KINETICS AND MECHANISM OF THE REVERSIBLE DECOMPOSITION OF CERTAIN NITROALCOHOLS IN WATER

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The condensation of nitro-compounds with aldehydes is a convenient model reaction for investigating problems associated with the basicity and nucleophilicity of carbanions with respect to carbon [1, 2]. The mechanism of this process is described by the general scheme of aldol condensation [2-5], where the first step is ionization of the nitro-compound under the action of bases. Nucleophilic addition of carbanions of nitro-compounds to an aldehyde is the limiting step of the entire process. In aqueous solutions in the case of a low concentration of the reagents and high pH, the equilibrium of the reaction is strongly shifted in the direction of the starting materials. Therefore it is considerably more convenient to investigate the reverse reaction – decomposition of nitroalcohols [2-5]. The equilibrium constant of this process is expressed as follows [1]

$$K_{\text{equil}} = \frac{k_{-1}}{k_1}\frac{[\mathrm{A}^-][\mathrm{C}]}{[\mathrm{AH}][\mathrm{OH}^-]},$$

where [AH] is the concentration of the nitroalcohol in the mixture at equilibrium; [A$^-$] is the concentration of the anion of the nitro-compound; [C] is the concentration of the aldehyde; k_1 is the rate constant of decomposition of the nitroalcohol; k_{-1} is the rate constant of interaction of the anion of the nitroalcohol with the aldehyde. The values of k_{-1} can be found directly by calculating the kinetic curves of the decomposition of the nitroalcohol under conditions when this process does not go to completion [2, 3].

In this work we are reporting data on the decomposition of α-nitro-β-hydroxybutyric ester (I), α-nitro-α-methyl-β-hydroxybutyric ester (II), α-nitro-α-methyl-β-hydroxypropionic ester (III), and 3-nitro-3-methylbutanol-2 (IV). We had performed measurements for α-nitro-β-hydroxybutyric ester (I) and α-nitro-α-methyl-β-hydroxybutyric ester (II) earlier on a pH-stat in unbuffered media [6]. Under these conditions the inertia of the glass electrode is high, and the rate constants obtained from the kinetic curves of the consumption of the titrant with time are elevated. Moreover, the acidity constant of (II) was determined incorrectly. This value was obtained by extrapolating the curve of the change in the pH of the mixture of (II) with a solution of KOH with respect to time to zero time. Here we erroneously assumed that the change in the pH of the medium occurs on account of the formation of α-nitropropionic ester, which is less acidic than (II), as a result of the decomposition. A more detailed analysis of the data obtained indicated that under these conditions the decomposition of (II) occurs very rapidly with the formation of the anion of α-nitropropionic ester. The recombination of this compound under the action of hydroxonium ions is actually the cause of the change in the pH of the medium. In other words, extrapolation of the curves of the pH change obtained by mixing a weighed sample of (II) and a solution of KOH to zero time does not characterize the acidity of the hydroxyl group of the nitroalcohol. In view of this we were forced to repeat the measurements for (I) and (II), using a spectrophotometric method.

TABLE 1. Dependence of k_{eff} of the Decomposition of (I) on the Buffer Capacity of the Medium (pH 5.0, acetate buffer, $\mu = 0.5$)

Concentration of base, M	$k_{\text{eff}} \cdot 10^3$, sec^{-1}
0.3	1.75
0.03	1.67
0.003	1.70

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TABLE 2. Decomposition of (I) in Buffered Aqueous Solutions at 25° and $\mu = 0.5$

pH	$k_{eff} \cdot 10^3$, sec^{-1}	Error·10^3*	Buffer
5.0	1.75	0.07	Acetate
5.65	6.80	0.08	Mixed acetate–phosphate
6.0	14.30	0.2	Phosphate
6.2	20.0	0.5	The same
6.37	22.0	0.8	" "
6.52	35.0	1.5	" "
6.75	42.0	1.0	" "
6.95	41.0	0.6	" "

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* Mean square error of the arithmetic mean.

EXPERIMENTAL

All the reagents used were cp grade. The water was redistilled twice before use, the second time in a stream of nitrogen.

