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Kinetics of Neptunium(VI) Reduction by Kojic Acid

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The kinetics for Np(VI) reduction by kojic acid, HK, have been studied at tracer level concentrations of Np(VI) in aqueous chloride media. The empirical rate expression for the reaction was found to be $-d[\mathrm{Np(VI)}]/dt = k[\mathrm{Np(VI)}][\mathrm{HK}]_T/[\mathrm{H}^+]$, where T denotes the total concentration. Rate constant and activation parameters have been determined at an ionic strength of 1.0 M (NaCl) and 25.0 °C to be $k = 1.63 \pm 0.08\ \mathrm{s}^{-1}$, $\Delta H^* = 82.7 \pm 3.4$ kJ/mol, and $\Delta S^* = 34 \pm 12$ J/(mol·K). The rate decreases with increasing ionic strength. A reaction mechanism is discussed.

Introduction

It has been reported that ethylenediaminetetraacetic,[1] oxalic,[2] and alkanedicarboxylic acids[3] reduce Np(VI) to Np(V) in acid solution. Hydroquinones[4] also reduce Np(VI) and Pu(VI) to lower oxidation states. A study from this laboratory has shown that organic compounds with phenolic groups, with or without carboxylate groups, reduce Np(VI) but alcohols and methoxy compounds do not.[5] No reduction of Np(VI) by phthalic and benzoic acids and similar reduction rates with the different phenolic reductants suggested a redox intermediate from interaction between $\mathrm{NpO_2}^{2+}$ and a phenolic group rather than with a carboxylate group. From spectral changes at 400 nm, the growth and the subsequent decay of an intermediate species were followed in the reaction of $\mathrm{NpO_2}^{2+}$ with isomers of hydroxybenzoic acid.[6] It was found that the rate of Np(V) formation is lower than the rate of the formation of the intermediate species.

This paper reports a study of the kinetics of Np(VI) reduction by kojic acid with a solvent extraction technique. Kojic acid, 5-hydroxy-2-hydroxymethyl-4-pyrone (Figure 1), is a nonaromatic cyclic compound with a hydroxyl group that is more acidic ($\mathrm{p}K_a \sim 7.67$) than phenol ($\mathrm{p}K_a = 9.82$). The influence, if any, of a carbonyl group on the Np(VI) reduction could be studied with this ligand.

Experimental Section

Reagents and Equipment. All the chemicals employed were reagent grade, and all aqueous solutions were prepared from triply distilled water pretreated with $\mathrm{KMnO_4}$ and passed through a Barnstead Cartridge with HN Ultrapure-mixed resin (Sybron Corp.) after distillation. Glassware was pretreated with hot $\mathrm{HNO_3}$ and $\mathrm{NaBrO_3}$ solutions and rinsed carefully with the deionized distilled water. These pretreated glass vials were silanized prior to use in the solvent extraction experiments.[7]

The stock solution of ^{237}Np was prepared in 1.0 M HCl from high-purity neptunium-237 oxide (Oak Ridge National Laboratory). A working solution of ^{237}Np tracer in 0.1 M HCl was passed through a column (2 mm × 80 mm) of Bio-Rad AG 50-X4 (100–200 mesh) cation-exchange resin at a flow of 0.05 mL/min to remove ^{233}Pa.[8] The completeness of removal of ^{233}Pa was confirmed by checking for its 0.31-MeV γ-peak with a Ge(Li) detector and a multichannel analyzer. Oxidation to the hexavalent state was achieved by fuming the neptunium solution to near dryness several times after additions of aliquots of concentrated perchloric acid. The residue was then dissolved in triply distilled water.

Thenoyltrifluoroacetone, TTA (Aldrich Chemical Co.), was purified by vacuum sublimation at 45 °C. The pale greenish yellow crystals of purified TTA were stored in the dark. The TTA/toluene solution was filtered through 0.45-μ Millipore filter to remove any particulate matter before use. Crude kojic acid, HK (Eastman), was crystallized from a minimum amount of hot water.[9] White needlelike crystals of pure HK were obtained by ether extraction in a Soxhlet apparatus. Working solutions of HK were prepared by dissolving appropriate amounts of such crystals. The pH of the working solutions was adjusted with either HCl or NaOH, and the ionic strength was adjusted with NaCl.

