

Kinetics and mechanism of redox reactions of the uranium(III) ions with monobromoacetic and monoiodoacetic acid

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The kinetics and mechanism of redox reactions of the U(III) ions with monobromoacetic and monoiodoacetic acid have been studied. A probable reaction mechanism of these reactions is proposed and the results of kinetic measurements obtained with all three monohalogen acetic acids are generally compared. The study of the influence of the binary water—*tert*-butyl alcohol mixture on kinetic parameters of these reactions as well as the application of the Marcus relation to expressing the ratio of rate constants of the outer-sphere reactions evidences that the reduction of the halogen acetic acids with the U(III) ions follows an outer-sphere mechanism.

Была изучена кинетика и механизм окислительно-восстановительной реакции ионов U(III) с монобромуксусной и моноиодуксусной кислотами. Был предложен вероятный механизм этих реакций и сравниваются результаты кинетических измерений для трех моногалогенкислот. Изучение влияния бинарной смеси вода—трет-бутиловый спирт на кинетические параметры этих реакций и также применение формулы Маркуса для выражения отношения констант скорости внесферных реакций доказывают, что восстановление галогенуксусных кислот ионами U(III) протекает по внесферному механизму.

The topic of this paper is a kinetic study of the redox oxidation of the U(III) ions with monobromoacetic and monoiodoacetic acid which is a continuation of our preceding studies dealing with the oxidation of the U(III) ions by chloroacetic acids [1, 2].

Experimental

The U(III) solutions were prepared by reduction of $\text{UO}_2(\text{ClO}_4)_2$ with zinc amalgam in 1 M-HClO₄. As the U(III) ions rapidly react with oxygen, an inert nitrogen atmosphere was used. The concentration of the U(III) solutions was determined spectrophotometrically (the coefficient of absorption in 0.1 M-HClO₄, $\epsilon = 1620 \text{ M}^{-1} \text{ cm}^{-1}$ at 350 nm) and polarographically.

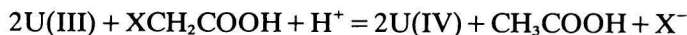
Monobromoacetic acid and monoiodoacetic acid were prepared daily by weighing crystalline anal. grade reagents and dissolving them in redistilled water. All other chemicals used were anal. grade reagents. The kinetics was studied polarographically by investigating the time dependence of limiting diffusion current of the anodic wave of the U(III) ions under conditions of a pseudo-first-order reaction. Monobromoacetic acid and monoiodoacetic acid were in excess in comparison with the U(III) ions. For the reaction of the U(III) ions with monobromoacetic acid the mercury dropping electrode was used as an indication electrode and the measurements were carried out at the potential of -0.1 V against SCE. For the reaction of the U(III) ions with monoiodoacetic acid the platinum vibration electrode of the frequency of 50 Hz, 10 mm length and 1 mm width served as an indication electrode.

The reaction vessel was a Kalousek polarographic vessel adapted for water thermostating. The measurements were performed on a polarograph OH-102 (Radelkis, Budapest) in combination with a thermostat U-10 (Prüfgeräte, Medingen). In potentiometric titrations the electromotive force was measured with a pH-meter Universal, type OP-204/1 (Radelkis, Budapest).

Results

Stoichiometry

The stoichiometry of redox reactions of the U(III) ions with halogen acetic acids was determined by polarometric titration (Fig. 1). The stoichiometric ratio corresponds to two U(III) ions for 1 mole of halogen acetic acid in conformity with the reaction



X = Cl, Br or I.

The reaction products found are in agreement with the above stoichiometric equation. The concentrations of halogenides were determined by potentiometric titrations. The U(IV) ions were estimated by polarographic analysis.

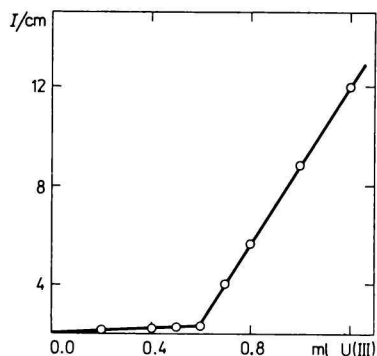


Fig. 1. Polarometric titration of 10 ml of 1.5×10^{-3} M solution of monobromoacetic acid with 0.05 M solution of the U(III) ions.

