

Kinetics of the redox reaction of the U(III) ions with hydrazoic acid

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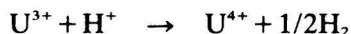
Received 9 December 1976

The kinetics and mechanism of the redox reaction of the U(III) ions with hydrazoic acid was studied. The kinetics of this reaction is led by the rate equation $-d[U(III)]/dt = k[U(III)][HN_3]$. The activation parameters in the 0.4 M solution of HCl are: $\Delta H^\ddagger = 43.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -142.3 \text{ J mol}^{-1} \text{ K}^{-1}$. The probable reaction mechanism and the influence of the nature of solvent in binary solvent mixtures (water—methanol, water—ethanol, water—*isopropyl alcohol*) are discussed.

Была изучена кинетика и механизм окислительно-восстановительной реакции ионов U(III) с азотистоводородной кислотой. Ее кинетика подчиняется уравнению $-d[U(III)]/dt = k[U(III)][HN_3]$. Параметры активации в растворе 0,4 М-НСl следующие: $\Delta H^\ddagger = 43,1 \text{ кДж моль}^{-1}$ и $\Delta S^\ddagger = -142,3 \text{ Дж моль}^{-1} \text{ К}^{-1}$. Обсуждается вероятный механизм реакции и влияние характера растворителя в двойных системах растворителей (вода с метиловым, этиловым или изопропиловым спиртами).

The U(III) ions in aqueous solutions show strong reduction properties, the redox potential of the system U(IV)/U(III) in 1 M-HClO₄ being 0.63 V [1]. For instance, they are able to reduce the Cr(III) and H₃O⁺ ions.

Thus far, the kinetics and mechanism of the redox reactions of the U(III) ions have been little investigated. *Peretrukhin* [2] measured the rate constants of the redox reaction



and obtained $k = 1.81 \times 10^{-5} \text{ s}^{-1}$ in 0.5 M-HClO₄ and $k = 1.73 \times 10^{-4} \text{ s}^{-1}$ in 3.5 M-HClO₄. *Sato* observed [3] that the U(III) ions in a 0.5 M solution of HCl and inert atmosphere oxidized at 25°C by about 2% in the interval of 24 hrs. Since the oxidation of the U(III) ions proceeds faster in the presence of perchloric acid than in the presence of hydrochloric acid, *Peretrukhin* [4] came to the conclusion that not only the H⁺ ions but also the ClO⁻ ions functioned as oxidants of the U(III) ions. The kinetics of the reactions in the systems U(III)—U(VI) and Np(III)—Np(VI) was studied in the medium of perchloric acid [5]. The rate constant of the reaction in the system U(III)—U(VI) in 0.1 M-HClO₄ at 25°C is $1.1 \times 10^4 \text{ mol}^{-1} \text{ s}^{-1} \text{ l}$.

Other kinetic studies deal with the reduction of the *cis*-Co(NH₃)₅(H₂O)₂³⁺ ions by the U³⁺ ions [6] and the reduction of the Co(NH₃)₅X²⁺ complexes by the U(III)

ions where X^- stands for halogenide, acetate, azide, cyanide or thiocyanate ions [7].

Espenson and Wang [8] investigated the kinetics of the reactions among the U^{3+} ions and Cr(III) halogenide complexes in the medium of $HClO_4$. On the basis of kinetic results they came to the conclusion that all reactions followed an inner-sphere mechanism. The kinetics and mechanism of the redox reaction of the U(III) ions with the V(III), V(IV), and Fe(III) ions were also described [9]. Recently, we published the results of the kinetic study dealing with the redox reaction of the U(III) ions with benzaldehyde and salicylaldehyde [10].

This paper is concerned with the kinetics of the redox reaction between the U(III) ions and hydrazoic acid.

Experimental

The solutions of the U^{3+} ions were prepared from $UO_2(ClO_4)_2$ of anal. grade by reduction with zinc amalgam in 1 M- $HClO_4$ and were kept in contact with amalgam during use. The solutions of the U(III) ions have to be constantly bubbled through with nitrogen of electric bulb industry and every manipulation with these solutions has to be done in an inert atmosphere. The preparation of the U(III) solutions was described in more detail in [10]. The concentration of the U(III) ions was determined polarographically. Sodium azide and other chemicals used were of anal. grade.