Table I. Rate Constants for Np(VI) Reduction by Kojic Acid ($T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ M (NaCl))

$10^5[\mathrm{Np(VI)}]_0$, M	$10^4[\mathrm{HK}]$, M	$[\mathrm{H}^+]$, M	10^3k_0, s^{-1}	k, s^{-1}	cc
2.16	1.117	0.10	1.29 ± 0.05	1.15 ± 0.05	0.995
1.08	1.117	0.10	1.64 ± 0.06	1.47 ± 0.05	0.996
0.755	1.117	0.10	1.63 ± 0.06	1.46 ± 0.05	0.996
0.957	0.580	0.30	0.37 ± 0.01	1.91 ± 0.07	0.995
0.820	0.580	0.192	0.53 ± 0.02	1.75 ± 0.08	0.994
0.956	0.580	0.095	1.09 ± 0.06	1.79 ± 0.09	0.993
0.928	0.580	0.047	2.44 ± 0.11	1.98 ± 0.09	0.994
0.873	0.580	0.030	4.11 ± 0.17	2.13 ± 0.09	0.997
1.11	4.641	0.10	6.49 ± 0.22	1.40 ± 0.05	0.997
1.05	2.231	0.10	3.62 ± 0.36	1.62 ± 0.16	0.985
1.14	0.291	0.10	0.36 ± 0.02	1.24 ± 0.06	0.994

Procedures. A solvent extraction technique was applied to the study of tracer level Np(VI) reduction to Np(V) by HK. The reaction was started by adding Np(VI) tracer solution to 5.0 mL of a known concentration of kojic acid solution in a 20.0-mL pretreated glass vial that was immersed in a constant water bath. At fixed time intervals, 0.5-mL aliquots from the reaction vessel were placed in an extraction vial containing 1.00 mL of 0.5 M TTA/toluene and 0.5 mL of 0.25 M sodium acetate/acetic acid buffer (pH 4.6). The glass vials used in the extraction and as containers of Np(VI) tracer or TTA/toluene solutions were protected from light. After 5 min of shaking, the phases were separated by centrifugation. Aliquots (0.5 mL) from each phase were placed in counting vials, mixed thoroughly with 5.0 mL of Handifluor liquid scintillation counting solution (Mallinckrodt) and counted for α radioactivity in a liquid scintillation spectrometer (Packard Tri-Carb). In this extraction Np(IV) and -(VI) are extracted quantitatively into the organic phase, while Np(V) is retained completely in the aqueous phase.[10]

The pH change of the aqueous phase was measured with a combination glass electrode and a PHM 84 research pH meter (Radiometer) after each kinetic run.

The same procedure was applied to the rate measurements at different temperatures and to experiments at different ionic strengths. Investigations were conducted in this same manner to ascertain if Np(IV) is formed in Np(VI) reduction by kojic acid, if the sodium acetate/acetic buffer solution interfered, and if Np(VI) reduction occurred in the absence of HK.

Corrections for TTA quenching effects in the α counting and all calculations on the raw counting data were performed on an IBM-XT-PC. Rate constants, their standard deviations, and the correlation coefficients (cc's) were obtained from linear regression on the CYBER 760 of the Florida State University Computing Center using the statistical package MINITAB.

Results

The extraction experiments confirmed that Np(V) and not Np(IV) is the product of $\mathrm{NpO_2}^{2+}$ reduction by kojic acid. Also, Np(VI) was not reduced by 0.125 M sodium acetate buffer solution (pH 4.6). Had Np(IV) formed in these studies, the amount of Np extracted in the organic phase would have decreased initially due to Np(V) formation and then increased at later times due to Np(V) → Np(IV).