Oxidation of the uranium(III) ions with monobromoacetic acid

The kinetics of redox reaction of the U(III) ions with monobromoacetic acid was investigated in the medium of perchloric acid. The monobromoacetic acid was in excess (10^{-3} – 10^{-2} M) with respect to the concentration of the U(III) ions (5×10^{-4} M). The value of rate constant was evaluated by means of the kinetic equation of the first-order reaction. The dependence of rate constant (s^{-1}) on concentration of monobromoacetic acid expressed graphically is a straight line passing through the origin. The value of rate constant k was determined from the slope of this straight line. Thus it was found $k = 2.9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in 1 M-HClO₄ at 288.15 K.

The rate equation for a given concentration of the H₃O⁺ ions assumes the form

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

At a constant ionic strength, the rate constant slightly decreases with increasing concentration of the hydrogen ions (Table 1). The measured rate constant slightly decreases with increasing ionic strength of the solution. At 0.1 M concentration of the H₃O⁺ ions and temperature of 288.15 K, the rate constants found for ionic strengths $I = 0.1 \text{ mol dm}^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$ are $k = 4.8 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ and $k = 3.24 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$, respectively.

The activation parameters were determined by means of the Eyring equation on the basis of the temperature dependence of the rate constant (Table 2).

The influence of the character of solvent on this redox reaction was investigated in binary solvent mixtures, *i.e.* water—methanol, water—ethanol, water—*isopropyl* alcohol, and water—*tert*-butyl alcohol. In the medium water—methanol the

Table 1

Variation of rate constant with concentration of the hydrogen ions
 5×10^{-4} M-U(III), 5×10^{-3} M-BrCH₂COOH, $I = 2.0 \text{ mol dm}^{-3}$, 288.15 K
 5×10^{-4} M-U(III), 1×10^{-3} M-ICH₂COOH, $I = 2.0 \text{ mol dm}^{-3}$, 278.15 K

H ₃ O ⁺	$k_{\text{BrCH}_2\text{COOH}}$ mol ⁻¹ s ⁻¹ dm ³	$k_{\text{ICH}_2\text{COOH}}$ mol ⁻¹ s ⁻¹ dm ³
0.04	3.8	111
0.08	3.48	
0.1	3.24	99
0.4	3.1	78
1.0	2.86	70
1.6	2.8	
2.0	2.74	67

Table 2

Kinetic parameters of the oxidation of the U(III) ions with halogen acetic acids
0.4 M-HClO₄, 288.15 K

Oxidation agent	k mol ⁻¹ s ⁻¹ dm ³	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹
ClCH ₂ COOH	0.018	55.4	- 85.7
BrCH ₂ COOH	3.1	38.4	- 102.5
ICH ₂ COOH	155	36.5	- 76.4

measured rate constant is almost independent of mole fraction of methanol. The relationships between the logarithm of rate constants and mole fraction of other alcohols exhibit a minimum (Fig. 2).

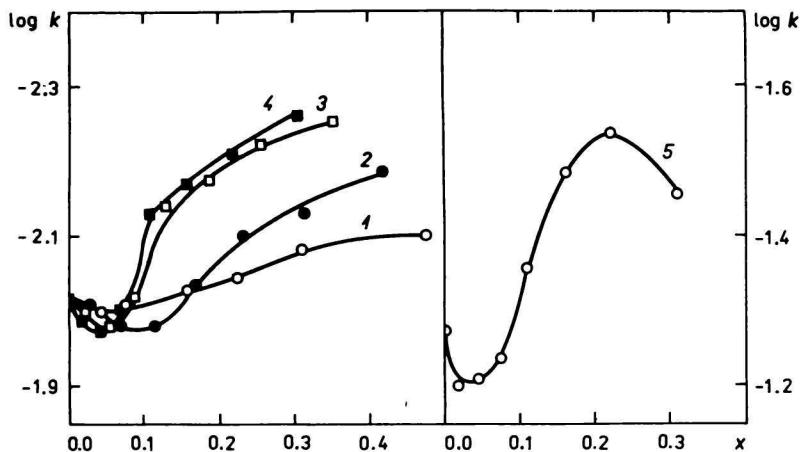


Fig. 2. Logarithm of the rate constants as a function of mole fraction of alcohols.

