

KINETIC STUDY OF A REDOX REACTION OF U(III) IONS WITH BENZALDEHYDE AND SALICYLALDEHYDE

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The authors studied the kinetics, stoichiometry and mechanisms of redox reactions of U(III) ions with benzaldehyde and with salicylaldehyde in perchloric acid solutions. They examined the forms of the rate laws and determined the stoichiometry with the help of polarometric titration and analysis of reaction products. The first reaction is acid catalysed, while the rate of the other reaction depends only very slightly on the concentration of hydrogen ions. Kinetic data, obtained polarographically, give the basis for discussion of the possible reaction mechanisms.

The chemistry of solutions of U(III) ions is not yet well known because of the instability of these ions, and experimental data are therefore mostly of a qualitative character. Because of the thermodynamical instability of U(III) it is impossible to reduce U(IV) to U(III) quantitatively by electrolysis of aqueous solutions. Peretruchin and coworkers¹⁻⁵ found that the maximum yield of U(III) can be expected in diluted solutions of hydrochloric or sulphuric acid, where U(III) is most stable. The degree of reduction increases as the catholyte volume decreases, the cathode area increases and the speed at which the catholyte is stirred increases. Peretruchin² calculated the rate constants of the redox reaction of U^{3+} in perchloric, sulphuric and chloride media.



The rate constant in 0.5M-HClO₄ is $k = 1.81 \cdot 10^{-5} s^{-1}$ and in 3.5M-HClO₄ it is $k = 1.73 \cdot 10^{-4} s^{-1}$. Sato⁶ observed that in a 0.5M-HCl solution at 25°C in an inert atmosphere U(III) is oxidized only to about 2% in 24 hours and to about 6% in 72 hours. In all media studied, in the absence of air, the stability of U(III) decreases with increasing concentration of hydroxonium ions. In solutions of glacial acetic acid⁷ the U(III) is also unstable, and is gradually oxidized to U(IV). The rate of this reaction is proportional to $[U(III)]^2$. The kinetics of the reactions of U(III) — U(VI) and Np(III) — Np(VI) was studied in perchlorate medium⁸. The change in hydrogen ion concentration has only the slightest effect on both reactions. The rate constant of the system U(III)—U(VI) in 0.1M-HClO₄ at 25°C is $1.1 \cdot 10^4 M^{-1} s^{-1}$. The activation parameters and the effect of ionic strength were determined for both reactions. Another kinetic study⁹ is concerned with the reaction of U^{3+} with *cis*-Co(NH₃)₄(H₂O)₂³⁺ in perchlorate medium. Wang and Espenson¹⁰ worked on the kinetics and mechanism of the reduction of Co(III) complexes by U(III). The reaction rate of complexes of the Co(NH₃)₅X²⁺ type point strongly to an inner-sphere mechanism. If X stands for H₂O the dependence on hydrogen ion concentration accords with the notion of the formation of an OH-bridged intermediary complex, whose stability considerably affects the kinetics of the reaction.

Both redox equilibria and the kinetics of the redox processes of U(III) have been very little studied so far. No kinetic study of the redox reaction of U(III) with organic substances has yet been published. We therefore decided to investigate the reduction of two basic aromatic aldehydes, benzaldehyde and salicylaldehyde, by U(III) ions. The kinetics of these reactions is presented in this paper.

EXPERIMENTAL

The U^{3+} ions were prepared from $UO_2(ClO_4)_2$ of analytical grade purity by reduction in $1M-HClO_4$ on zinc amalgam and were maintained in contact with the amalgam while in use. Zinc had no effect on the rates measured. U(III) were also prepared from uranyl perchlorate by electrolytic reduction in $1M-HClO_4$ on a mercury cathode ($0.024 A/cm^2$). Using both methods of preparation of U(III), the same results of kinetic measurements were obtained. In most cases we used second method of preparation. U(III) is a very strong reducing agent, but can be kept quite well in acid solutions in absence of oxygen. Oxygenfree nitrogen, further purified by solutions of chromium(II), was constantly passed through the U(III) solutions. The Cr^{2+} solution was prepared by reducing $1M-Cr_2(SO_4)_3$ by zinc amalgam in $2M-HClO_4$. All manipulation with U(III) solutions was performed in an inert atmosphere. The distribution of nitrogen by polythene tubes was controlled by a three-way stopcock. Beyond the polarographic vessel appropriate valves were placed, to prevent reverse diffusion of oxygen. The concentration of U(III) was determined spectrophotometrically and polarographically. All chemicals used were of analytical grade purity, benzaldehyde and salicylaldehyde were also freshly distilled before use.