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Table II. Ionic Strength Effects on the Rate of Np(VI) Reduction by Kojic Acid[a]

10^5[Np(VI)]$_0$, M	μ	$\mu^{1/2}/(1 + \mu^{1/2})$	k, s^{-1}	log k	cc
1.067	0.03	0.148	0.666 ± 0.028	−0.177 ± 0.042	0.995
1.088	0.06	0.197	0.637 ± 0.039	−0.196 ± 0.061	0.990
1.045	0.10	0.240	0.522 ± 0.044	−0.282 ± 0.084	0.980
1.110	0.20	0.309	0.478 ± 0.030	−0.321 ± 0.063	0.990
1.104	1.00	0.500	0.409 ± 0.017	−0.388 ± 0.041	0.996

[a] Conditions: $T = 15.0 \pm 0.1$ °C; $[H^+] = 0.03$ M, $[HK] = 1.117 \times 10^{-4}$ M, and ionic strength was adjusted with NaCl.

Table III. Rate Constants at Different Temperatures (μ = 1.0 M (NaCl))

T, °C	10^5[Np(VI)]$_0$, M	10^4[HK]$_0$, M	[H$^+$], M	k, s^{-1}	cc
0.0	1.04	4.641	0.10	0.066 ± 0.002	0.998
15.0	1.04	1.117	0.10	0.43 ± 0.01	0.997
25.0	1.04	1.117	0.10	1.47 ± 0.05	0.996
35.0	1.04	1.117	0.10	3.53 ± 0.09	0.998
45.0	1.04	1.117	0.10	14 ± 1	0.986

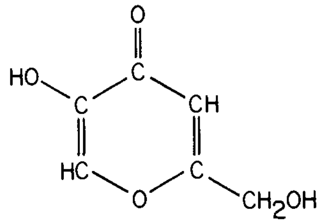

Figure 1. Kojic acid.

The disappearance of Np(VI) was studied at $[HK]_T/[Np(VI)]_0 = 3$–42. Linear plots of ln $(E_t - E_0)$ (E_t and E_0 = percent extraction of Np(VI) into the organic phase at time = t and 0, respectively) vs time confirmed that the reduction reaction is first-order with respect to the analytical Np(VI) concentration, $[Np(VI)]_T$. At constant [H$^+$] and [HK], the linearity was the result of pseudo-first-order conditions.

The calculated rate constants at hydrogen ion concentrations from 0.03 to 0.30 M at constant [HK] and those for varied concentrations of HK at constant hydrogen ion concentration, i.e., 0.1 M, are listed in Table I. The rate of Np(VI) reduction increased with pH and with HK concentration with dependences respectively of −1.05 ± 0.03 and 1.01 ± 0.08. The intercept of the plot of the apparent rate constant, k_0, versus total concentration of kojic acid was zero. From these data the rate of Np(VI) reduction by kojic acid is given by

$$\text{rate} = k_0[\text{Np(VI)}] = k[\text{Np(VI)}][\text{HK}]_T/[\text{H}^+] \qquad (1)$$

The average rate constant, k, is 1.63 ± 0.08 s^{-1} at 25 °C, 1.0 M (NaCl) ionic strength, and $[Np(VI)] \approx 10^{-5}$ M.

The slope of log k vs the square root of the ionic strength ($\mu^{1/2}$) or vs $\mu^{1/2}/(1 + \mu^{1/2})$ at constant temperature gives the value of Z_AZ_B, where Z_A and Z_B are the ionic charges of the reactants that form the activated complex.[11] Table II lists the values of log k for ionic strengths from 0.03 to 1.0 M (NaCl). The inverse correlation of log k with $\mu^{1/2}/(1 + \mu^{1/2})$ provides support that NpO_2^{2+} interacts with the kojate anion to form the activated complex $[NpO_2K^+]^*$.

