum-chemical calculation. In the zeroth approximation of the mean perturbation-theory energy, the changes in the order of the B–F bond (ΔP) and the electronic stabilization energy (E) in the transition state can be evaluated on the basis of the initial step of the elimination of F^- according to the formula $\Delta P \sim \pi\Delta\alpha$ and $E \sim \pi\Delta\alpha\Delta\beta$, where $\pi \sim P_{B\text{-}F}(P_F - 1)$ is an analog of the polarizability for an atom (F) or a bond (B–F) [10], and a positive value for the increment of the resonance integral $\Delta\beta$ corresponds to weakening of the B–F bond during dissociation. Since the order of the B–F bond ($P_{B\text{-}F}$), the value of $P_F - 1$ (the electron density on F^- is significantly greater than unity), and the mean value of the one-electron perturbation $\bar{\Delta\varepsilon}$ are also possible, $\Delta P < 0$ and $E < 0$. It follows from the results of the calculations performed that P_F and $P_{B\text{-}F}$ are practically independent of the substituent. The largest contribution to $(\bar{\Delta\varepsilon})^{-1}$ is made by the difference between the energies of the low unoccupied and highest occupied molecular orbitals ($\bar{\Delta\varepsilon} \sim \Delta\varepsilon = \varepsilon_{LUMO} | - \varepsilon_{HOMO}$), which varies appreciably for different substituents. Thus, the rate constant increases antibatically as $\Delta\varepsilon$ decreases, as is confirmed by the data in Table 1.

In contrast to the case considered of a series of monosubstituted derivatives, in which the calculated charge of the boron atom q_B changes slightly, this magnitude is very sensitive to the degree of substitution. Thus, in the series $BF_4^- \to BF_3OCH_3^- \to BF_2(OCH_3)_2^- \to BF(OCH_3)_3^-$ q_B is equal to 0.373, 0.344., 0.307, 0.278. This allows us to compare q_B to the strength of the B–F bond, since the charge on the fluorine atom remains practically constant in all the compounds calculated (−0.32 to −0.35) due to the high electronegativity of this atom, and the value of q_B actually reflects the energy of this predominantly ionic bond. Therefore, the increase in the reaction rate along a series of polysubstituted derivatives is attributable mainly to the relative increase in the height of the base of the barrier to the reaction, while in the case of the series of monosubstituted derivatives considered above, it is completely determined by the decrease in the energy of the transition state. The latter effect is also observed in the case of $BF_{4-n}(OCH_3)_n^-$, but in a less pronounced form: $\Delta\varepsilon$ takes on the values 14.19, 13.78, and 13.302 eV as n is varied from 1 to 3. The absence of a correlation between the value of $\Delta S^{\neq}$ and the basicity of the substituent in the series of alkoxytrifluoroborate anions is observed. The values of $\Delta S^{\neq}$, which are significant in magnitude and negative in sign are undoubtedly caused by solvation effects, i.e., the enhancement of the hydration of the transition state following the removal of a fluoride ion from the inner coordination sphere [11]. It is interesting that the transition from the tetrafluoroborate anion to BF_4OR^- is accompanied by the observation of an increase in $\Delta S^{\neq}$, which is probably caused by some enhancement of the hydration of the original complexes. The slight decrease in $\Delta S^{\neq}$ along the series $BF_4^- \to BF_3OCH_3^- \to BF_3OC_2H_5^-$ may be caused by a decrease in hydration as a result of the incresae in the length of the hydrocarbon radical.

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