KINETICS AND MECHANISM OF REDOX REACTION OF U(III) IONS WITH TRICHLOROACETIC ACID

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The kinetics and mechanism of redox reaction of U^{3+} ions with trichloroacetic acid in the medium of perchloric acid were studied. The form of the dependence of the rate constant on the concentration of H_3O^+ ions suggests that the U^{3+} ion reacts in the first elementary step with the $CCl_3.COO^-$ anion under formation of an intermediary radical which reacts rapidly in the second step. The results of kinetic measurements of all three chloro substituted acetic acids are compared. A detailed study of the influence of binary mixtures on kinetic parameters of the studied reaction (especially of water–tert-butanol mixtures) shows that the reduction of chloroacetic acids with U^{3+} ions proceeds by the outer sphere mechanism of the electron transfer.

Kinetic studies of the mechanism of redox reactions of U^{3+} ions were described in our preceding communications[1-4]. The present work is a continuation of the study[4] of the kinetics and mechanism of redox reactions of U^{3+} ions with mono- and dichloroacetic acids. Also in this case we concentrated on the influence of H_3O^+ ions and organic solvent–water mixtures on the studied redox reaction.

EXPERIMENTAL

Chemicals. The preparation and handling of easily oxidizable U^{3+} ions solutions was described earlier[1]. Their concentration was determined polarographically and spectrophotometrically at 350 nm (coefficient of absorbancy in $0{\cdot}1\text{M-HClO}_4$, $1620\ \text{M}^{-1}\ \text{cm}^{-1}$). Trichloroacetic acid (Reanal, Budapest) and other chemicals were of reagent grade, solutions were prepared from redistilled water. All solutions contained perchloric acid and their ionic strength was adjusted by the addition of sodium perchlorate.

Kinetics. Kinetic measurements were done polarographically: the time dependence of the limiting diffusion current of the anodic wave of U^{3+} ions at $-0{\cdot}1$ V (S.C.E.) was recorded, and this until the reaction did not proceed to at least 80 percent. The rate constants were evaluated from this dependence with the use of the integrated form of the kinetic equation of the first order, provided that trichloroacetic acid was in excess against U^{3+} ions. A Kalousek cell with a thermostated mantle served as reaction vessel. An OH-102 type polarograph (Radelkis, Hungary) and a U-10 type thermostat (Prüfgeräte-Werk, Medingen, GFR) were used.

Identification of reaction products. Analysis of inorganic reaction products was done both polarographically and potentiometrically. Analysis of organic reaction products was carried out on a gas chromatograph of the type Carlo Erba GI 450 with the use of a flame ionization detector. The inlet pressure of nitrogen (as carrier) was 0·1 MPa. The column was 80 cm long, its inner diameter was 2 mm and it was filled with Porapak Q of grain size 80 – 100 mesh. The column temperature was 200°C. Ether served as extracting agent. The rate constants used in the dependences are averages from three independent measurements whose accuracy was ±5 percent.

RESULTS

In solutions containing $1 . 10^{-3}$M-U^{3+} and 0·005 – 0·04M-CCl_3COOH, the rate constant is a linear function of the concentration of trichloroacetic acid in the whole studied range. The slope of this linear dependence gives the rate constant $k = 0{\cdot}88$ . . $mol^{-1}\,dm^3\,s^{-1}$ in 1M-$HClO_4$ at 283·15 K. The rate equation at a given concentration of H_3O^+ ions is

$$-d[U^{3+}]/dt = k[U^{3+}]\,[CCl_3COOH]\,.$$

The rate constant decreases with increasing concentration of hydrogen ions at constant ionic strength (Table I); its reciprocal value is proportional to the concentration of hydrogen ions. With increasing ionic strength at constant concentration of hydrogen ions, the rate constant diminishes somewhat. Cl^- ions exert a moderate inhibiting effect on the studied reaction (Table I).

TABLE I

Dependence of Rate Constant on Concentration of H_3O^+ and Cl^- Ions
$1 . 10^{-3}$M-U^{3+}, 0·01M-CCl_3COOH, 10°C.