The effect of temperature on the rate constants is presented in Table III. A plot of ln (k/T) vs $1/T$ was linear and gave

$$\Delta H^* = 82.7 \pm 3.4 \text{ kJ/mol} \qquad \Delta S^* = 34 \pm 11 \text{ J/(mol·K)}$$

Discussion

The radioactive nature of neptunium restricts our use of macroconcentrations. An attempt was made to cause sufficient reaction to allow identification of some of the products of the oxidation of the kojic acid. Unfortunately, for the concentration of product obtained, spectroscopic identification was unsuccessful. Consequently, the stoichiometry of the redox reaction was not determined and the only product identified was NpO_2^+, formed by a one-electron reduction of NpO_2^{2+} by HA. In a similar one-electron reduction of Co(III) by salicylic acid, *cis,cis*-muconic acid was obtained, which indicated ring opening in the organic oxidation.[12] However, oxidation of phenolic compounds by a variety of metal ions[13-23] results in the formation of phenoxy

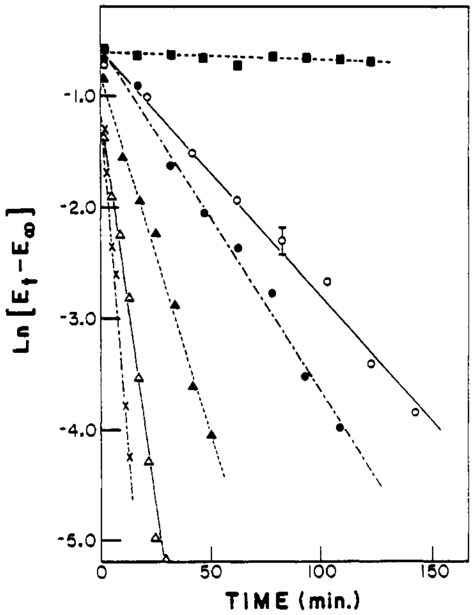

Figure 2. Reduction of Np(VI) by 5.801 × 10^{-5} M kojic acid with μ = 1.0 M (NaCl), at 25.0 °C. $[Np(VI)]_0 = 9.245 \times 10^{-6}$ M, [H$^+$] = 0.3 M (○), 0.2 M (●), 0.1 M (▲), 0.05 M (△), 0.03 M (×), and blank (■).

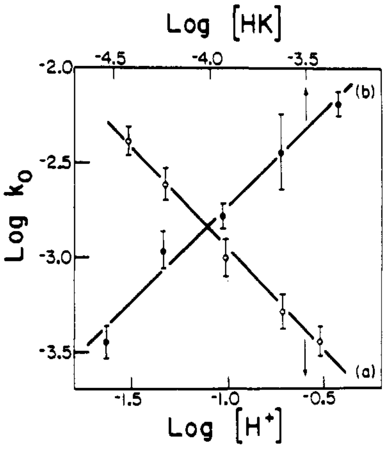

Figure 3. Plot of log of the apparent rate constant, k_0, vs (a) log of the hydrogen ion concentration for reduction of Np(VI) by 0.580 × 10^{-4} M kojic acid and (b) log of the kojic acid concentration at 0.1 M hydrogen ion concentration.

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radicals; analogous products were observed by ESR spectrometry in the oxidation of kojic acid by Ce(IV).[24] We assume that such radicals are formed in the reduction of Np(VI) by HK. Such phenoxy radicals would be unstable because the nonbonding orbital of the oxygen atom does not overlap with the π-bonding orbitals of the ring. There may be ring cleavage in the subsequent reaction of the phenoxy radical of kojic acid.

The empirical rate law, eq 1, as well as the linear plot of the ln (k/T) vs $1/T$ data, excludes a mechanism consisting either of successive steps or of two or more competing parallel pathways with transition states of different composition. The inverse hydrogen ion dependence on the rate indicates the existence of an equilibrium preceding the rate-limiting step with the hydrogen ion produced as a byproduct in this equilibrium. Such a deprotonation is most likely associated with formation of kojate anions from kojic acid. The effect of ionic strength is consistent with the interaction of the kojate anions with NpO_2^{2+} to form the activated complex. These considerations lead to the mechanism

$$\mathrm{HK} \xrightleftharpoons{K_a} \mathrm{H^+ + K^-} \tag{2}$$

$$\mathrm{NpO_2^{2+} + K^-} \xrightleftharpoons{\beta_1} [\mathrm{NpO_2K^+}] \rightleftharpoons [\mathrm{NpO_2K^+}]^{\ddagger} \tag{3}$$

