

DISTINGUISHING BETWEEN OUTER-SPHERE AND INNER-SPHERE REDOX MECHANISM ON THE BASIS OF THE SOLVENT EFFECT

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During kinetic studies of redox reactions of U^{3+} ions, we paid special attention to the influence of water-alcohol binary mixtures on the reaction rate. Kinetic data suggest that the water-tert-butanol system is of a high diagnostic value. The dependence of $\log k_{exp}$ on the molar fraction of tert-butanol passes through a characteristic minimum in the case of an outer-sphere mechanism, whereas in the other case it decreases monotonously.

Two mechanistic categories are sufficient to classify the mechanisms of redox reactions: an "inner-sphere" and an "outer-sphere" mechanism. The latter is defined so that the electron transfer between two reactants proceeds through their intact inner coordination spheres. An inner-sphere mechanism is defined so that the electron transfer takes place through a common ligand forming a bridge between two reactants. Since the criteria enabling a unique classification of both these mechanisms failed in the case of many studied redox systems, a considerable effort has been spent in developing new "criteria of reactivity" enabling such distinguishing¹.

The same goal is the object of the present work, where we present kinetic data obtained with numerous reactions in binary mixtures of water with tert-butanol. Our aim was to find out a correlation between the redox mechanism and the character of the dependence of the rate constant on the mole fraction of the cosolvent.

EXPERIMENTAL

Solutions of U^{3+} ions were prepared from uranyl perchlorate of reagent grade by reduction with a zinc amalgam in 1M-HClO₄. The olive-green solution obtained was constantly bubbled with pure nitrogen which was additionally purified by bubbling through a solution of Cr²⁺ ions. U^{3+} ions decompose slowly water with the formation of U^{4+} ions and hydrogen; this reaction is in acidic medium so slow that it has no influence on the measured rates². Solutions of U^{3+} ions can be stored in an inert atmosphere³. Their concentration was determined spectrophotometrically (at 350 nm; extinction coefficient 1620 mol⁻¹ cm⁻¹ in 0.1M-HClO₄) and polarographically.

The kinetics of redox reactions of U^{3+} ions with NH₂OH, N₃H, mono-, di-, and trichloroacetic acids, monobromacetic acid, and Cr³⁺ ions were studied polarographically with an OH-102 type polarograph (Radelkis). The time dependence of the limiting diffusion current

of the anodic wave of U^{3+} ions from zero to -0.5 V was recorded (s.c.e) and from this the rate constants were evaluated. The kinetics of the redox reaction of Fe^{2+} with $[Co(NH_3)_5Cl]^{2+}$ ions was followed spectrophotometrically (Specord UV VIS, Zeiss, Jena). The values of rate constants given are averages from three independent measurements which were precise to within $\pm 5\%$. The Kalousek electrolytic cell was tempered by means of an U 10 type ultrathermostat (Prüfgerätewerk, Medingen).

RESULTS AND DISCUSSION

The dependence of the experimental rate constant on pH and the kinetics of the redox reaction of U^{3+} ions with hydroxylamine⁴, hydrazoid acid⁵, chloro and bromo substituted acetic acids⁶⁻⁸, Cr^{3+} and $Cr(H_2O)_5Cl^{2+}$ ions⁹ were already studied and discussed. All these reactions are of the first order with respect to both U^{3+} ions and oxidant.

The dependence of the logarithm of experimental rate constant on mole fraction of the cosolvent is significant (Fig. 1). Similar dependences of activation parameters on mole fraction of binary mixtures were summarized recently by Blandamer and Burgess¹⁰⁻¹¹. The characteristic dependence with a minimum and a maximum can be interpreted as follows. The added organic solvent influences not only the dielectric constant but also the solvation of the reactants in the initial and transition states. At low mole fractions of the alcohol, the typically aqueous mixtures exert a structure-forming action¹². At a certain value of the mole fraction of the cosolvent, x_2^* there is a lack of water to preserve the three-dimensional network of hydrogen bridges and the structure-breaking action takes place. The value of x_2^* corresponds to the minimum on our curves (Fig. 1). Hence, the increasing value of x_2^* influences the reaction rate not only through a change in the dielectric constant and in the solvation of the reactants, but also through a change in the water structure (ordering of H_2O molecules by a network of hydrogen bonds). This latter effect can be expected, from the point of view of the modern theory of the electron transfer, in the case of the outer-sphere redox mechanism.

The most pronounced effect can be observed with water-tert-butanol binary mixtures. Iwasaki and Fujiyama¹³ discussed their light-scattering spectrums of these mixtures in terms of the existence of clathrates (hydrates). The mole fraction $x_2^* = 0.05$ corresponds to the clathrate $(H_2O)_{21}TBA$ (TBA denotes tert-butanol). According to Hvidt and coworkers¹⁴, this value of x_2 corresponds to the minimum value of the molar volume of tert-butanol. Kingston and Symons¹⁵ concluded from their NMR studies of aqueous tert-butanol that the effect of the water structure is here most significant. Harvey and coworkers¹⁶ found from their NMR and IR studies of interactions in water-alcohol mixtures also a clathrate cage effect at the mentioned mole fraction of tert-butanol.

