Kinetic solvent isotope effect on the redox reaction of U(IV) ions with ferricyanide ions

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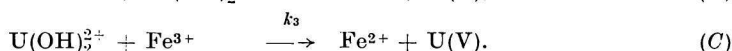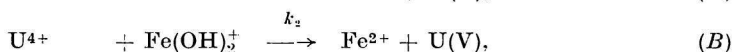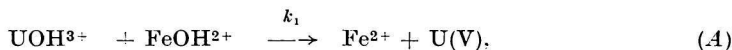
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Dedicated to Professor M. Dillinger on his 70th birthday

The kinetic solvent isotope effect on the redox reaction of U(IV) ions with ferricyanide ions was studied. The measured temperature-dependent values of k_{H_2O}/k_{D_2O} as well as the values of $\delta\Delta H^+$ and $\delta\Delta S^+$ were interpreted from the point of view of the proposed reaction mechanism. The increase in activation enthalpy in heavy water by 2.5 kcal mol^{-1} when compared with light water supports the idea of the electron transfer between U(IV) and $HFe(CN)_6^{2-}$ ions by the $-OH$ (or $-OD$) bond mechanism.

Betts [1] studied the mechanism of the redox reaction of U(IV) ions with Fe(III) ions by kinetic methods. With respect to the observed overall reaction order ($n = 2$) he assumed the one-electron transfer to be a slow rate-determining step. But it was not possible to explain unambiguously the second order reaction with respect to the concentration of hydrogen ions. According to [1] this reaction order should comply with one of the following competitive reactions

$$UOH^{3+} \;+\; FeOH^{2+} \;\xrightarrow{k_1}\; Fe^{2+} + U(V), \qquad (A)$$

$$U^{4+} \;+\; Fe(OH)_2^+ \;\xrightarrow{k_2}\; Fe^{2+} + U(V), \qquad (B)$$

$$U(OH)_2^{2+} + Fe^{3+} \;\xrightarrow{k_3}\; Fe^{2+} + U(V). \qquad (C)$$

These reactions are kinetically equivalent and for this reason it was not possible to decide which of these steps prevailed. Recently *Regnault* and *Kikindai* [2, 3] described the effect of butanol and degradation products of tributylphosphate on the kinetics of this reaction. In our preceding paper [4] we presented the results of the kinetic study of the reaction of U(IV) ions with ferricyanide ions. On the basis of the kinetic data obtained in aqueous solutions we determined the thermodynamic quantities of hydrolytic equilibrium of U^{4+} ions as well as the activation parameters of the elementary reaction, *i.e.* the interaction between $HFe(CN)_6^{2-}$ and UOH^{3+} ions.

With regard to the possibility of generalizing the mechanism proposed for the redox processes of U(IV) ions we considered it useful to study this reaction also in D_2O and thus to elucidate its mechanism in more detail on the basis of kinetic solvent isotope effect.

Experimental

The kinetics of the oxidation of U(IV) ions with ferricyanides was studied polarographically by recording the time dependence of limiting diffusion current of ferricyanides at the potential of -0.08 V against SCE. The measurements were done with a polarograph OH-102, Radelkis.

A Kalousek vessel with a separated calomel electrode prepared in D_2O was used as an electrolytic vessel. During kinetic measurements the vessel was kept at constant temperature by means of a Hoeppler thermostat. The indication electrode was a dropping mercury electrode with the outflow velocity $m = 1.0$ mg s^{-1} and the drop time $t_1 = 5$ s in distilled water and in currentless state at $h = 50$ cm. The measured solution was kept in an atmosphere of pure nitrogen.

The solution of U(IV) ions was prepared as described in [4]. All chemicals used were of anal. grade. Heavy water (99.86%) (Institute for the Research and Utilization of Radioisotopes, Prague) was used as a solvent. Other experimental conditions were the same as described in paper [4].

The rate constants involved in individual relationships are the average values of four independent measurements accurate to $\pm 7\%$.

Results and discussion

The redox reaction of U(IV) ions with ferricyanide ions is also in D_2O solutions of perchloric acid of the first order regarding the concentration of ferricyanides as well as that of U(IV) ions. To determine the first order rate constant (s^{-1}) a kinetic equation of the first order was used in the form

$$\ln i/i_0 = k\,t. \tag{1}$$

The measured rate constant (s^{-1}) is linearly proportional to the concentration of U(IV) ions, the coefficient of proportionality being the rate constant k_2 (s^{-1} mol^{-1} l). The ratio of the rate constant k_2 in light and heavy water under equal conditions expresses the kinetic solvent isotope effect k_{H_2O}/k_{D_2O} (Table 1).

Table 1

Values of the kinetic solvent isotope effect k_{H_2O}/k_{D_2O} at different temperatures

5×10^{-4} M-U(IV), 10^{-3} M-$K_3Fe(CN)_6$, 1 M-H_3O^+ ions, $\mu = 2.0$

| T [K]	k_{H_2O}/k_{D_2O}
288.16	2.48
298.16	2.33
313.16	1.85

The rate constant k_2 decreases with increasing concentration of hydrogen ions at constant ionic strength in the solutions of light [4] and heavy water (Fig. 1). It follows from the logarithmic analysis that the reaction order equals -1 with respect to the concentration of hydrogen ions and is temperature independent.

