The purpose of this work was to study the kinetic principles and mechanism of the hydrolysis of an N-methyl-substituted anilide in aqueous solutions of potassium hydroxide and to verify the applicability of the alkalinity function $B_0$ [1, 2] to the description of the dependence of the effective reaction rate constant $k_{\text{eff}}$ on the alkali concentration in aqueous solution.

**EXPERIMENTAL METHOD**

N-Methylorthonitroacetanilide was synthesized by alkylation of ortho nitroacetanilide with methyl iodide in anhydrous acetone medium in the presence of powdered potassium hydroxide.

Chemically pure potassium hydroxide, produced in the German Democratic Republic, was used. A saturated aqueous solution of KOH was prepared, it was freed of carbonate impurities by filtration. More dilute solutions were prepared from this solution by the addition of the required amount of double-distilled water by weight. The alkali concentration was determined by titration with sulfuric and hydrochloric acids. The kinetic measurements were performed by the spectrophotometric method. The degree of conversion of the anilide to the reaction products was determined according to the change in the optical density of the solution at $\lambda = 410$ nm. The experiments were conducted in quartz cuvettes, which were thermostatically controlled with an accuracy of $\pm 0.1^\circ$. The anilide was introduced into an aqueous solution of alkali in the form of an aqueous solution. The concentration of the anilide in the optical cuvette was $\sim 10^{-4}$ M. The rate of hydrolysis is described by a first-order equation with respect to the anilide. As a result of hydrolysis, N-methyl ortho nitroaniline and potassium acetate are formed. Judging by the absorption spectra of the reaction products in the visible region, the process is irreversible.

Figure 1 presents a typical kinetic curve of the hydrolysis of N-methyl orthonitroacetanilide. The rate constant was calculated according to the equation for first-order reactions:

$$k_{\text{eff}} = \lg \frac{D_0 - D_c}{D_\infty - D_c}$$

where $D_0$, $D_c$, and $D_\infty$ are the initial, current, and final optical densities, respectively. $k_{\text{eff}}$ remains constant all the way up to complete conversion of the anilide to the hydrolysis products. Figure 1 also presents a logarithmic plot of the kinetic curve (straight line in a plot of $-\log (D_\infty - D_c)$ versus t).

**DISCUSSION OF RESULTS**

Table 1 presents the rate constants of the hydrolysis of N-methyl orthonitroacetanilide in aqueous solutions of potassium hydroxide at $25^\circ$. As can be seen from these data, increasing the alkali concentration in aqueous solution leads to a sharp increase in $k_{\text{eff}}$. In

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Fig. 2. Dependence of the value of $\frac{b^2a_{H_2O}}{k_{eff}}$ on the alkalinity of the medium $b_0$ for the concentration interval 11.5–35.0% KOH.

relatively dilute solutions of potassium hydroxide, $k_{eff}$ increases practically as the square of the alkalinity of the medium.

$$\frac{k_{eff}}{b_0^2a_{H_2O}} = (8.4 \pm 0.2) \times 10^{-4} \text{ min}^{-1}$$

(1)

Eq. (1) is satisfactorily observed up to a 10% solution of KOH in water. In more concentrated solutions $k_{eff}$ increases more slowly than should have been expected according to Eq. (1), while in highly concentrated solutions of alkali (in the range 34–40.8% KOH), the effective rate constants of hydrolysis and the alkalinity of the medium $b_0$ are related by the function

$$\frac{k_{eff}}{b_0a_{H_2O}} = (7.8 \pm 0.8) \times 10^{-3} \text{ min}^{-1}$$

(2)

To explain such a complex dependence of $k_{eff}$ on the properties of the solution, we should consider the following circumstances. On the basis of the results of experiments on the measurement of the coefficients of distribution of N-methylorthonitroacetanilide between aqueous solutions of potassium hydroxide and carbon tetrachloride, it must be considered that in relatively dilute solutions of KOH, the anilide exists practically entirely in a nonionized form. With a small error, it can also be assumed that in relatively dilute alkalies, the ratio of the activity coefficients in the kinetic equation is constant. On the basis of the aforementioned, to explain the dependence (1) it must be assumed that the activated state of the hydrolysis of N-methylorthonitroacetanilide is formed from the doubly ionized form of the anilide and two molecules of water. The singly ionized form can be formed only by the addition of a hydroxyl ion to the carbonyl group of the anilide.

$$H_3C \quad N-C-C-O^- + OH^- \rightleftharpoons H_3C \quad N-C-C-\bar{O}^- + H_2O$$

Let us denote the first ionization constant as $K_1$

$$K_1 = \frac{a_Ba_{OH}}{a_Ba_{H_2O}} \cdot \frac{C_B}{C_{BOH}} = \frac{f_B}{f_{BOH}} = K_1 = \frac{C_B}{C_{BOH}} - b_0$$

$a_B$, $a_{BOH}$, $a_{OH}$ are the activities of the nonionized and ionized form of the anilide and hydroxyl ions, respectively; $f_B$ and $f_{BOH}$ are the activity coefficients of the nonionized and singly ionized forms of the anilide.

Let us replace the quantity $a_{OH}f_B/f_{BOH}$ by the alkalinity $b_0$. The twice ionized form can be formed in the interaction of the hydroxyl ion with the singly ionized form

$$H_3C \quad N-C-C-O^- + \bar{O}H \rightleftharpoons H_3C \quad N-C-C-\bar{O}^- + H_2O$$

The equilibrium constant of the reaction of formation of the twice ionized form will be denoted as $K_2$

$$K_2 = \frac{a_{BOH}a_{OH}}{a_{BOO}a_{H_2O}} \cdot \frac{C_{BOO}}{C_{BOOH}} = \frac{f_{BOOH}}{f_{BOO}} = \frac{C_{BOOH}b_0}{C_{BOOH}a_{H_2O}} = K_2$$

$a_{BOO} = f_{BOOH} = c_{BOO} = $ are the activity, activity coefficient, and concentration of the doubly ionized form. If the activated state of the reaction is formed from the twice ionized form and two molecules of water, then [5]