5×10^{-4} M-U(III), 3×10^{-3} M-BrCH₂COOH, 0.4 M-HClO₄, 288.15 K. 1. Methanol; 2. ethanol; 3. isopropyl alcohol; 4. *tert*-butyl alcohol.

10^{-4} M-U(III), 5×10^{-4} M-ICH₂COOH, 0.4 M-HClO₄, 278.15 K; 5. *tert*-butyl alcohol.

Oxidation of the uranium(III) ions with monoiodoacetic acid

The kinetics of redox reaction of the U(III) ions with monoiodoacetic acid was investigated in the presence of excess concentration of this acid in the medium of perchloric acid with 5×10^{-4} M initial concentration of the U(III) ions and 8×10^{-4} — 3×10^{-3} M initial concentrations of monoiodoacetic acid. By using the

integral method, it was found that the partial reaction order with respect to either reactant was equal to one.

The rate equation for a given concentration of the H_3O^+ ions may be written in the form

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

The value of the rate constant k for 0.4 M- HClO_4 and 278.15 K is $k = 87 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$.

At a constant ionic strength, the rate constant very slightly decreases with increasing concentration of the hydrogen ions (Table 1). The measured rate constant slightly decreases with increasing ionic strength of the solution. At 0.1 M concentration of the hydrogen ions and 278.15 K, we found $k = 112 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ and $k = 83 \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ for the ionic strengths $I = 0.1 \text{ mol dm}^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$, respectively. The activation parameters of this reaction are given in Table 2. The oxidation of the U(III) ions with monoiodoacetic acid was investigated in the binary water—*tert*-butyl alcohol mixture (Fig. 2).

Discussion

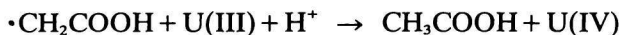
The rate equations obtained for these reaction systems imply a bimolecular interaction between the U(III) ions and oxidants. The small influence of concentration of the H_3O^+ ions on the measured rate constant may be explained by the fact that the U(III) ions react with the undissociated forms of monobromoacetic and monoiodoacetic acid. If the U(III) ions reacted in two parallel reaction steps with the undissociated and dissociated form of the acid, the following equation would be valid for the experimental rate constant

$$k = \frac{k_1 + k_2 K_r [\text{H}_3\text{O}^+]}{1 + K_r [\text{H}_3\text{O}^+]}$$

The symbols k_1 and k_2 stand for the rate constants of reduction of the dissociated and undissociated form respectively and K_r is the reciprocal value of the dissociation constant K_a ($K_a = 1.33 \times 10^{-3} \text{ mol dm}^{-3}$ for monobromoacetic acid at 288.15 K and $K_a = 7.87 \times 10^{-4} \text{ mol dm}^{-3}$ for monoiodoacetic acid at 278.15 K). When we plotted $k(1 + K_r[\text{H}_3\text{O}^+])$ against $[\text{H}_3\text{O}^+]$, we obtained straight lines passing through the origin. It means that the rate constant k_1 is equal to zero.

The reactions are likely to obey these mechanisms





where X = Cl, Br or I.

A small influence of ionic strength on the experimental rate constant is in agreement with the idea that an ion reacts with a dipole. The rate constants of oxidation of the U(III) ions with halogen acetic acids are different (Table 2). The slowest reaction is the reaction of the U(III) ions with monochloroacetic acid whereas the reaction of the U(III) ions with monoiodoacetic acid is the fastest one. In the same sense, the polarizability of the C—halogen bond increases. This polarizability is one of the major factors effecting a heterolytic destruction of the bond.