α-Nitro-β-hydroxybutyric and α-nitro-α-methyl-β-hydroxybutyric esters were produced and purified as described in [6]. α-Nitro-α-methyl-β-hydroxypropionic ester was produced according to the procedure of [7] from formaldehyde and α-nitropropionic ester; bp 77-78° (0.5 mm); n_D^{20} 1.4489. Found: C 36.72; 36.78; H 5.61; 5.60; N 9.42; 9.13%. $C_4H_9NO_3$. Calculated: C 36.8; H 5.52; N 8.58%. 3-Nitro-3-methylbutanol-2 was produced according to the procedure of [8], using acetic acid for the acidification of the reaction mass, bp 59° (1 mm); n_D^{20} 1.4462. According to the data of [9]: bp 64° (2 mm); n_D^{26} 1.4469; [10]: n_D^{25} 1.4457.

All the spectrophotometric measurements were conducted on an EPS-3 recording spectrophotometer in quartz cuvettes, placed in a thermostatically controlled cuvette holder. The pH was measured on a PHM-4 "Radiometer" instrument. The dissociation constant of the nitropropionic ester was determined by the usual method [11] on a PHM-4 "Radiometer" instrument. The value of K_a found was equal to $4.0 \cdot 10^{-7}$ M.

DISCUSSION OF RESULTS

The decomposition of (I) was studied spectrophotometrically in aqueous buffered solutions with $\mu = 0.5$ at 25°C. The use of this method was possible because the nitroacetic ester obtained as a result of the reaction is sufficiently ionized in the range of pH 5.0-7.0, and the absorption of its anion is great ($\varepsilon = 1.4 \cdot 10^4$, $\lambda_{max} = 295$ nm) in comparison with the absorption of the initial nonionized nitroalcohol (at 295 nm, $\varepsilon \approx 20$). In the solutions with the concentrations that we used (10^{-4} M), the decomposition of (I) goes practically entirely to acetaldehyde and nitroacetic ester. This was demonstrated by the fact that the UV spectrum of the final decomposition product of (I) is identical with the spectrum of nitroacetic ester under the same conditions. The experimental procedure and calculation of the rate constants were the same as in [4]. The decomposition of (I) obeys the principles of first-order kinetics. In this case no dependence of the rate of the process on the buffer capacity of the medium and on the composition of the buffer is observed (Table 1). The calculated values of k_{eff} are cited in Table 2.

The dependence of k_{eff} on the activity of hydroxyl ions is presented in Fig. 1. The curve obtained is evidence that at high pH values the rate of decomposition of (I) ceases to depend on the activity of hydroxyl ions in solution. The dependence of $1/k_{eff}$ on the activity of hydroxonium ions (in the system) represents a straight line with correlation coefficient 0.99 (Fig. 2). The slope of the straight line is equal to $(5.56 \pm 0.1) \cdot 10^7$ $mole^{-1} \cdot sec$. The segment intercepted is equal to 16.72 ± 2.3 sec. The absence of a dependence of the rate of the process on the buffer capacity of the system and the characteristic dependence of $1/k_{eff}$ on $a_{H_3O^+}$ (see Fig. 2) confirm the fact that the decomposition of (I) is described by a scheme in which the rates of establishment of acid – base equilibria leading to a reactive particle are sufficiently high in comparison with the rate of its decomposition. In this case the characteristic dependence of k_{eff} on $OH^{\ominus}$ in the region of high pH can be explained in two ways. In the first place, it is possible that at high pH values the concentration of O-anions of the nitroalcohol becomes comparable with the concentration of the initial compound, and this leads to the fact that a further increase in the pH of the medium does not accelerate the process [12]. However, the data on the decomposition of compound (II), the acidity of the hydroxyl group of which should

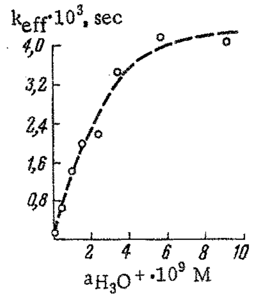

Fig. 1. Dependence of k_{eff} of the decomposition of (I) on the activity of hydroxyl ions.

TABLE 3. Decomposition of (II) in Water at 25°C and μ = 0.5

pH	k_{eff}, sec^{-1}	Error $\cdot10^3$*	Buffer solution
4,8	$3{,}20\cdot10^{-4}$		Acetate
5,4	$1{,}10\cdot10^{-3}$	0,03	The same
5,7	$2{,}42\cdot10^{-3}$	0,02	Acetate-phosphate
6,0	$4{,}55\cdot10^{-3}$	0,05	The same
6,32	$8{,}80\cdot10^{-3}$	0,1	Phosphate
6,85	$22{,}50\cdot10^{-3}$	0,3	The same
7,12	$60{,}00\cdot10^{-3}$	1,0	" "

* Mean square error of the arithmetic mean.