Kinetics of U(III) oxidation by benzaldehyde and salicylaldehyde was studied by polarography, recording the limiting diffusion current of the U(III) anodic wave in relation to time, at potential $-0.3 V$ and $0.0 V$ vs saturated calomel electrode. Measurements were performed on a polarograph OH-102, Radelkis. The Kalousek polarographic vessel was tempered during measurements by an ultrathermostat Höppler. Flow rate of the mercury dropping electrode was $1.3 mg/s$, drop time $5s$ (in distilled water, mercury column height $50 cm$). Constant value of ionic strength was maintained by sodium perchlorate. The value of rate constants appearing in the plots are the averages of four independent measurements, accurate to $\pm 6\%$.

Analysis of inorganic products was performed spectrophotometrically and polarographically. Analysis of organic products was performed by gas-chromatography. In both cases dichlormethane was used for extraction. In the case of benzyl alcohol a Perkin-Elmer model F 11 was used, with a flame ionization detector, using nitrogen as carrier gas. The column was $2 m$ long, $2 mm$ in diameter, packed with Chromosorb W, $0.16-0.20 mm$ range, coated with 10% of diethyleneglycol succinate. Temperature of the column was $130^\circ C$. For identifying salicyl alcohol a Fractovap model GI was used, with a flame ionization detector and nitrogen as carrier gas. Salicyl alcohol, as a trimethylsilyl derivative, was analysed on a glass column ($80 cm$ long, $3 mm$ in diameter) packed with 3% SE 30, at $100^\circ C$ and nitrogen pressure at the head of the column $0.5 kp/cm^2$. The stoichiometry of the reaction was determined by polarometric titration of U(III): using a special ultramicroburette, Hamilton-Bonaduz, Switzerland, of a $10 \mu l$ content, divided per $0.1 \mu l$, microlitre portions of benzaldehyde or salicylaldehyde were added, and the corresponding lowering of the anodic wave of U(III) was recorded.

RESULTS

Reduction of Benzaldehyde

Benzaldehyde in solution of perchloric acid is reduced by U(III) according to the rate law:

$$v = k [\text{U(III)}] [\text{benzaldehyde}] \quad (1)$$

First order kinetics of the reaction, with respect to U(III) concentration, was proved by the integral method. The limiting anodic diffusion current, corresponding to electrooxidation of U^{3+} to U^{4+} , decreases in time according to a first order kinetic law during the first two half-times. However, if a sufficient excess of benzaldehyde is used, the rate constant thus obtained increases linearly with increasing benzaldehyde concentration (Fig. 1). When the concentrations of U(III) and benzaldehyde are equivalent the plot of U(III) concentration vs time agrees with second order kinetics. The second order rate constant is given by the ratio of the first order rate constant to benzaldehyde concentration. The rate constant ($\text{s}^{-1} \text{mol}^{-1}$) increases linearly with increasing hydrogen ion concentration and does not depend on ionic strength in the range of 0.05 to 0.55. Its value decreases with increasing U(IV) concentration. Thus for instance for U(IV) concentrations $1.5 \cdot 10^{-4} \text{M}$ and $6 \cdot 10^{-3} \text{M}$ the rate constants are $k = 2.7 \cdot 10^{-2} \text{s}^{-1}$ and $k = 1.26 \cdot 10^{-2} \text{s}^{-1}$ respectively (for $5 \cdot 10^{-3} \text{M}$ benzaldehyde and 0.1M-HClO_4). From the temperature dependence of the rate constant, using Eyring's equation, activation parameters were determined: $\Delta H^\ddagger = 3.8 \pm \pm 0.6 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -55 \pm 1.2 \text{ cal K}^{-1} \text{ mol}^{-1}$. Stoichiometry of the

