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MECHANISM AND KINETICS OF THE NITRATION OF METHANOL.

COMMUNICATION 1. KINETICS OF THE NITRATION REACTION

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The nitration of alcohols in acid media has been studied by many workers [1-3]. However, our understanding of the mechanism of this reaction and role of the different species present is not yet complete. In the present work, we studied the kinetics of the nitration of alcohols in a broad nitric acid concentration range in order to elucidate the nature of the individual reaction steps.

EXPERIMENTAL

The kinetics of the nitration of methanol by aqueous nitric acid with HNO_3 concentration (C_{HNO_3}) from 65.86 to 79.01 mass % and HNO_3–H_2SO_4 with C_{HNO_3} from 5.31 to 23.71 mass % was studied on a calorimetric device analogous to that described by Eremenko et al. [4]. A sample of 100% HNO_3 was prepared and analyzed according to Karyakin and Angelov [5]. A sample of 100% H_2SO_4 was prepared and analyzed according to Bass et al. [6]. The applicability of the calorimetric method for the study of the kinetics of methanol nitration was justified by Eremenko et al. [4]. The selection of the upper limit for C_{HNO_3} in aqueous nitric acid was determined by the time constant of the measurement scheme (4 sec). For the HNO_3–H_2SO_4 system, the rates could not be measured (fast reaction). The initial alcohol concentration C_{CH_3OH} was about 0.037 mole/liter The HNO_3 concentration in the systems used was about 400 times greater than the CH_3OH concentration and hardly changed during the nitration. Bimolecular nitration under these conditions follows first-order kinetics. The rate constant retains its value to conversions of about 0.85 (Table 1).

We also studied the kinetics of the nitration of CH_3OH by HNO_3–H_2SO_4–H_2O with $C^0_{HNO_3}$ = 64.47 mass % (Table 2). This reaction is also described by first-order kinetics.

RESULTS AND DISCUSSION

The major protolytic equilibria in nitric acid solutions are:

$$2HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \tag{1}$$

$$NO_2^+ + NO_3^- \rightleftarrows N_2O_5 \tag{2}$$

$$HNO_3 + H_2O \rightleftarrows NO^-{}_3 + H_3O^+ \tag{3}$$

$$HNO_3 + H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^- \tag{4}$$

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TABLE 1. Rate Constants for the Nitration k_{ef} of Methanol by HNO_3—H_2O and HNO_3—H_2SO_4

Composition mass, %		$k_{ef} \cdot 10^3$, sec^{-1}	Composition mass, %		$k_{ef} \cdot 10^3$ sec^{-1}
HNO_3	H_2O		HNO_3	H_2O	
65.86	34.14	1,86	74,23	25,77	44,7
66.55	33.45	2,60	75,23	24,77	48,4
66,65	33.35	5,12	75,98	24,02	33,9
69,18	30,82	3.09	76,5	23,5	58,9
69,43	30,57	3,90	76.91	23.09	102
69.6	36,4	7,95	78.02	21,98	100
69,91	30.09	9,12	78,46	21,54	70,7
71,6	28.4	9,03	78,79	21.21	154
71,93	28.07	7,38	5,34–23,71 *	0	≫170
73.19	26,81	10,0			

*For the HNO_3—H_2SO_4 system.

TABLE 2. The Nitration of Methanol by HNO_3—H_2O—H_2SO_4 Mixtures

Composition mass, %			$k_{ef} \cdot 10^3$, sec^{-1}	Composition mass, %			$k_{ef} \cdot 10^3$ sec^{-1}
HNO_3	H_2O	H_2SO_4		HNO_3	H_2O	H_2SO_4	
59,1	33,4	7,5	0,59	39,2	22,2	38,6	22
59,1	33,4	7,5	0,63	33,6	19,0	47,4	15
53,3	30,1	16,6	4,3	27,1	15,4	57,5	17
47,6	26,9	25,6	16				

$$CH_3OH + HA \rightleftarrows CH_3OH_2^+ + A^- \qquad (5)$$

The equilibrium concentrations of the corresponding species may be obtained from data on the acidity, composition and thermal decomposition of nitric acid relative to its analytical concentration [7-16].