Like in oxidation of the U(III) ions with dichloroacetic and trichloroacetic acid, a nonlinear character of the relationship between the logarithm of rate constant and mole fraction of the corresponding binary mixture is also to be observed in these reactions. According to [3], the organic solvent has a "structure-forming" effect at low values of the mole fraction while the "structure-breaking" effect starts at the mole fraction $x_{\frac{1}{2}}$ and reaches the maximum value at $x_{\frac{1}{2}}^*$. It may be assumed that the dilute aqueous solutions containing the molecules of *tert*-butyl alcohol and stabilized by hydrogen bonds of the adjacent water molecules form clathrate cages. A clathrate consisting of one molecule of *tert*-butyl alcohol and 21 water molecules [4] should correspond to the mole fraction $x_{\frac{1}{2}} = 0.05$. As to the oxidation of the U(III) ions with monobromoacetic acid at 288.15 K, it is $x_{\frac{1}{2}} = 0.09$ for ethanol, $x_{\frac{1}{2}} = 0.06$ for isopropyl alcohol, and $x_{\frac{1}{2}} = 0.045$ for *tert*-butyl alcohol. For the oxidation of the U(III) ions with monoiodoacetic acid at 278.15 K, we observed the minimum $x_{\frac{1}{2}} = 0.045$ in the binary water—*tert*-butyl alcohol mixture (Fig. 2). A change in structure of solvent which takes place at the mole fraction $x_{\frac{1}{2}}$ manifests itself kinetically especially in redox reactions with outer-sphere mechanism. The outer-sphere mechanism of electron transfer is, therefore, very likely to occur in the redox reactions of halogen acetic acids with the U(III) ions.

According to the Marcus theory, the rate constant of a reaction with outer-sphere electron transfer is governed by the equation

$$k_{AB} = (k_{AA}k_{BB}K_{AB}f)^{1/2} \quad (1)$$

where K_{AB} is the equilibrium constant of the reaction, k_{AB} is the rate constant of the reaction between the reactants A and B, and k_{AA} and k_{BB} are the rate constants of exchange reactions of the reactants. Furthermore, it is valid

$$\ln f = \frac{(\ln K_{AB})^2}{4 \ln (k_{AA}k_{BB}z^{-2})}$$

where z is a measure for the number of collisions between two neutral particles in a volume unit of solution and in a time unit ($z \doteq 10^{11} \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$).

If two equal oxidants are reduced by two different reductants and both reductions follow an outer-sphere mechanism, the ratio of the rate constants may be expressed by the following equation [5]

$$\frac{k_{AB}}{k_{AC}} = \frac{k_{BB}}{k_{CC}} K \quad (2)$$

The constant K expresses the difference between reduction abilities of the reductants B and C . The right side of eqn (2) is independent of character of the oxidant and the ratio of the rate constants of the outer-sphere reactions $A + B$ and $A + C$ should be constant. The V(II) ions were used as a reductant C . Provided the reductions by the V(II) ions are fast enough, they must be outer-sphere reactions owing to a relatively low substitution rate of the V(II) ions. Table 3 contains the

Table 3

Rate constants of the reduction of some substances with the U(III) and V(II) ions (298.15 K)

Oxidant	$k_{U(III)}$ $\text{mol}^{-1} \text{s}^{-1} \text{dm}^3$	$k_{V(II)}$ $\text{mol}^{-1} \text{s}^{-1} \text{dm}^3$	$k_{U(III)}/k_{V(II)}$
$\text{Co}(\text{NH}_3)_6^{3+}$	1.32	3.7×10^{-3}	3.6×10^2
$\text{Co}(\text{en})_3^{3+}$	0.133	2.0×10^{-4}	6.7×10^2
Cl_3CCOOH	8.4	0.025	3.4×10^2
BrCH_2COOH	4.2	7.7×10^{-3}	5.5×10^2
$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$	1.08×10^6	13	831×10^2
$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	5.4×10^5	2.6	2077×10^2

rate constants of the reduction of some substances by the U(III) and V(II) ions. The reduction of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ ions by the U(III) [6] and V(II) [7] ions follows an outer-sphere mechanism. As the ratios of the rate constants $k_{U(III)}/k_{V(II)}$ are approximately equal for the investigated reactions with monobromoacetic acid and trichloroacetic acid [2], we may confirm the assumption that the reactions of the U(III) ions with halogen acetic acids involve an outer-sphere mechanism. The reductions of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ by the U(III) [6] and V(II) [7] ions do not follow an outer-sphere mechanism. The values of the ratio of the rate constants of these reactions significantly differ from the above-mentioned values.

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