Cl^- M	I mol . dm^{-3}	H_3O^+ M	k_{exp} $mol^{-1}\,s^{-1}\,dm^3$
0	2·0	0·04	1·5
0	2·0	0·08	1·5
0	2·0	0·1	1·45
0	2·0	0·2	1·36
0	2·0	0·4	1·2
0	2·0	0·8	1·05
0	2·0	1·0	0·95
0	2·0	1·6	0·77
0	2·0	2·0	0·68
0	1·0	0·1	1·6
0·1	1·0	0·1	1·4
0·6	1·0	0·1	1·1
1·0	1·0	0·1	0·98

In mixtures of water with ethanol, isopropanol and tert-butanol, the dependence of the logarithm of the rate constant on the mole fraction of these alcohols passes through a characteristic minimum and a maximum (Fig. 2), whereas the same dependence in the case of methanol does not show such extremums.

The stoichiometry of the studied reaction was determined by polarometric titration of U^{3+} ions and of trichloroacetic acid. In the first case, we followed the decrease of the anodic wave of U^{3+} during gradual addition of the acid, while in the second case we followed the decrease of the cathodic wave of the acid during gradual addition of U^{3+} ions. This method revealed the following stoichiometrical reaction:

$$2\,U^{3+} + CCl_3COOH + H^+ = 2\,U^{4+} + Cl^- + CHCl_2COOH$$

which is in agreement with the found reaction products. Gas chromatography showed the main product to be dichloroacetic acid, potentiometric titration with a silver electrode showed the formation of Cl^- ions, and polarographic analysis revealed U^{4+} ions.

DISCUSSION

According to the mentioned rate equation, we assume a bimolecular reaction between U^{3+} ions and trichloroacetic acid. This reaction proceeds apparently in two steps with the formation of intermediary radicals:

$$U^{3+} + Cl_3CCOO^- \rightarrow U^{4+} + {}^{\bullet}Cl_2CCOO^- + Cl^-\,,$$

$$U^{3+} + {}^{\bullet}Cl_2CCOO^- + 2\,H^+ \rightarrow U^{4+} + Cl_2CHCOOH\,.$$

The influence of the concentration of hydrogen ions on the measured rate constant

TABLE II

Kinetic Parameters for Reduction of Chloroacetic Acids with U^{3+} Ions

k_1Rate constant for reduction of dissociated, k_2 of undissociated form; $1\,.\,10^{-3}$ M-U^{3+}, 0·4M-$HClO_4$, 15°C.

Oxidant	k $mol^{-1}\,s^{-1}\,dm^3$	$\Delta H^{\ddagger}$ $kJ\,mol^{-1}$	$\Delta S^{\ddagger}$ $J\,K^{-1}\,mol^{-1}$	k_1 $mol^{-1}\,s^{-1}\,dm^3$
$CH_2ClCOOH$	0·018	55·4	−85·7	0
$CHCl_2COOH$	0·23	46·2	−94·6	0·5
CCl_3COOH	1·9	54·7	−50·4	2·5

can be attributed to the fact that U^{3+} ions react only with the CCl_3COO^- anion. The rate equation can be hence written as

$$-d[U^{3+}]/dt = k[U^{3+}][CCl_3COO^-], \qquad (1)$$

or

$$-d[U^{3+}]/dt = k[U^{3+}]KS/(K + [H^+]) = k_{exp}S[U^{3+}], \qquad (2)$$

where the experimental rate constant k_{exp} fulfils the relation

$$1/k_{exp} = 1/k + [H^+]/kK, \qquad (3)$$

k is the rate constant of the elementary reaction step, K dissociation constant of trichloroacetic acid, and S its analytical concentration. The latter equation is in good agreement with our experimental results; this dependence measured at three different temperatures leads to the value of $K = 1{\cdot}6\ dm^3/mol$ (15°C) and to the following values of k(for $1 \,.\, 10^{-3}$M-U^{3+}, $8 \,.\, 10^{-3}$M-CCl_3COOH, $I = 2{\cdot}0$M):

T, K:	283·15	288·15	293·15
k, $mol^{-1}\ s^{-1}\ dm^3$	1·54	2·50	4·65

The corresponding activation parameters were determined as $\Delta H^{\ddagger} = 49{\cdot}9\ kJ\ mol^{-1}$ and $\Delta S^{\ddagger} = -61{\cdot}3\ J\ K^{-1}\ mol^{-1}$.