Hence, we can conclude that the solvent structure changes significantly at the molar fraction x_2^* and an influence of this effect on the rate of redox reactions with an outer-

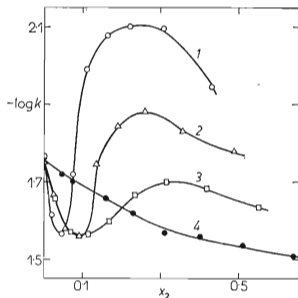


Fig. 1

Dependence of Logarithm of Rate Constants on Mole Fraction of Alcohols

$1 \cdot 10^{-3} \text{M-U}^{3+}$, $8 \cdot 10^{-3} \text{M-CCl}_3\text{COOH}$, 0.4M-HClO_4 ; 288.15 K; 1 tert-butanol, 2 iso-propanol, 3 ethanol, 4 methanol.

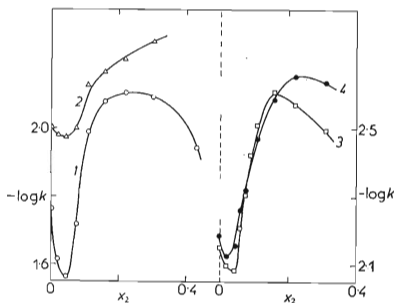


Fig. 2

Dependence of Logarithm of Rate Constants on Mole Fraction of Tert-Butanol

$1 \cdot 8 \cdot 10^{-3} \text{M-CCl}_3\text{COOH}$, $1 \cdot 10^{-3} \text{M-U}^{3+}$, 0.4M-HClO_4 ; 288.15 K; 2 $3 \cdot 10^{-3} \text{M-CH}_2\text{BrCOOH}$, $5 \cdot 10^{-4} \text{M-U}^{3+}$, 0.4M-HClO_4 ; 288.15 K; 3 $2 \cdot 10^{-2} \text{M-CHCl}_2\text{COOH}$, $1 \cdot 10 \cdot 10^{-3} \text{M-U}^{3+}$, 0.4M-HClO_4 ; 293.15 J; 4 $8 \cdot 10^{-2} \text{M-NaN}_3$, $1 \cdot 10^{-3} \text{M-U}^{3+}$, 0.4M-HClO_4 , 298.15 K.

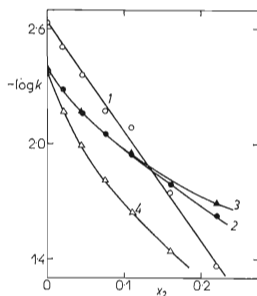


Fig. 3

Dependence of Rate Constants on Mole Fraction of Tert-Butanol

1 0.1M-Cr^{3+} , $1 \cdot 10^{-3} \text{M-U}^{3+}$, 0.4M-HClO_4 ; 293.15 K; 2 $0.4 \text{M-NH}_2\text{OH}$, $1 \cdot 10^{-3} \text{M-U}^{3+}$, 0.4M-HClO_4 ; 298.15 K; 3 about $4 \cdot 10^{-3} \text{M-CrCl}_2^{2+}$, $1 \cdot 10^{-3} \text{M-U}^{3+}$, 0.4M-HClO_4 ; 293.15 K; 4 0.05M-Fe^{2+} , $3 \cdot 10^{-3} \text{M-Co(NH}_3)_5\text{Cl}^{2+}$, 0.4M-HClO_4 ; 296.15 K.

-sphere mechanism can be expected. According to our experimental results (Fig. 2), the redox reactions of U^{3+} ions with dichloroacetic⁶, trichloroacetic⁷ and monobromoacetic acids⁸ or with hydrazoic acid,⁵ proceeding *via* an outer-sphere mechanism, can be distinguished from reactions of U^{3+} ions with hydroxylamine⁴, $Cr \cdot (H_2O)_6^{3+}$ or $Cr(H_2O)_5Cl^{2+}$ ions and of Fe^{2+} with $[Co(NH_3)_5Cl]^{2+}$ ions, proceeding *via* an inner-sphere redox mechanism (Fig. 3), which was assumed by other authors^{17,18}.

Based on our results, it can be expected that the dependence of the logarithm of the rate constant on the mole fraction of tert-butanol can be of diagnostic value in distinguishing the principal redox mechanisms. A more pronounced effect of the solvent structure on outer-sphere than on inner-sphere redox reactions can be expected also from the point of view of the electron transfer theories according to Marcus¹⁹ and Levich and Dogonadze²⁰.

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