# KINETICS AND MECHANISM OF REDOX REACTIONS OF U(III) IONS WITH MONOCHLOROACETIC AND DICHLOROACETIC ACIDS

Ľubica ADAMČÍKOVÁ and Ľudovít TREINDL

*Department of Physical Chemistry,*
*Comenius University, 816 50 Bratislava*

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The kinetics and mechanism of the redox reactions of $U^{3+}$ ions with mono- and dichloroacetic acids were studied. The influence of pH was observed mainly in the second case and led to the determination of the rate constants and activation parameters corresponding to two parallel steps, namely oxidation of $U^{3+}$ with $CHCl_2COO^-$ ions and oxidation of $U^{3+}$ with $CHCl_2.COOH$ molecules. The influence of binary mixtures of water with methanol, ethanol, isopropanol, or tert- butenol on the reaction rate was followed. Increasing alcohol concentration influences the rate constant not only through changing dielectric constant and solvation of the reactants but also through a change of the solvent structure which plays a role in reactions with an outer sphere mechanism of the electron transfer.

Uranium(III) ions are a strong reducing agent which can reduce many transition metal ions at measurable rates. The kinetics and mechanism of their redox reaction with Fe(III), V(V), and V(III) ions were studied in detail by Ekstrom and coworkers[1]. Oxidation of U(III) ions with Co(III) in a perchlorate solution proceeds analogously[2] as with Fe(III) by an outer sphere mechanism. Ekstrom and coworkers[3] studied the kinetics and mechanism of reduction of Tl(III) and Cr(III) ions with U(III) in perchlorate solutions. Other authors were concerned with the reactions of U(III) with the *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ complex ions[4], with complexes of the type $[Co(NH_3)_5X]^{2+}$, where X denotes halide, acetate, azide, cyanide, or thiocyanate ions[5], and with complexes of the type $[Cr(H_2O)_5X]$, where X denotes water, halide, azide, thiocyanate, or isothiocyanate ions[6]. The authors concluded that all reactions proceeded by an inner sphere mechanism in which $OH^-$ ions play the role of a bridge. The kinetics of reactions of $U^{3+}$ ions with $UO_2^{2+}$ and $Np^{3+}$ with $NpO_2^{2+}$ were studied in solutions of perchloric acid[7]. Adegite and coworkers[8] described the kinetics and mechanism of oxidation of $U^{3+}$ ions with iodine and bromine in acidic medium. The first step of the two-step oxidation of $U^{3+}$ with $Br_2$, $I_2$ or $I_3^-$ has an outer-sphere character. The authors determined the homonuclear exchange rate constant $k_{ex}$ for the reaction of $U^{3+}$ with $U^{4+}$.

The present work is a continuation of our previous communications about redox reactions of uranium(III) ions[9-11] with special regard to the influence of binary water–alcohol mixtures.

## EXPERIMENTAL

Solutions of $U^{3+}$ ions were prepared from uranyl perchlorate of reagent grade by reduction with a zinc amalgam in 1M-$HClO_4$ and were kept in contact with the amalgam in an atmosphere of pure nitrogen. Water is decomposed by $U^{3+}$ ions very slowly without influencing the measured rates.

The concentration of $U^{3+}$ ions was determined polarographically and spectrophotometrically (at 350 nm, the extinction coefficient was equal to 1 620 $mol^{-1}\,dm^3\,cm^{-1}$ in 0·1M-$HClO_4$). Mono- and dichloroacetic acids were of reagent grade as other chemicals. Solutions were prepared from redistilled water. The ionic strength was adjusted by the addition of sodium perchlorate.

The kinetic measurements were carried out by recording the time dependence of the polarographic diffusion current of the anodic wave of U(III) ions at −0·1 V against saturated calomel electrode, while the reaction proceeded to at least 80%. The first-order kinetic equation in the integrated form was used to evaluate the rate constant. The reaction proceeded in a Kalousek polarographic cell with a thermostated mantle. The polarograph was of the type OH-102 (Radelkis), thermostat was U-10 (Prüfgeräte-Werk Medingen).