In principle, a nitroester may be formed upon the reaction of any pair of species given

$$CH_3OH + HNO_3 \rightarrow CH_3ONO_2 + H_2O \qquad (6)$$

$$CH_3OH_2^+ + HNO_3 \rightarrow CH_3ONO_2 + H^+(H_2O) \qquad (7)$$

$$CH_3OH + NO_3^- \rightarrow CH_3ONO_2 + OH^- \qquad (8)$$

$$CH_3OH_2^+ + NO_3^- \rightarrow CH_3ONO_2 + H_2O \qquad (9)$$

$$CH_3OH + NO_2^+ \rightarrow CH_3ONO_2 + H^+ \qquad (10)$$

$$CH_3OH_2^+ + NO_2^+ \rightarrow CH_3ONO_2 + 2H^+ \qquad (11)$$

$$CH_3OH + N_2O_5 \rightarrow CH_3ONO_2 + HNO_3 \qquad (12)$$

$$CH_3OH_2^+ + N_2O_5 \rightarrow CH_3ONO_2 + HNO_3 + H^+ \qquad (13)$$

Under certain conditions, the formation of nitrating agents along with the formation of a nitrate may be the rate-limiting step. On the basis of the strong dependence of the nitration rate on C_{HNO_3} and the existence of concentration ranges, in which the nitration rate is first- or zero-order relative to C_{CH_3OH}. Ingold et al. [1] concluded that NO_2^+ is the active species and the nitroester is formed by reaction according to Eq. (10). When zero-order is found, the mechanism is the same but the rate-limiting step is the formation of the nitronium cation. Genich and Kustova [2] came to an analogous conclusion upon observing a transition of the zero-order reaction realized in less concentrated HNO_3 solution with high $C^0_{CH_3OH}$ to a reaction first-order relative to C_{CH_3OH}. Eremenko [3] noted the protonization of alcohols in acids and the low probability of reaction (11) and proposed reaction (7) as rate-limiting. However, taking account of reactions (6) and (7) does not explain the strong dependence of the reaction rate on C_{HNO_3} and the acidity of the medium as well as boundary transitions. Reactions (8) and (9) are not in accord with the observations, which should give maximum rate and maximum concentration of the nitrate ions with a strong drop in the rate upon going to 100% HNO_3.

Figure 1a gives the dependence of log k_{ef} on log $C_{N_2O_5}$ in the range of HNO_3 solutions studied. The $C_{N_2O_5}$ value at 25°C in HNO_3 solutions [7]: $-dC_{HNO_3}/dt = kC_{N_2O_5}$, where k is the rate constant for the decomposition of N_2O_5 in the gas or inert solvents [8] and $C_{N_2O_5}$ is the equilibrium concentration of N_2O_5 in HNO_3 solution. Beginning at 70 mass %, the reaction rate is proportional to $C_{N_2O_5}$. The rate constant of the reaction step of $CH_3OH_2^+$ with N_2O_5 found from the linear dependence is $6.3 \cdot 10^5$ liters/mole•sec. The data on the activities of the free $HNO_3{*}$ and $H_2O{*}$ molecules found from the experimental vapor tensions of HNO_3 and H_2O above the solutions may also be used for calculating the change in $C_{N_2O_5}$ in the range of HNO_3 solutions studied [9]. Pure HNO_3 and H_2O liquids were taken as the standard state. Activity coefficients equal to unity may be taken for the free $HNO_3{*}$ and $H_2O{*}$ molecules. In accord with equilibria (1) and (2), $C_{N_2O_5}$ is proportional to $C^2_{HNO_3{*}}/C_{H_2O{*}}$. The difference in the slope of the dependences for k_{ef} for methanol nitration on $C_{N_2O_5}$ and $C^2_{HNO_3{*}}/C_{H_2O{*}}$ is about 5%, which may be related to the necessity of extrapolating the temperature dependences over a large temperature range in the case of finding $C_{N_2O_5}$. When the nitric acid concentration is less than 70 mass %, k_{ef} falls less sharply with increasing dilution than would be expected for a first-order mechanism relative to $C_{N_2O_5}$. Such a dependence may be explained by a shift in the mechanism for the nitration reaction. The $C_{ROH}/C_{ROH_2^+}$ ratio increases with increasing dilution of HNO_3 by water and decreasing acidity. In the entire concentration range, $C_{NO_2^+} > C_{N_2O_5}$, and $C_{NO_2^+}/C_{N_2O_5}$ also increases with increasing dilution. Thus, descending from 70 mass %, we initially encounter reaction (10). In this concentration range, k_{ef} is linearly dependent on $C_{NO_2^+}$ (see Fig. 1b). Kargin et al. [10] have determined $C_{NO_2^+}$ in the range of HNO_3 concentrations from 100 to 85 mass %. Using these data and the values for $C_{NO_3^-}$ [11], $C_{HNO_3{*}}$ and $C_{H_2O{*}}$, we found that the constant for equilibrium (1) K_1 in this range remains invariant and close to the value found for 100% HNO_3 [12]. When C_{HNO_3} is less than 70 mass %, $C_{NO_2^+}$ was found assuming the invariance of K_1. The rate constant for the reaction step of NO_2^+ with CH_3OH determined using this dependence is equal to $1.1 \cdot 10^5$ liters/mole•sec. A shift in the reaction mechanisms is also indicated by the finding that k_{ef} when C_{HNO_3} is less than 70 mass % is proportional to $(C_{HNO_3{*}}/C_{H_2O{*}})^{3/2}$, which, in turn, in accord with Eqs. (1) and (3), is proportional to $C_{NO_2^+}$.