Even for D_2O it may be written

$$\frac{1}{k_2} = \frac{1}{k^0} + \frac{[H^+]}{k^0\,K}. \tag{2}$$

Fig. 1. Dependence of the rate constant on the concentration of hydrogen ions in D_2O.
5×10^{-4} M-U(IV), 10^{-3} M-$K_3Fe(CN)_6$, $\mu = 2.0$.
1. 15°C: *2.* 25°C; *3.* 40°C.
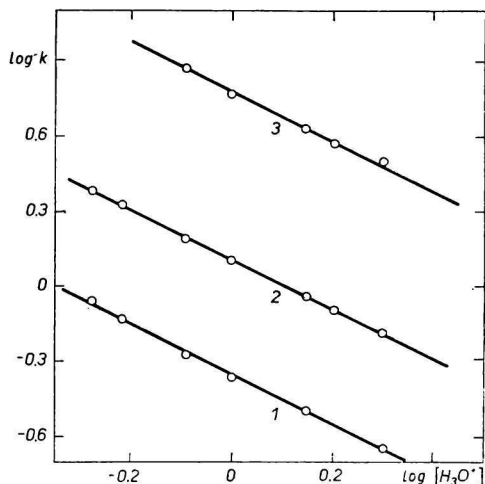
With the aid of this equation the rate constant of the elementary step k^0 and the equilibrium constant K of hydrolysis may be determined by the least squares method

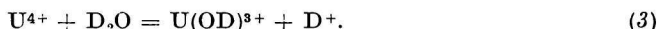$$U^{4+} + D_2O = U(OD)^{3+} + D^+. \tag{3}$$

Table 2 contains the values of the rate constant for the elementary step of redox reaction k^0, which corresponds very likely to the interaction of UOD^{3+} ions with $HFe(CN)_6^{2-}$

Table 2

Values of the rate constants for the elementary step of redox reaction k^0 and kinetic isotope effect $k^0_{H_2O}/k^0_{D_2O}$ at different temperatures

T [K]	$k^0_{D_2O}$ [s^{-1} mol^{-1} l]	$k^0_{H_2O}/k^0_{D_2O}$
288.16	21.1	2.78
298.16	33.9	2.53
316.16	58.9	2.0

ions [4], as well as the values of $k^0_{H_2O}/k^0_{D_2O}$. By using the Eyring equation, the activation parameters of elementary step, *i.e.* activation enthalpy $\Delta H^{\ddagger}_{D_2O}$ and activation entropy $\Delta S^{\ddagger}_{D_2O}$ were evaluated from the temperature dependence of the rate constant k^0 and the kinetic solvent isotope effect was expressed according to [5] as $\delta\Delta H^{\ddagger} = \Delta H^{\ddagger}_{D_2O} - \Delta H^{\ddagger}_{H_2O}$ and $\delta\Delta S^{\ddagger} = \Delta S^{\ddagger}_{D_2O} - \Delta S^{\ddagger}_{H_2O}$ (Table 3). On the basis of the temperature dependence of the equilibrium constant of hydrolysis K, the thermodynamic constants of the hydrolysis of U^{4+} ions with D_2O were evaluated (Table 4).

From these results it follows that the kinetic solvent isotope effect expressed in Table 1 does not involve the isotope effect of solvent on the value of the equilibrium constant of hydrolysis. The values of thermodynamic constants of the hydrolysis of U^{4+} ions in D_2O agree practically with the values of these constants found in H_2O (Table 4).

The results in Tables 2 and 3 demonstrate that the retarding effect of D_2O on the rate of the investigated reaction is a real kinetic solvent isotope effect represented by the ratio of rate constants of the elementary step in both media, *i.e.* $k^0_{H_2O}/k^0_{D_2O}$. The values of $\delta\Delta H^{\pm}$ and $\delta\Delta S^{\pm}$ (Table 3) estimated on the basis of the temperature dependence of the ratio $k^0_{H_2O}/k^0_{D_2O}$ enable us to study deeper the kinetic solvent isotope effect on the

Table 3

Activation parameters of elementary redox step in light and heavy water*

$\Delta H^{\pm}_{H_2O}$ [kcal mol^{-1}]	4.2 ± 0.6	$\Delta S^{\pm}_{H_2O}$ [cal K^{-1} mol^{-1}]	− 35 ± 1.8
$\Delta H^{\pm}_{D_2O}$ [kcal mol^{-1}]	6.7 ± 0.6	$\Delta S^{\pm}_{D_2O}$ [cal K^{-1} mol^{-1}]	− 29 ± 1.8
$\delta\Delta H^{\pm}$ [kcal mol^{-1}]	2.5	$\delta\Delta S^{\pm}$ [cal K^{-1} mol^{-1}]	6

* Activation parameters in H_2O solutions are based on the results of paper [4] which were calculated by the method of least squares.

Table 4

Thermodynamic constants of hydrolysis $U^{4+} + D_2O = UOD^{3+} + D^+$

$K_{25°C}$	ΔG^0 [kcal mol^{-1}]	ΔH^0 [kcal mol^{-1}]	ΔS^0 [cal K^{-1} mol^{-1}]
0.039 ($\mu = 2.0$)	1.9	11.8 ± 0.5	33.3 ± 1.3

investigated reaction and thus also its mechanism. The fact that the activation enthalpy of the elementary step is in D_2O by 2.5 kcal mol^{-1} higher than in H_2O favours the idea of the electron transfer between U(IV) and HFe(CN)$_6^{2-}$ ions by the −OH (or −OD) bond mechanism. The value of the activation entropy of the elementary step which is by 6 entropy units higher in D_2O than in H_2O may be caused by a more stable solvation shell of U(IV) ion in D_2O when compared with the one existing in H_2O.

References

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