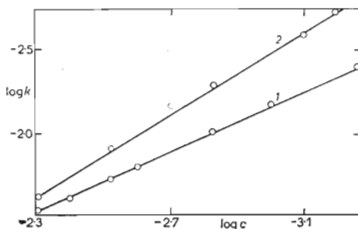


FIG. 1

Dependence of the Rate Constant (s^{-1}) on the Concentration of 1 Benzaldehyde and 2 Salicylaldehyde

$1.5 \cdot 10^{-4} \text{M-U(III)}$, 0.1M-HClO_4 , 15°C , $I = 0.1$.

reaction, determined polarometrically, indicates a consumption of two U(III) ions per molecule of benzaldehyde. Gas chromatographic analysis of the reaction mixture showed the main product of the reaction to be benzyl alcohol (60–70%). U(IV) was the only product of oxidation of U(III) found in the reaction mixture by polarographic and spectrophotometric methods of analysis.

Reduction of Salicylaldehyde

The reduction of salicylaldehyde also exhibits first order kinetics with respect to U(III) concentration. The rate constant (s^{-1}) increases with increasing salicylaldehyde concentration. Logarithmic analysis gave the order $n = 1.2$ (Fig. 1). Hydrogen ions catalyse the reaction to a lesser degree than in the case of benzaldehyde ($1.5 \cdot 10^{-4}M$ -U(III), $5 \cdot 10^{-3}M$ salicylaldehyde, $15^\circ C$, $I = 0.5$):

H_3O^+ , M	0.05	0.1	0.2	0.3	0.5
$k \cdot 10^2, s^{-1}$	1.24	1.38	1.49	1.68	1.84

The effect of U(IV) is in this case more pronounced than in the former reaction. While for concentration $2.5 \cdot 10^{-4}M$ -U(IV) the rate constant was $k = 3.24 \cdot 10^{-2} s^{-1}$, the constant for $2.2 \cdot 10^{-3}M$ -U(IV) was only $k = 1.5 \cdot 10^{-2} s^{-1}$ ($5 \cdot 10^{-3}M$ salicylaldehyde and $0.1M$ -HClO₄). For higher concentrations of U(IV) the order of the reaction with respect to U(III) changes from $n = 1$ to $n = 2$. If, however, we analyse the plot of limiting diffusion current *vs* time by the differential method, the same change of reaction order is noticeable even for lower U(IV) concentrations. The rate constant obtained is again independent of ionic strength. Activation parameters: $\Delta H^\ddagger = 3.9 \pm 0.6 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -54 \pm 1.2 \text{ cal K}^{-1} \text{ mol}^{-1}$. Polarometric titration gave a stoichiometric ratio of two U(III) ions per molecule of salicylaldehyde. Gas chromatographic analysis showed salicyl alcohol (70–75%) in the reaction mixture, polarographic and spectrophotometric analysis showed U(IV).

DISCUSSION

The present kinetic study is another proof of the strong reducing qualities of U(III) ions. In the case of reduction of benzaldehyde by U(III), the reaction is of first order with respect both to oxidizer and reducer. The reaction is catalysed by hydrogen ions. The effect of hydrogen ion concentration on the experimental rate constant can be explained if we assume that the U(III) reacts in two parallel reaction paths, with benzaldehyde and with protonized benzaldehyde.

