KINETICS AND MECHANISM OF THE HYDROLYSIS OF N-METHYLPARANITROACETANILIDE AND N-METHYLMETANITROACETANILIDE IN AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE

A. Kh. Pochikyan and M. I. Vinnik

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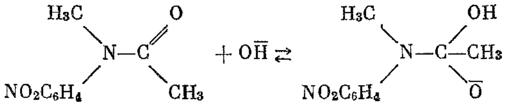
In contrast to nitroacetanilides, where ionization at the –N–H– and –C = O bonds is possible, in the case of N-methyl-substituted nitroanilides, the ionization can be explained only by the addition of a hydroxyl ion to the carbonyl group



In this work we studied the kinetic principles of the hydrolysis of N-methylparanitroacetanilide and N-methylmetanitroacetanilide to determine their ionization constants in solutions of potassium hydroxide and to determine the mechanism of the limiting step of hydrolysis.

EXPERIMENTAL METHOD

N-Methylparanitroacetanilide was synthesized from methylaniline by acylation with acetic anhydride [1] and nitration with a nitrating mixture [2]. N-Methylmetanitroacetanilide was synthesized from m-nitroaniline by acylation with acetic anhydride and alkylation with methyl iodide in acetone in the presence of KOH powder [3]. The products were recrystallized from a mixture of ethanol and water and identified according to the melting points, which corresponded to the data of [4].

Solutions of alkali were prepared from cp. KOH. The solution was filtered until a transparent homogeneous solution was obtained, and its concentration was determined by titration with acid according to phenolphthalein. More dilute solutions were prepared from the initial solution by dilution with water by weight. The kinetics of the process was studied by a spectrophotometric method, according to the change in the optical density at 370-410 nm, where a maximum difference of the molar absorption coefficients of the corresponding anilides and anilines is observed.

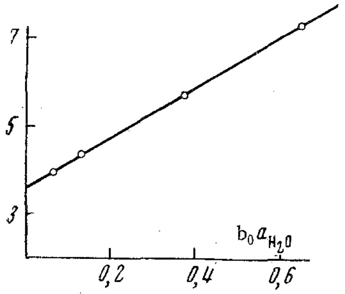


Fig. 1. Dependence of the value of $10^6 \cdot k_{eff}/b_0$ on $b_0 a_{H_2O}$ for the hydrolysis of N-methylmetanitroacetanilide in the interval 0.46-5% KOH at 25°.

The experiments were conducted in thermostatically controlled quartz cuvettes; the temperature was controlled with an accuracy of ±0.1°; the anilide concentration was $\sim 10^{-4}$ M, and its influence on the medium can be neglected. The anilide was introduced into the cuvette with the alkali in the form of an aqueous solution with a concentration $\sim 10^{-2}$ M. As a result of the reaction, the anilides are entirely converted to anilines and the potassium salt of acetic acid. The process is first order with respect to the anilide, and the kinetic curves are well described by the equation for monomolecular reactions.

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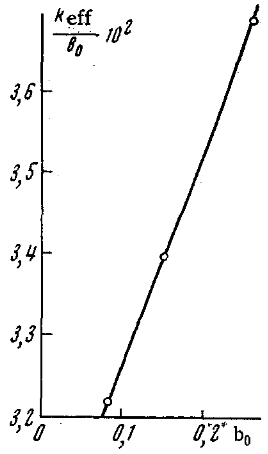