$$[\mathrm{NpO_2K^+}]^{\ddagger} \xrightarrow{k_1} \mathrm{NpO_2^+} + {}^{\bullet}\mathrm{K} \tag{4}$$

$${}^{\bullet}\mathrm{K} \rightarrow \text{products} \tag{5}$$

The rate equation derived from this mechanism is

$$\text{rate} = k_1\beta_1 \frac{[\mathrm{Np(VI)}][\mathrm{HK}]_\mathrm{T}}{1 + K_a[\mathrm{H^+}] + \beta_1[\mathrm{HK}]} \tag{6}$$

where k_1 is the rate constant for the rate-limiting step, β_1 is the stability constant for formation of NpO_2K^+, and K_a is the association constant for kojic acid. From log K_a = 7.67 and log β_1 = 7.1 (the value for formation of $[UO_2K^+]$[25,26]) the rate equation, for our conditions, can be reduced to

$$\text{rate} = \frac{k_1\beta_1}{K_a} \frac{[\mathrm{Np(VI)}][\mathrm{HK}]_\mathrm{T}}{[\mathrm{H^+}]} \tag{7}$$

From eq 1 and 7, we derive the relationship $k = k_1\beta_1/K_a$, which results in a value of $k_1 = 6.06 \pm 0.30$ s^{-1} at 25 °C and μ = 1.0 M (NaCl).

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Registry No. Np, 7439-99-8; kojic acid, 501-30-4.

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Non-Metal Redox Kinetics: Oxidation of Iodide by Hypochlorous Acid and by Nitrogen Trichloride Measured by the Pulsed-Accelerated-Flow Method

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The very rapid reaction between HOCl and I^- is general-acid- (HA-) assisted. The proposed mechanism is

$$\mathrm{HOCl + I^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HOClI^-}$$

$$\mathrm{HOClI^-} \xrightarrow{k_0} \mathrm{HO^- + ICl}$$

$$\mathrm{HOClI^- + HA} \xrightarrow{k_{HA}} \mathrm{H_2O + ICl + A^-}$$

$$\mathrm{ICl + 2I^-} \xrightarrow{\text{fast}} \mathrm{I_3^- + Cl^-}$$

where a stability constant (k_1/k_{-1} = 220 M^{-1}) is determined for the $HOClI^-$ intermediate from kinetic data and the limiting rate constant at high $[H^+]$ is $k_1 = 4.3 \times 10^8$ M^{-1} s^{-1}. Values for third-order rate constants (with the general form $k_1k_{HA}/(k_0 + k_{-1})$ (M^{-2} s^{-1}) at 25.0 °C, μ = 0.1) are evaluated for H_3O^+ (3.5×10^{11}), CH_3COOH (3.2×10^{10}), and $H_2PO_4^-$ (2.6×10^{10}) and give a Brønsted α value of 0.11, which indicates a small degree of proton transfer in the transition state. For the H_2O path, $k_0k_1/(k_0 + k_{-1}) = 1.4 \times 10^8$ M^{-1} s^{-1}. The reaction between trichloramine and iodide exhibits saturation kinetics due to the formation of NCl_3I^- ($K_1 = 6 \times 10^3$ M^{-1}), which undergoes first-order decomposition ($k_2 = 1.5 \times 10^4$ s^{-1} at 25.0 °C and μ = 0.1) to $HNCl_2$ and ICl. Acids do not affect the rate of NCl_3I^- decomposition. For these two studies first-order rate constants fall in the range of 10 000–142 000 s^{-1} and are measured by pulsed-accelerated-flow spectroscopy.

Introduction

Stopped-flow studies showed[1] that the reaction between OCl^- and I^- is general-acid-assisted with a Brønsted α value of 0.75. The third-order rate constant for $H_3O^+ + OCl^- + I^-$ is so large (4.4×10^{15} M^{-2} s^{-1}) that it is necessary to assume HOCl forms first (which is not the case for other acids) and that its reaction with I^- has a second-order rate constant of 1.4×10^8 M^{-1} s^{-1}. In the present study we examine the direct reaction between HOCl and I^- by use of pulsed-accelerated-flow (PAF) methods[2,3] and

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