## RESULTS

### *Oxidation of* U(III) *with Monochloroacetic Acid*

In solutions of the initial composition $1 \,.\, 10^{-3}$M-$U^{3+}$ and 0-08 − 0·5M-$CH_2ClCOOH$ in the presence of perchloric acid, the reaction order with respect to both reactants was found by the integral method as equal to one. Hence, the rate equation can be written at constant pH in the form

$$-\mathrm{d}[U^{3+}]/\mathrm{d}t = k[U^{3+}]\,[CH_2ClCOOH]\,. \qquad (1)$$

The rate constant was found as $k = 2{\cdot}7 \,.\, 10^{-2}\ mol^{-1}\,s^{-1}\,dm^3$ in 0·4M-$HClO_4$ at 293·15 K, and decreases slightly with increasing concentration of hydrogen ions at constant ionic strength (Table I). The value of $k$ decreases somewhat with increasing ionic strength: $k = 4{\cdot}2 \,.\, 10^{-2}\ mol^{-1}\,s^{-1}\,dm^3$ at $I = 0{\cdot}04\ mol/dm^3$, whereas $k = 3{\cdot}2 \,.\, 10^{-2}\ mol^{-1}\,s^{-1}\,dm^3$ at $I = 2{\cdot}0\ mol/dm^3$.

From the temperature dependence of the rate constant and the Eyring equation, we found $\Delta H^{\ddagger} = 55{\cdot}4$ kJ/mol and $\Delta S^{\ddagger} = -95{\cdot}8$ J/K . mol.

TABLE I

Dependence of Rate Constant on Hydrogen Ions Concentration for $1 \,.\, 10^{-3}$M-$U^{3+}$, 0·1M-$CH_2ClCOOH$, $I = 2{\cdot}0\ mol/dm^3$, 293·15 K

| $[H_3O^+]$ | 0·02 | 0·04 | 0·08 | 0·2 | 0·4 | 2·0 |
|---|---|---|---|---|---|---|
| $k \,.\, 10^3, s^{-1}$ | 3·4 | 3·2 | 2·9 | 2·6 | 2·7 | 2·6 |

In the water–methanol medium, the measured rate constant does not depend on the mole fraction of the alcohol. In the water–tert-butanol medium the dependence of the rate constant on the mole fraction of the alcohol is nonlinear.

### *Oxidation of* U(III) *with Dichloroacetic Acid*

This reaction was studied in perchloric acid solutions. The limiting anodic diffusion current corresponding to oxidation of $U^{3+}$ to $U^{4+}$ ions decreases with time according to a first-order kinetic equation at an excess of dichloroacetic acid. The reaction order with respect to this acid was determined by logarithmic analysis as 1. The kinetic equation has the form:

$$-\mathrm{d}[U^{3+}]/\mathrm{d}t = k'[U^{3+}]\,[CHCl_2COOH]\,. \qquad (2)$$

The value of $k'$ is equal to $0{\cdot}36\ \mathrm{mol^{-1}\ s^{-1}\ dm^3}$ at 293·15 K in $0{\cdot}4\text{M-HClO}_4$ and $1\,.\,10^{-3}\text{M-U}^{3+}$. The value of $k'$ decreases with increasing concentration of hydrogen ions more than in the case of monochloroacetic acid. The rate constant also decreases slightly with increasing ionic strength: $k' = 5{\cdot}1\,.\,10^{-1}\ \mathrm{s^{-1}\ mol^{-1}\ dm^3}$ at $I = 0{\cdot}2\ \mathrm{mol/dm^3}$ and $k' = 4{\cdot}5\,.\,10^{-1}\ \mathrm{s^{-1}\ mol^{-1}\ dm^3}$ at $I = 2{\cdot}2\ \mathrm{mol/dm^3}$. The values of $k'$ are not influenced by $Cl^-$ ions.

We measured the $k'$ values in binary mixtures of water with methanol, ethanol, isopropanol, and tert-butanol. The dependences of log $k'$ on the mole fraction of the alcohol show a minimum and a maximum (Fig. 1).

## DISCUSSION

The influence of pH on the measured rate constant of oxidation of U(III) ions with dichloroacetic acid can be explained on the assumption that these ions react in two

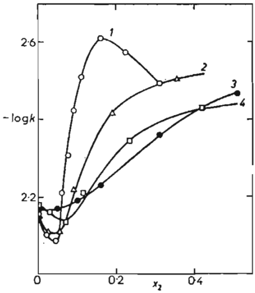

FIG. 1

Dependence of Logarithm of Rate Constants on Mole Fraction of Alcohol

Solution of $1\,.\,10^{-3}\text{M-U}^{3+}$, $0{\cdot}02\text{M-CHCl}_2.$ $.\text{COOH}$, $0{\cdot}4\text{M-HClO}_4$ at 293·15 K. *1* Tert-butanol, *2* isopropanol, *3* ethanol, *4* methanol.

parallel reaction steps – both with the acid and its anions:

$$-\mathrm{d}[\mathrm{U}^{3+}]/\mathrm{d}t = k_1[\mathrm{U}^{3+}]\,[\mathrm{CHCl_2COO^-}] + k_2[\mathrm{U}^{3+}]\,[\mathrm{CHCl_2COOH}]\,. \quad (3)$$