Fig. 2

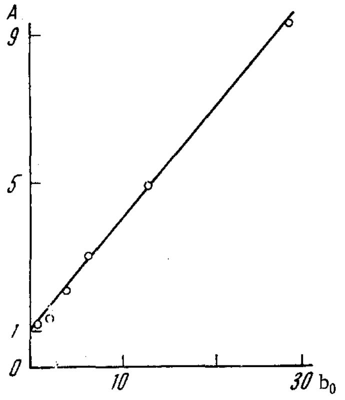

Fig. 3

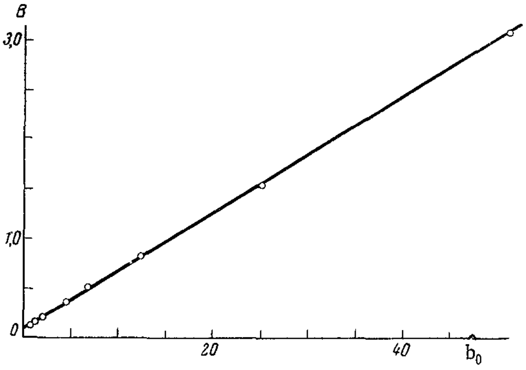

Fig. 4

Fig. 2. Dependence of the value of k_{eff}/b_0 on the alkalinity of the medium b_0 for the hydrolysis of N-methylparanitroacetanilide in the interval 0.60-1.97% KOH at 25°.

Fig. 3. Determination of the true rate constants and equilibrium constants of the formation of the singly ionized form in the hydrolysis of N-methylmetanitroacetanilide (25°).

$$A - \frac{b_0}{k_{\text{eff}}} \cdot 3.6 \cdot 10^{-3} + \frac{b_0^2 a_{\mathrm{H_2O}}}{k_{\text{eff}}} \cdot 5.85 \cdot 10^{-3}$$

Fig. 4. Determination of the true rate constants and equilibrium constants of the formation of the singly ionized form during the hydrolysis of N-methylparanitroacetanilide (25°).

$$B = \frac{b_0}{k_{\text{eff}}} \cdot 3 \cdot 10^{-2} + \frac{b_0^2 a_{\mathrm{H_2O}}}{k_{\text{eff}}} \cdot 2.7 \cdot 10^{-2}$$

TABLE 1. Effective Rate Constants of the Hydrolysis of N-Methylparanitroacetanilide in Aqueous Solutions of KOH at 25°

KOH content, % by mass	k_{eff}, min^{-1}	b_0	$a_{\mathrm{H_2O}}$
0,60	$2,67 \cdot 10^{-3}$	$8,3 \cdot 10^{-2}$	1,0
1,14	$5,10 \cdot 10^{-3}$	0,15	1,0
1,97	$9,60 \cdot 10^{-3}$	0,26	1,0
3,02	$1,56 \cdot 10^{-2}$	0,43	0,995
5,02	$2,77 \cdot 10^{-2}$	0,71	0,980
7,98	$5,02 \cdot 10^{-2}$	1,26	0,955
11,1	$8,21 \cdot 10^{-2}$	2,11	0,935
16,8	$1,72 \cdot 10^{-1}$	4,58	0,86
19,9	0,24	6,92	0,82
24,4	0,43	12,4	0,76
29,7	0,775	25,2	0,66
34,5	1,33	51,3	0,56

Note: The activities of water were taken from [5]. The values of b_0 for 25° were calculated as average ionic activities of KOH for this temperature. The activity of KOH was taken from [6]. The values of $b_0 = a\pm$ for diluted solutions were taken from the book [7].

DISCUSSION

Tables 1 and 2 present the experimental values of the effective rate constants of hydrolysis (k_{eff}) of N-methylparanitroacetanilide and N-methylmetanitroacetanilide in aqueous solutions of potassium hydroxide at 25°. As can be seen from the tables, with increasing alkali concentration the effective rate constant k_{eff} increases. In the hydrolysis of N-methylorthonitroacetanilide [8], the kinetic curves are described by a scheme according to which the singly ionized form does not possess reactivity. The activated state of the reaction is formed from the doubly ionized form of the anilide and two molecules of water. The singly ionized form of N-methylorthonitroacetanilide is nonreactive, apparently on account of the formation of a hydrogen bond between the oxygen of the nitro group and the hydrogen of the carboxyl group. Probably if there were no hydrogen bond, the singly ionized form would possess reactivity.

It is natural to assume that as a result of the ionization of N-methyl-m- and p-nitroacetanilides in alkaline solution, singly and doubly ionized particles can be formed. However, in the case of the p-nitro derivatives, in our opinion, the singly ionized form should possess reactivity, since no hydrogen bond can be formed between the hydrogen of the carboxyl group and the nitro group. In the m-nitro derivative, there is a possibility of formation of a hydrogen bond, but it is weaker than in the o-nitro derivative.

