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Chapter 28

Reduction of Neptunium(VI)
by Organic Compounds

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The kinetics and mechanism of the reduction of NpO_2^{2+} by dicarboxylic acids and hydroxylic compounds are reviewed, and new data on reduction by hydroxybenzoic acids are discussed. Maxima in log k_{obs} as a function of pH for the alkyl dicarboxylic acids have been interpreted as resulting from reduction via NpO_2L formation with inhibition by $NpO_2L_2^{2-}$. Reduction of NpO_2^{2+} by hydroxyl compounds was studied by solvent extraction and spectrophotometric techniques. Data of the primary salt, kinetic solvent isotope, micelle effects, and of the products of the analogous reaction between Ce(IV) and o-hydroxybenzoic acid are consistent with interaction of NpO_2^{2+} with the hydroxyl group. This interaction results in redox reaction with the formation of hydroxyl radicals. A correlation between the rate constants and the basicity of the hydroxyl group and an isokinetic relationship between the enthalpy and entropy of activation are discussed in terms of the proposed mechanism.

Redox reactions between metal cations and organic compounds have attracted the attention of chemists for both fundamental and practical reasons. Among the topics of fundamental interest are questions about the nature of the transition state, the mode of electron transfer, and the rearrangement or dissociation of the organic reagent. Organic reductants may be chosen to serve as models for reactants in biological and environmental systems in which electron-transfer reactions play significant roles.

The redox reactions of some lighter actinides (e.g., neptunium and plutonium) offer particularly challenging systems; they can exist in as many as four oxidation states in aqueous solution. The An(IV)–An(III) and the An(VI)–An(V) couples involve simple electron loss or gain. The An(VI)–An(IV) and An(V)–An(IV) half-reactions include metal–oxygen bond formation or rupture, as well as electron gain or loss, because of the dioxo structure of the actinyl ions $An(V)O_2^+$ and $An(VI)O_2^{2+}$. The redox behavior of the actinides is complicated further by the possibility of disproportionation reactions at macro- (but not at micro-) concentrations.

Benzoic acid was not found to reduce NpO_2^{2+} (*1*), whereas oxalic acid reduces both NpO_2^{2+} (*2*) and PuO_2^{2+} (*3*). The product was reported to be An(IV); however, the probability of concurrent disproportionation reactions limited the value of these studies. Hydroquinones reduce NpO_2^{2+} and PuO_2^{2+} (*4*), as do compounds with phenolic groups (*1*).

The environmental behavior of actinide ions involves hydrolysis, as well as complexation with organic and inorganic ligands. One of the significant organic species is humic acid, for which the overall features of interaction with actinide ions have been discussed elsewhere (5). Studies of the redox behavior of hexavalent actinide ions (UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}) with humic acid showed that NpO_2^{2+} is reduced to NpO_2^+ and PuO_2^{2+} to Pu^{4+}, although UO_2^{2+} is not reduced (6). A detailed kinetic analysis of the reduction of NpO_2^{2+} proved fruitless. However, an understanding of the kinetics of the reduction of hexavalent actinide ions by simple organic molecules with functional groups similar to the reactive ones in humic acid could serve to clarify the nature of the interaction with humic acid.

In this chapter we review studies of Np(VI) reduction at tracer concentrations by dicarboxylic acids (7) and by several types of hydroxylic reductants (1, 8–12). New data on reduction by hydroxybenzoic acids are included. The experimental procedures, similar in all studies from this laboratory, are described with particular attention to the new studies with the hydroxybenzoates.

We conducted experiments to test the sensitivity to light of the redox reactions between Np(VI) and the organic compounds under investigation. At pH 1.4 and total organic acid concentrations of $(1–5) \times 10^{-3}$ M, no effect of room light on the reduction rate was measured. Subsequently, all experiments were performed without taking special precautions to avoid light exposure.

In our experiments, a constant $[H^+]$ and a relatively large excess of the reducing agent were used. The reaction order with respect to [Np(VI)] was derived from the variation of ln $([Np(VI)]/[Np]_{total})$ with time. A linear relationship was obtained for all the organic systems investigated, which indicated that the reaction was pseudo-first-order in [Np(VI)]. From the slope, k_{obs}, the pseudo-first-order constant was calculated for each system.