The kinetics of the oxidation of the U(III) ions with hydrazoic acid in the medium of hydrochloric, perchloric, and sulfuric acids was studied polarographically by recording the time dependence of the limiting diffusion current of anodic wave of the U(III) ions at the potential of -0.3 V against the potential of a saturated calomel electrode. The measurements were performed on a polarograph OH-102, Radelkis. The electrolytic cell was a Kalousek vessel held at constant temperature in an ultrathermostate U 10.

The values of rate constants in individual relationships are average values of the three independent measurements accurate to $\pm 5\%$.

Results

The integral method was used to determine the partial reaction order of the reaction studied with respect to the concentration of the U(III) ions as well as to the concentration of hydrazoic acid. In both cases the reaction order was found to be equal to one for a 10^{-3} M concentration of the U(III) ions and 0.01–0.3 M concentration of sodium azide in 0.4 M- $HClO_4$. Hence the rate equation may be written in the form

$$-\frac{d[U(III)]}{dt} = k[U(III)] [\text{hydrazoic acid}].$$

For the 10^{-3} M concentration of the U(III) ions in a 0.4 M solution of HCl (or 0.4 M- $HClO_4$) the value of the rate constant is $k = 8.8 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C. In a 0.4 M solution of H_2SO_4 the value of the rate constant is fourfold with respect to the preceding case. The rate constant found does not change with ionic strength in the range from 0.4 M to 1.4 M (NaCl). The value of the rate constant decreases slightly (at a constant ionic strength $I = 2.0$ M) with increasing concentration of the H_3O^+ ions (Table 1). On the basis of the temperature dependence of the rate constant in the above-mentioned

Table 1

Dependence of the rate constant on hydrogen ion concentration
 10^{-3} M-U(III) ions, 2×10^{-1} M- NaN_3 , 2 M- Cl^- ions, $I = 2.0$ M, $t = 25^\circ\text{C}$

$[\text{H}_3\text{O}^+]$ M	k 10^2 s $^{-1}$
0.2	2.1
0.4	1.9
1.0	1.8
1.6	1.6
2.0	1.6

solutions the following activation parameters were determined by means of the Eyring equation: $\Delta H^\ddagger = 43.1$ kJ mol $^{-1}$, $\Delta S^\ddagger = -142.3$ J mol $^{-1}$ K $^{-1}$ in a 0.4 M solution of HCl and $\Delta H^\ddagger = 43.1$ kJ mol $^{-1}$, $\Delta S^\ddagger = -133.9$ J mol $^{-1}$ K $^{-1}$ in a 0.4 M solution of H_2SO_4 (Fig. 1).

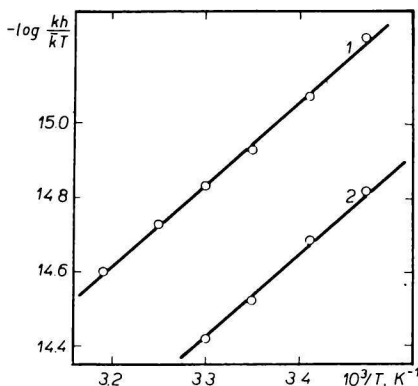


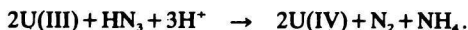
Fig. 1. Dependence of the rate constants on temperature.

10^{-3} M-U(III) ions, 8×10^{-2} M- NaN_3 , $I = 0.4$ M.

1. 0.4 M-HCl; 2. 0.4 M- H_2SO_4 .

The influence of the nature of solvent on the redox reaction investigated was examined by means of the kinetic isotopic effect of solvent as well as in some binary mixtures of solvents: water—methanol, water—ethanol, and water—*isopropyl alcohol*. The value of the kinetic isotopic effect of solvent was evaluated for two temperatures: $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.08$ at 25°C and $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.1$ at 40°C . The dependences of the rate constant on the component ratio of the above binary solvent mixtures are nonlinear and pass through a maximum at higher temperatures (Fig. 2). On the basis of the temperature dependence of the rate constants in individual mixtures the activation parameters were evaluated (Table 2).

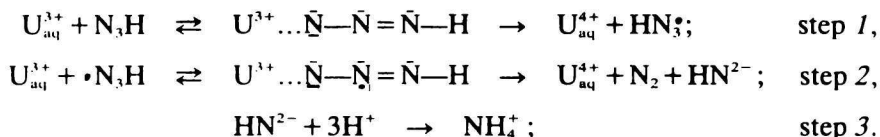
By polarometric titration the stoichiometry of the following reaction was determined



Discussion

No adequate attention has been paid to the reduction of molecules by the U(III) ions as yet. As soon as the kinetics of the redox reaction of the U(III) ions with benzaldehyde and salicylaldehyde has been described [10], such studies became desirable even from the view-point of the comparison of these reactions with the reduction reactions of Cr(II).