The recordered rate of oxidation of U(III) by benzaldehyde can be expressed by the equation:

$$-\frac{d[U(III)]}{dt} = k_1 [U(III)] [\text{benzaldehyde}] + k_2 [U(III)] [BH^+].$$

Protonation is fast and is characterized by an equilibrium dissociation constant

$$K_a = \frac{[\text{benzaldehyde}] [H^+]}{[BH^+]},$$

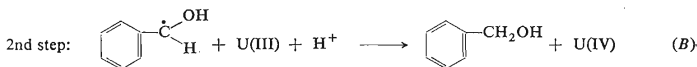
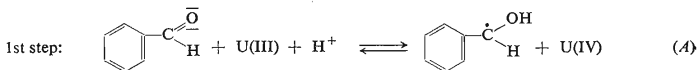
where BH^+ is the protonated form of benzaldehyde. The rate law can then be expressed as:

$$-\frac{d[U(III)]}{dt} = k_1 [U(III)] [\text{benzaldehyde}] + \frac{k_2}{K_a} [\text{benzaldehyde}] [U(III)] [H^+].$$

By comparing this equation with Eq. (1) we obtain:

$$k = k_1 + \frac{k_2}{K_a} [H^+].$$

From this equation we can determine the values of both rate constants. The rate constant for the reduction of benzaldehyde by U(III), k_1 , is $3.7 \text{ s}^{-1} \text{ mol}^{-1} \text{ l}$ at 20°C . From the slope of the linear plot of the experimental rate constant *vs* hydrogen ion concentration we determined the rate constant of the reaction of protonated benzaldehyde with U(III), $k_2 = 1.3 \cdot 10^8 \text{ s}^{-1}$, assuming the dissociation constant $K_a = 10^{7.1}$ (ref.¹¹). Activation parameters corresponding to rate constant k_1 , $\Delta H^\ddagger = 3.4 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = -44 \text{ cal K}^{-1} \text{ mol}^{-1}$, were determined from the effect of temperature on the dependence of the experimental rate constant on hydrogen ion concentration. As the nature of the dependence of the equilibrium dissociation constant of protonation of benzaldehyde on temperature is not known, it was impossible to calculate the activation parameters corresponding to k_2 . Since benzyl alcohol is the predominant reaction product in the observed reaction, we can assume that the reduction of benzaldehyde by U(III) is a consecutive two-electron process with two protons, as given below:



where the first step is slow and therefore rate determining. Knowing that the experimental rate constant decreases with increasing U(IV) concentration we can assume that the first step is reversible. Acid catalysis of the reaction (corresponding to rate constant k_2) can be explained if we imagine the proton and aldehyde group of the protonated form to be in close contact. The considerable negative value of activation entropy ($\Delta S^\ddagger = -44 \text{ cal K}^{-1} \text{ mol}^{-1}$) agrees with the great decrease of entropy of the given system on its path from the initial to the transition state. This is probably due to very high degree of order in the activated complex which contains one molecule of benzaldehyde, one proton and an U^{3+} ion with at least six coordinated molecules of water.

Reduction of salicylaldehyde by U(III) probably proceeds by an analogous mechanism. For lower hydrogen ion concentrations and identical conditions, both reactions proceed with identical reaction rates which correspond to practically identical activation parameters. This is probably because the elementary step of the reaction includes still unprotonated aldehyde groups. The hydrogen bond between the neighbouring —OH group and the oxygen of the aldehyde group does not, contrary to expectation, affect the values of rate constant or activation parameters¹². Our observations, however, agree with the results of Udupa and coworkers¹³ on the electrochemical reduction of benzaldehyde and salicylaldehyde. It is interesting that the reaction rate depends relatively less on hydrogen ion concentration than in the previous case. The small effect of hydrogen ion concentration may be due to negligible protonation of salicylaldehyde, because the aldehyde group is compensated by a hydrogen bond from the neighbouring —OH group. The effect of U(IV) is more pronounced in the reduction of salicylaldehyde than in the reduction of benzaldehyde. As in the previous case, this fact may be explained as due to greater value of the rate of the reverse reaction of the first step in the process. The same holds for the change of reaction order with respect to U(III) from $n = 1$ to $n = 2$ and for the value of reaction order with respect to salicylaldehyde ($n_s = 1.2$). The fact that both reactions are independent of ionic strength agrees with the assumed mechanism. In both cases, for lower hydrogen ion concentrations, the interaction of the molecule with an ion in the first (rate determining) step depends very slightly on ionic strength.

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