Figure 2 gives the dependence of log k_{ef} on the analytical concentration of HNO_3 in H_2O and H_2SO_4. In addition, this figure gives the values for log k_{ef} calculated for equilibria (7), (10) and (13) using equations

$$\log\left(\frac{1}{C^0_{CH_3OH}}\frac{dC}{dt}\right) = \lg k_{ef} = \lg\left[k_{HNO_3}C_{HNO_3{*}}/(1 + 10^2/h_0)\right] \qquad (14)$$

$$\log k_{ef} = \log\left[k_{NO_2^+}K_1C^2_{HNO_3{*}}/(1 + h_0/10^2)\,C_{H_2O{*}}C_{NO_3^-}\right] \qquad (15)$$

$$\log k_{ef} = \log\left[k_{N_2O_5}K_1K_2C^2_{HNO_3{*}}/(1 + 10^2/h_0)\,C_{H_2O{*}}\right] \qquad (16)$$

where h_0 is the acidity of the medium [15, 16], 10^2 is the ionization constant of $CH_3OH_2^+$ [13] and K_2 is the constant for equilibrium (2). Since the true rate constant for the reaction step involving HNO_3 is unknown, the calculated curve for HNO_3 was "linked in" to the experiment at the point of shift of the mechanism. The curves calculated for equilibria (6) and (12) are not given. They apparently lie below the curves for equilibria (7) and (13), respectively, due to the strong drop in C_{CH_3OH} with increasing acidity of the medium.

In strongly acidic media, the calculations carried out on the assumption of a predominant role for reaction (13) with N_2O_5 as the nitrating agent are in good accord with the experimental results. This is also indicated by the finding that the nitration rate in HNO_3—H_2SO_4 is greater than would be expected from calculations for HNO_3 and NO_2^+. When C_{HNO_3} is less than 70 mass %, the experimental points lie near the calculated curve for the rates of the reaction of NO_2^+ with CH_3OH.

Figure 3 shows the dependence of log $C_{N_2O_5}$ in HNO_3—H_2SO_4—H_2O. The reaction rate was proportional to $C_{N_2O_5}$. The rate constant of the nitration step in the ternary mixture is $1.5 \cdot 10^5$ liters/mole•sec, which is about four times less than the analogous value in the HNO_3—H_2O system. We may consider that within the error for the determination of $C_{N_2O_5}$ using the temperature dependences for the rate constants for the thermal decomposition of HNO_3 solutions, the rate constants for nitration by N_2O_5 in both media are similar. If the nitration in this system proceeded by an additional reaction, for example, by the action of acid nitronium sulfate which exists in equilibrium with the protonated