The redox reaction of the U_{aq}^{3+} ions with hydrazoic acid is likely to proceed in the following steps



The sum of all three steps corresponds to the overall stoichiometric equation. As the reaction is of the first order with respect to the concentration of the U(III) ions, one of the first two steps is slow and determines the reaction rate. The rate constant does not depend on ionic strength in a broad interval (from 0.4 to 1.4 M) and this fact confirms the assumption of an interaction between the U_{aq}^{3+} ions and a HN_3 molecule (the dipole moment of which is relatively low: 0.847 ± 0.005 [11]). The low value of the kinetic isotopic effect of solvent does not indicate an OH or OD bridge transfer. A slight decrease in the rate constant with increasing concentration

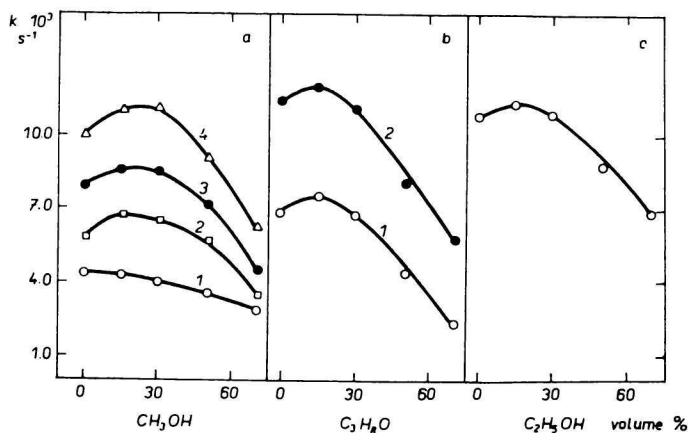


Fig. 2. Rate constants in binary mixtures of solvents.
 10^{-2} M-U(III) ions, 8×10^{-2} M- NaN_3 , 0.4 M- $HClO_4$.
 a) 1. 20°C; 2. 25°C; 3. 30°C; 4. 35°C. b) 1. 25°C; 2. 35°C. c) 35°C.

Table 2

Activation parameters in the mixtures methanol—water
 10^{-3} M-U(III) ions, 8×10^{-2} M-NaN₃, 0.4 M-HClO₄

Methanol volume %	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹
0	43.1	-140.6
15	43.9	-139.8
30	43.9	-139.8
50	43.1	-144.8
70	38.3	-164.1

of the H₃O⁺ ions may be related to the corresponding decrease in the equilibrium concentration of the HN₃ molecules brought about by their partial protonation.

The catalytic effect of the sulfate ions consists not in the change of activation enthalpy but in a decrease of the negative value of activation entropy by two units. Therefore, it does not consist in the change of activation process but rather involves the difference between the hydration entropies of the starting ions (U_{aq}³⁺, USO_{4aq}⁻, and UHSO_{4aq}²⁺).

The results of the kinetic measurements in binary mixtures of solvents (water—methanol, water—ethanol, water—*isopropyl alcohol*) characterized by the plots of rate constant vs. the ratio of both solvents (showing a maximum at higher temperatures) are analogous to the observations of *Rykov* and co-workers [12, 13]. On the basis of their observations these authors reject the classical electrostatic model for the interpretation of the Gibbs activation energy of redox reactions and put forward the assumption of a charge transfer between reacting ions through the molecules of solvent. Such way of electron transfer which was accepted by several authors [14—16] may be effective in the investigated reaction, too.

The most important factor which determines the entropy of the activated complex is its charge. According to *Newton* and *Rabideau* [17], the formal entropy (S^*) of the activated complex is given by the expression

$$S^* = \Delta S^\ddagger + \Sigma S_r^0 - \Sigma S_p^0,$$

where ΔS^\ddagger is the activation entropy and ΣS_r^0 , ΣS_p^0 stand for the sums of standard entropies of the reactants or products taking part in the formation of the activated complex. The value of the formal entropy of the activated complex determined in this work, $S^* = -36$, corresponds to the activated complex bearing a charge 3⁺ [18].

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Translated by R. Domanský