From Table 2 it is evident that in the case of N-methylmetanitroacetanilide, even in dilute solutions of alkali, where the activity of water is practically constant, there is no linear relationship between k_{eff} and b_0. Similarly to the case of N-methylorthonitroacetanilide, as the alkali concentration is increased, k_{eff} increases more rapidly than b_0. Constancy of k_{eff}/b_0 is observed only in concentrated solutions of

TABLE 2. Effective Rate Constants of the Hydrolysis of N-Methylmetanitroacetanilide in Aqueous Solutions of KOH at 25°

KOH content, % by mass	k_{eff}, min^{-1}	b_0	a_{H_2O}
0,46	$2,6 \cdot 10^{-4}$	0,065	1,0
0,95	$5,8 \cdot 10^{-4}$	0,13	1,0
2,94	$2,12 \cdot 10^{-3}$	0,37	0,99
2,95	$2,23 \cdot 10^{-3}$	0,37	0,99
5,00	$4,60 \cdot 10^{-3}$	0,64	0,98
10,1	$1,58 \cdot 10^{-2}$	1,82	0,93
15,4	$4,00 \cdot 10^{-2}$	3,71	0,89
19,1	$7,05 \cdot 10^{-2}$	6,24	0,83
24,7	0,158	12,8	0,76
30,4	0,342	28,2	0,66

KOH (15.4-30.4% KOH). To explain such a dependence of k_{eff} on b_0, let us assume that in solutions of alkali, the singly and doubly ionized forms possess reactivity

$$B + \overline{OH} \rightleftarrows B\overline{OH} \qquad K_1 = \frac{C_B b_0}{C_{B\overline{OH}}}$$

$$B\overline{OH} + \overline{OH} \rightleftarrows BOO^{=} + H_2O \qquad K_2 = \frac{C_{B\overline{OH}}\ b_0}{C_{BOO^{=}}\, a_{H_2O}}$$

K_1 is the equilibrium constant of formation of the singly ionized form; K_2 is the equilibrium constant of formation of the doubly ionized form from the singly ionized form; C_B, $C_{B\overline{OH}}$, $C_{BOO^{=}}$ are the concentrations of the nonionized, singly ionized, and doubly ionized forms, respectively; b_0 is the alkalinity of the medium.

Let us assume also that the singly ionized form undergoes monomolecular decomposition to the reaction products, while the doubly ionized form forms an activated complex with two water molecules, and that in the kinetic equation, the ratio of the activity coefficients does not depend on the composition of the medium [9]. Then the reaction rate is expressed as

$$W = k'_{true}\, C_{B\overline{OH}} + k''_{true}\, C_{BOO^{=}} a^2_{H_2O},$$

where k'_{true} and k''_{true} are the true rate constants of conversion of the singly and doubly ionized forms, respectively.

If the degree of ionization is negligible ($C_B \approx C_0$)

$$k_{eff} = \frac{k'_{true}}{K_1} b_0 + \frac{k''_{true}}{K_1 K_2} b_0^2 a_{H_2O}$$

or

$$\frac{k_{eff}}{b_0} = \frac{k'_{true}}{K_1} + \frac{k''_{true}}{K_1 K_2} b_0 \cdot a_{H_2O}. \tag{1}$$

Equation (1) describes the data up to 5% KOH (Fig. 1). In a plot of k_{eff}/b_0 versus $b_0 a_{H_2O}$, a straight line is obtained, and the values $k'_{true}/K_1 = 3.6 \cdot 10^{-3}$ and $k''_{true}/K_1K_2 = 5.8 \cdot 10^{-3}$ were determined by a graphical method. For N-methylparanitroacetanilide, Eq. (1) describes the data up to 2% KOH (Fig. 2): $k'_{true}/K_1 = 3.0 \cdot 10^{-2}$ and $k''_{true}/K_1K_2 = 2.7 \cdot 10^{-2}$. In concentrated solutions of alkali, the relative concentration of the singly ionized form should increase, and $C_0 = C_B + C_{B\overline{OH}}$. Considering ionization, the following expression is obtained for the effective rate constant

$$\frac{k'_{true}}{K_1} \cdot \frac{b_0}{k_{eff}} + \frac{k''_{true}}{K_1 K_2} \cdot \frac{b_0^2 a_{H_2O}}{k_{eff}} = \frac{1}{K_1} b_0 + 1. \tag{2}$$