Then the experimental rate constant is given as

$$k' = \frac{k_1 + k_2K_\mathrm{p}[\mathrm{H}^+]}{1 + K_\mathrm{p}[\mathrm{H}^+]}\,, \quad (4)$$

where $k_1$ and $k_2$ are rate constants corresponding respectively to the reduction of the dissociated and undissociated forms of the acid and $K_\mathrm{p}$ is the reciprocal dissociation constant $K_\mathrm{a}$ ($K_\mathrm{a} = 5{\cdot}1 \,.\, 10^{-2}$ mol/dm$^3$ at 298·15 K (ref.[12])). Eq. (*4*) fits well the experimental data. By a graphical analysis of the dependence of the experimental rate constant on pH, the values of $k_1$ and $k_2$ were determined at several temperatures (Table II). From this and the Eyring equation, the activation parameters were determined as $\Delta H_1^\ddagger = 65{\cdot}1$ kJ/mol, $\Delta S_1^\ddagger = -25{\cdot}2$ J mol$^{-1}$ K$^{-1}$ and $\Delta H_2^\ddagger = 50{\cdot}4$ kJ/mol, $\Delta S_2^\ddagger = -86{\cdot}1$ J mol$^{-1}$ K$^{-1}$.

It follows from Table II that the $\mathrm{U}^{3+}$ ions react more rapidly with the dissociated than with the undissociated acid. The influence of ionic strength on the experimental rate constant can be qualitatively elucidated by the interaction of oppositely charged ions. Monochloroacetic acid dissociates much less ($K_\mathrm{a} = 1{\cdot}55 \,.\, 10^{-3}$ mol/dm$^3$ at 293·15 K (ref.[12])) than dichloroacetic acid, hence the very small drop of the rate constant with increasing concentration of hydrogen ions can be understood.

The influence of binary mixtures of water and alcohols as co-solvents in the studied reactions can be discussed as follows. The dependence of the logarithm of the rate constant or activation Gibbs energy on the molar fraction of the alcohol is not linear, in contrast to the reaction of U(III) ions with hydroxylamine[11]. This nonlinear character is especially marked in the case of the reaction of U(III) ions with dichloroacetic acid, showing a characteristic minimum. (This consists of two

TABLE II

Dependences of Individual Rate Constants on Temperature (mol$^{-1}$ s$^{-1}$ dm$^3$) for 1 . $10^{-3}$M-$\mathrm{U}^{3+}$, 2 . $10^{-2}$M-$\mathrm{CHCl_2COOH}$, $I = 2{\cdot}0$ mol/dm$^3$

| $T$, K | $k_1$ | $k_2$ |
|---|---|---|
| 288 | 0·5 | 0·16 |
| 293 | 0·8 | 0·22 |
| 303 | 2·0 | 0·45 |

parallel reactions of U(III) ions with the anion and the undissociated molecule $CHCl_2COOH$.) Similar dependences of activation parameters on the molar fraction of the binary mixtures were observed also by other authors[13].

In interpreting our results, it is not sufficient to use the classical concept of electrostatic interactions and of the solution as a continuum with a macroscopic dielectric constant. The influence of the organic solvent is apparently related not only to a change of the dielectric constant but also to a change in the solvation of the reactants in the initial and transition states. According to Franks and Blandamer[14] the organic solvent has at low mole fractions a structure forming effect, while at mole fractions above a certain value, $x_2^*$, a structure breaking effect takes place, which attains a maximum at $x_2^{**}$. The values of $x_2^*$ and $x_2^{**}$ depend on the nature of the organic solvent and temperature. For example, $x_2^* = 0{\cdot}09$ for ethanol, 0·06 for isopropanol, and 0·04 for tert-butanol at 298·15 K. The dependence $\log k = f(x_2)$ shows a minimum (Fig. 1) corresponding to the value of $x_2$ for the corresponding mixture. It can be concluded that the change of the ratio of the components in the binary mixture influences the reaction rate not only through changing dielectric constant and reactant solvation but also by changing the structure of the aqueous solution or the degree of ordering of the hydrogen bonds. An influence of the solvent structure can be expected in an outer-sphere mechanism rather than in an inner-sphere (bridge) mechanism of the electron transfer. The former is hence more probable in the studied case than the latter, which would involve an intermediate complex such as $[U\text{-}CH_2ClCOO]^{2+}$ or $[U\text{-}CH_2ClCOOH]^{3+}$.

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