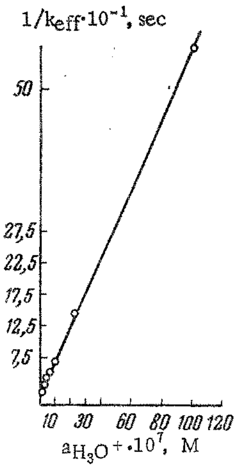

Fig. 2. Dependence of $1/k_{eff}$ of the decomposition of (I) on the activity of hydroxonium ions.

be the same as for (I), are not described by such a dependence on OH. The presence of acid – base equilibrium, leading to a C-anion of (I), which does not participate in the decomposition, is the second, most probable explanation. In this case the dependence of k_{eff} on the activity of hydroxonium ions will be described by the following formula [6]:

$$1/k_{eff} = \frac{K_1}{K_2k_3} + \frac{a_{H_3O^+}}{K_2k_3},$$

where K_1 is the constant of acid – base equilibrium, characterizing the acidity of the α-proton of (I); K_2 is the acidity constant of the OH group of (I); k_3 is the rate constant of the decomposition of the O-anion of (I). From this, using the dependence of $1/k_{eff}$ on $a_{H_3O^+}$ (see Fig. 2), we can find K_2k_3 and K_1. K_1 and K_2k_3 are equal to $(3.0 \pm 0.6)\cdot10^{-7}$ mole and $(1.79 \pm 0.02)\cdot10^{-8}$ mole·sec^{-1}, respectively.

The decomposition of (II) in water was studied spectrophotometrically according to the increase in the absorption at 290 nm (the maximum absorption of the anion of the nitropropionic ester). Buffered solutions with pH from 4.8 to 7.1 and μ = 0.5 were used. The measurements were conducted at 25°C. The decomposition of (II) at the concentration 10^{-4} M goes entirely to the final products, which was confirmed by a comparison of the UV spectra of the final product of the decomposition and the spectrum of the nitropropionic ester under the same conditions. The decomposition of (II) is complicated by the fact that this compound exists in the form of a mixture of approximately equal amounts of the diastereomers. In contrast to (I), the diastereomers of (III) cannot be interconverted on account of dissociation of the α-proton of this compound with the formation of a flat anion. However, the decomposition of the diastereomers of (II) occurs at approximately equal rates [6]. In other words, the presence of diastereomers does not complicate the kinetics of the decomposition of (II). The decomposition of (II) obeys the principles of first-order reactions. The kinetic curves were calculated by the usual method. The values obtained for k_{eff} are cited in Table 3.

A graph constructed as a plot of $1/k_{eff}$ versus $a_{H_3O^+}$ (Fig. 3) represents a straight line with slope $(1.97 \pm 0.04)\cdot10^8$ mole^{-1}·sec. The straight line passes through the origin within the limits of the experimental error. This is evidence that the decomposition of (II) is described by the usual scheme of decomposition of nitroalcohols [3, 4]. The equilibrium constant of the decomposition of (II) was determined potentiometrically on a "Radiometer" pH-stat. The method of determination of K_{equil} was the same as for 3,3-dinitrobutanol-2 [4]. K_{equil} obtained in this way is equal to $(6.3 \pm 3.0)\cdot10^5$. From this the rate constant of the interaction of the anion of nitropropionic ester with acetaldehyde is equal to 0.805 ± 0.5 sec^{-1}·mole^{-1}.

TABLE 4. Decomposition of (III) in Water at 25°C and $\mu = 0.1$

pH	$K_{equil} \cdot 10^{-3}$	k_{-1}, mole^{-1} $\cdot$sec^{-1}	Method
7,86	9,4		Polarographic
7,94	9,5		The same
7,50	12,1	0,17	Spectrophotometric
7,50	10,7	0,19	The same
7,50	9,95	0,21	" "
Average	$K_{equil} = 1{,}03 \cdot 10^4 \pm 0{,}1 \cdot 10^4$	0,19±0,06	

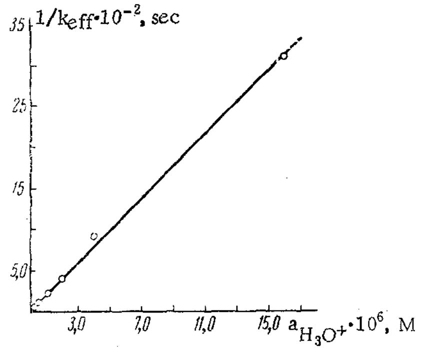

Fig. 3. Dependence of $1/k_{eff}$ of decomposition of (II) on the activity of hydroxonium ions.