Since the values of k'_{true}/K_1 and k''_{true}/K_1K_2 are known from dilute solutions, there is a possibility of graphical calculation of the values of K_1 and k'_{true} (Figs. 3 and 4).

For N-methylmetanitroacetanilide, $K_1 = 3.38$, $k'_{true} = 1.22 \cdot 10^{-2}$ min^{-1}; N-methylparanitroacetanilide, $K_1 = 1.8$, $k'_{true} = 5.33 \cdot 10^{-2}$ min^{-1}. However, the experimental data on the hydrolysis of N-methylparanitroacetanilide in aqueous solutions of alkali are also described according to another scheme. As can be seen from Table 1, in the case of N-methylparanitroacetanilide, up to 20% KOH, a linear relationship is observed between the effective rate constant and the alkalinity b_0. This can also be explained as follows: in this region of potassium hydroxide concentrations, the degree of ionization is negligible, while the ratio of the activity coefficients of the ionized form and of the activated complex is constant. In more concentrated solutions, k_{eff} increases more slowly than b_0. If we consider that in this region the substance is substantially ionized, then according to the equation

$$k_{eff} = k'_{true}\, b_0 / K_1 + b_0 \tag{3}$$

we can determine the values $K_1 = 104$, $k'_{true} = 4.0$ min^{-1}.

It should be mentioned that the experimental data on the hydrolysis of N-methylmetanitroacetanilide in aqueous solutions of potassium hydroxide are not described by Eq. (3).

Thus, on the basis of the kinetic data on the first and second mechanisms of the hydrolysis of N-methylparanitroacetanilide, the value of the ionization constant obtained is equal to 1.8 and 104, respectively.

Since direct methods of determining the equilibrium constant of ionization are unavailable in this case on account of the low solubility of the reagents, on the basis of the available data it is not yet possible to establish precisely which of the proposed mechanisms of the hydrolysis of N-methylparanitroacetanilide is actually realized in aqueous solutions of alkali.

CONCLUSIONS

1. The kinetic principles of the hydrolysis of N-methylmetanitroacetanilide and N-methylparanitroacetanilide in aqueous solutions of potassium hydroxide were studied by a spectrophotometric method at 25°.

2. The investigated anilides exist in aqueous solutions of potassium hydroxide in three forms: nonionized, singly ionized, and doubly ionized. The effective rate constant is determined by the relative concentrations of the singly and doubly ionized forms.

3. The true rate constants of hydrolysis and the equilibrium constants of the formation of the singly ionized form of N-methylmetanitroacetanilide and N-methylparanitroacetanilide were calculated.

LITERATURE CITED

1. R. Stormer, Ber., 31, 2529 (1898).
2. Yu. K. Yur'ev, Practical Studies in Organic Chemistry [in Russian], MGU, III (1961), p. 42.
3. I. J. Pachter and M. Kloetrer, J. Amer. Chem. Soc., 74, 1321 (1952).
4. Dictionary of Organic Compounds [in Russian], Moscow (1949).
5. E. Shibata, J. Kobayachi, and S. Fukinawa, J. Chem. Soc. Japan, 52, 404 (1931).
6. R. A. Robinson and R. M. Stokes, Trans. Faraday Soc., 45, 612 (1949).
7. R. Robinson and R. Stokes, Solutions of Electrolytes [Russian translation], IL (1963), p. 575.
8. M. I. Vinnik and A. Kh. Pochikyan, Izv. Akad. Nauk SSSR, Ser. Khim., 1213 (1971).
9. M. I. Vinnik and Y. V. Moiseyev, Tetrahedron, 19, 1441 (1963).