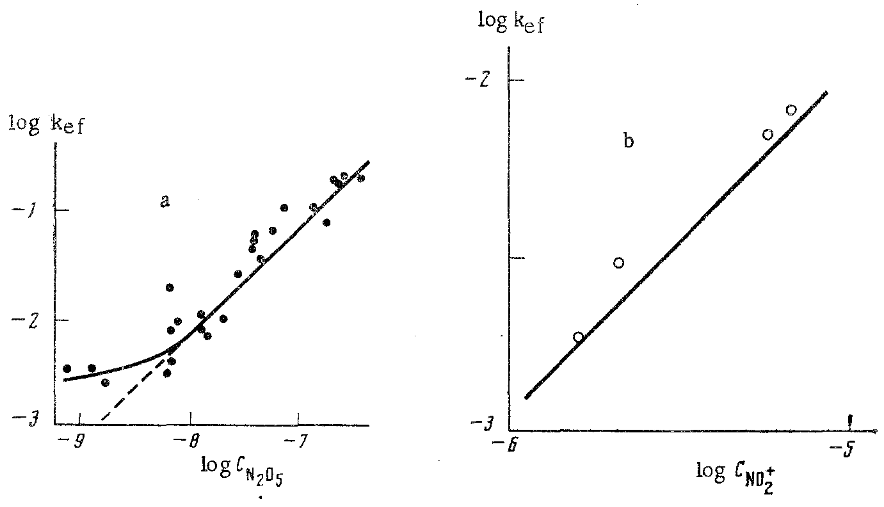

Fig. 1. The dependence of log k_{ef} on log $C_{N_2O_5}$ (a) and log $C_{NO_2^+}$ (b) in the nitration of methanol by aqueous HNO_3 solutions.

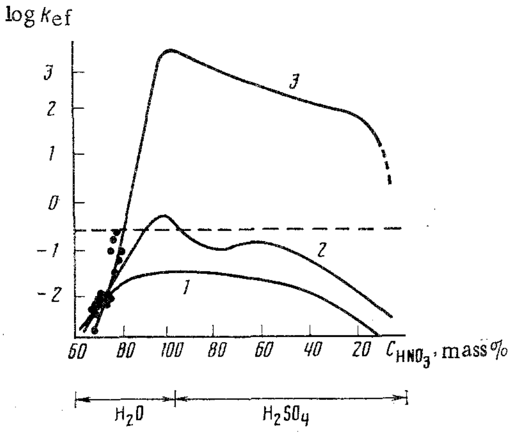

Fig. 2. Dependence of log k_{ef} on the composition of the nitrating mixture. The experimental data are given by the points and the calculated results are given by the lines: 1) Eq. (7), 2) Eq. (10), 3) Eq. (13). The dashed line gives the upper limit of the rate constants which could be measured.

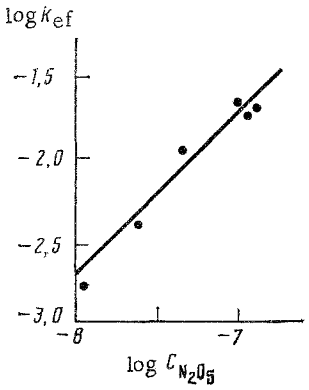

Fig. 3. Dependence of log k_{ef} on log $C_{N_2O_5}$ in the nitration of methanol by HNO_3—H_2SO_4—H_2O mixtures.

$$NO_2^+ + HSO_4^- \rightleftarrows NO_2HSO_4 \tag{17}$$

form of the alcohol, the rate constants for the ternary system would be enhanced. In fact, some decrease in the rate constant is found. Apparently, NO_2HSO_4 which is present in the system does not participate in the nitration of methanol.

CONCLUSIONS

1. The rate of formation of methyl nitrate in the $CH_3OH-H_2O-HNO_3$ system is a function of the reaction of N_2O_5 with $CH_3OH_2^+$ in solutions with HNO_3 concentration greater than 70 mass % and the reaction of NO_2^+ with methanol at lower concentrations. The rate constants for these reactions were determined.

2. The nitration mechanism is retained in the $HNO_3-H_2SO_4$ mixture; NO_2HSO_4 virtually does not participate in the nitration reaction in the concentration range studied.

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