TABLE 5. Decomposition of (IV) in Water at 25°C and $\mu = 0.1$

pH	$K_{equil} \cdot 10^{-4}$	$k_{-1} \cdot 10^3$, mole^{-1} $\cdot$sec^{-1}
9,2	2,22	5,22
9,4	1,72	5,70
9,4	2,22	7,20
9,5	1,93	7,70
9,5	1,64	6,07
9,6	1,66	7,10
Average	$(1{,}9 \pm 0{,}3) \cdot 10^4$	$(6{,}5 \pm 0{,}9) \cdot 10^{-3}$

The reversible decomposition of (III) was studied spectrophotometrically and polarographically in water at the temperature 25°C and $\mu = 0.1$ (Table 4). As in the case of (I) and (II), the process is not accompanied by side reactions and leads to the formation of α-nitropropionic ester (V) and formaldehyde. The esters (III) and (V) have the same $E_{1/2}$. However, as a result of the ionization of (V) under the experimental conditions, the value of the limiting current differs greatly for (III) and (V), which permits a determination of the concentrations of (III) and (V) in the system from the expression

$$i = i_A X + i_B \cdot (AH_0 - X)$$

where i, i_A, and i_B are the observable values of the limiting current, the limiting current of (V), and the limiting current of (III), respectively, under the experimental conditions (pH = 6.0-8.1, saturated calomel electrode −1.1 V); AH_0 is the initial concentration of the nitroalcohol; X is the concentration of (V) formed.

At a concentration of (III) > 10^{-3} M and pH 7.0-8.0, the decomposition of (III) is reversible. This permits a determination of the observable rate constant of the interaction of (V) with formaldehyde in a calculation of the kinetic curves of the decomposition of (III). To determine the true rate of interaction of the anion of (V) and formaldehyde, as well as the equilibrium constants, independent of the pH, it is necessary to consider the degree of ionization of (V)

$$K_{equil} = K^{eff}_{equil} \frac{K_a}{K_a + a_{H_3O^+} \gamma_{B^\ominus}},$$

where K_a is the acidity constant of (V), equal to $4.0 \cdot 10^{-7}$ M; $\gamma_B^\ominus$ is the activity coefficient of the anion (V); K^{eff}_{equil} is the observed equilibrium constant; K_{equil} is the true equilibrium constant of the process.

In view of the fact that the experimental errors in the determination of K^{eff}_{equil} are large, while $K_a > a_{H_3O^+} \gamma_B^\ominus$, we did not calculate $\gamma_B^\ominus$:

$$k_{-1} = k^{eff}_{-1} \frac{K_a + a_{H_3O^+} \gamma_{B^\ominus}}{K_a};$$

k_{-1} is the true rate constant of the interaction of the anion of (V) with formaldehyde; k^{eff}_{-1} is the observed rate constant of the interaction of (V) with formaldehyde. The equilibrium constant of the decomposition of (III) and k^{eff}_{-1} were determined spectrophotometrically according to the method of [4].

The decomposition of (IV) was studied by the method of pH determination at the temperature 25°C and $\mu = 0.1$ (Table 5). The experimental procedure, instruments, and calculation of the kinetic curves were the same as in [2]. The only difference lay in the fact that an excess of acetaldehyde was added to the reaction mixture to shift the equilibrium in the direction of (IV). Acetaldehyde was added directly to the solution, which was weighed before and after this.

CONCLUSIONS

1. The dissociation of α-nitro-β-hydroxybutyric ester (I), α-nitro-α-methyl-β-hydroxybutyric ester (II), α-nitro-α-methyl-β-hydroxypropionic ester (III), and 3-nitro-3-methylbutanol-2 (IV) to the starting materials in water under the action of bases was studied.

2. The equilibrium constants of the dissociation of (II), (III), and (IV) in water at 25°C were determined.

3. The rate constants of the interaction of the anion of nitropropionic ester with acetaldehyde and formaldehyde and the anion of 2-nitropropane with acetaldehyde were determined.

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