The mentioned value of K lies in the interval of values found by other authors[5]. The observed influence of ionic strength can be explained qualitatively by interaction of oppositely charged ions. A moderate inhibition effect of Cl^- ions may be due to

TABLE II
(*Continued*)

k_2 $mol^{-1}\ s^{-1}\ dm^3$	$\Delta H_1^{\ddagger}$ $kJ\ mol^{-1}$	$\Delta S_1^{\ddagger}$ $J\ K^{-1}\ mol^{-1}$	$\Delta H_2^{\ddagger}$ $kJ\ mol^{-1}$	$\Delta S_2^{\ddagger}$ $J\ K^{-1}\ mol^{-1}$
0·018	—	—	55·4	−85·7
0·16	65·1	−25·2	50·4	−86·1
0	49·9	−61·3	—	—

a shift in the equilibrium in favour of UCl^{2+} ions, which are apparently less reactive. The oxidation rate constants of chloroacetic acids with U^{3+} ions are summarized in Table II.

The dependence of the logarithm of the rate constant on the mole fraction of alcohol (Fig. 1) is interesting; the characteristic minimums and maximums can be explained qualitatively as in our preceding work[4]. This effect is most pronounced in aqueous tert. butanol. To elucidate it more thoroughly, we measured the temperature dependence of the rate constant at two mole fractions, x_2^* and x_2^{**}, corresponding the mentioned minimum and maximum (Fig. 2). The activation enthalpy is equal in both cases, $\Delta H^{\neq} = 55{\cdot}4$ kJ/mol. The activation entropy in the maximum of the curve is $\Delta S^{\neq} = -49{\cdot}8 \text{ J K}^{-1} \text{ mol}^{-1}$ and in the minimum $-43 \text{ J K}^{-1} \text{ mol}^{-1}$, i.e., less negative. This confirms our conclusion[4] according to which the effect of the alcohol is related not only to the change of the dielectric constant but also to the change in solvation of the reactants in the initial and transition states and to a change in the structure of the aqueous solution. These effects were in other systems pointed out by Blandamer and Burgess[6]. Pointud and Juillard[7] investigated recently solute–solvent interactions in tert-butanol–water mixtures on the basis of calorimetric measurements of excess Gibbs energies and entropies of some electrolytes. At a mole fraction x_2^* (corresponding to the minimum in Fig. 1), they observed the highest value of the excess entropy due to transfer of halides from water to aqueous tert-butanol and they discussed it in terms of the Atkinson's model of fluctuating cages.

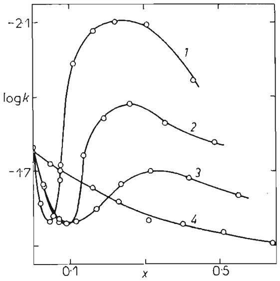

FIG. 1

Dependence of Logarithm of Rate Constant on Mole Fraction of Alcohol

$1 . 10^{-3}$M-U^{3+}, $8 . 10^{-3}$M-CCl_3COOH, 0·4M-$HClO_4$; 15°C. *1* tert-butanol; *2* isopropanol; *3* ethanol; *4* methanol.

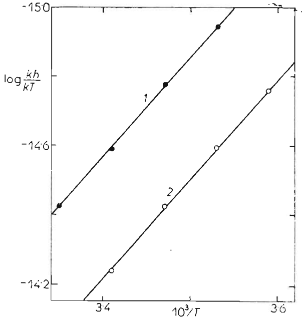

FIG. 2

Temperature Dependences of Rate Constants

$1 . 10^{-3}$M-U^{3+}, $8 . 10^{-3}$M-CCl_3COOH, 0·4M-$HClO_4$; 15°C. *2* In the minimum, *1* in the maximum of the curve (Fig. 1).

Iwasaki and Fujiyama[8] proved the formation of clathrates such as $(H_2O)_{21}.TBA$ or $(H_2O)_{105}.(TBA)_5$ (TBA = tert-butanol) in the mentioned binary mixture in dependence on the mole fraction. The former clathrate corresponds to the mole fraction $x_2 = 0{\cdot}05$, which in turn corresponds according to Hvidt and coworkers[9] to a minimum apparent volume of tert-butanol. The mentioned facts show that the structure of the solvent changes markedly at the mole fraction x_2^*, which is manifested on the kinetics mainly of redox reactions with an outer-sphere mechanism. This mechanism of the electron transfer is hence very probable in the case of the redox reactions between U^{3+} ions and chloroacetic acids and it can be expected also in the reduction of similar substrates with these ions.

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