Experimental Procedures

Reagents and Equipment

All the chemicals employed were reagent grade or better. Special precautions to ensure that reduction occurred only with the reducing agent under study included preparation of all solutions from water redistilled from basic permanganate solution and pretreatment of all glassware used in the reduction and extraction operations with hot HNO_3 + $NaBrO_3$ solutions, followed by rinsing with the redistilled water.

o-Hydroxybenzoic acid (*o*-HBA), *m*-hydroxybenzoic acid (*m*-HBA), and *p*-hydroxybenzoic acid (*p*-HBA) (Aldrich Chemical Co.) were recrystallized twice from redistilled water. Stock solutions of these compounds (0.01 M) were prepared by dissolving the purified compounds in redistilled water. Dilution with appropriate amounts of NaCl solution (to maintain the proper ionic strength) was used to prepare the working solutions. All the kinetic experiments, except those on the salt effect, were carried out at ionic strength $I = 0.10$ M. The pH adjustments were performed with reagent-grade NaOH and HCl solutions and a Corning 130 pH meter.

Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) (Aldrich Chemical Co.) were used without further purification in the experiments on micelle effect.

Thenoyltrifluoroacetone (HTTA) (Aldrich Chemical Co.) was purified by sublimation at about 60 °C. After preparation, the extractant solution of 0.50 M HTTA in toluene was shaken for 0.5 h with a solution of 0.01 M $NaBrO_3$ + 0.10 M HNO_3 to destroy reducing impurities. Washing with 0.01 M HNO_3 removed any bromate remaining in the organic phase.

The NpO_2^{2+} stock solution was prepared by procedures described in reference 7.

Ecolume (ICN Biomedicals) was used as the scintillation solution for counting the
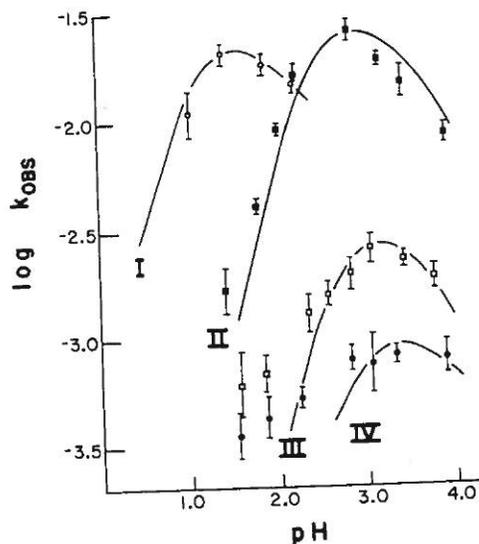
Figure 1. Variation of log k_{obs} with pH for the reduction of NpO_2^{2+} by dicarboxylic acids. I = 0.10 M (NaCl), T = 23 °C. Key: I, 1.0×10^{-3} M oxalic acid; II, 5.0×10^{-3} M malonic acid; III, 5.0×10^{-3} M methylmalonic acid; and IV, 5.0×10^{-3} M dimethylmalonic acid. (Reproduced from reference 7. Copyright 1984 American Chemical Society.)

The experiments on the micelle effect were performed at ambient temperature (~23 °C). A reactant, either NpO_2^{2+} tracer or the ligand acid, was mixed with the micelle-forming agent in a quartz cell of 1.0-cm optical path. After 0.5 h the other reactant was introduced into the cell with thorough mixing. The absorbance of NpO_2^+ in the mixed solution was followed on the Cary-14 spectrometer as a function of time. The results reported in this chapter are the average values of duplicate runs.

The procedures for separation and identification of the organic products of the reaction between Ce(IV) and o-HBA are presented in detail in reference 19. Two samples of the organic oxidation products were obtained from the reaction mixture by extraction with ethyl ether. A portion of one sample (I) was dissolved in ethyl ether and the solution used for GC–MS analysis. A small amount of the other sample (II) was placed directly on the MS probe and analyzed.

Reduction by Dicarboxylic Acids

The data for some dicarboxylic acids of the log k_{obs} at different pH values are shown in Figure 1. The maximum in these values could be interpreted as showing that formation of NpO_2L promotes reduction while formation of $NpO_2L_2^{2-}$ inhibits it. To test this interpretation, the formation of these complexes for these conditions was calculated as a function of pH. The resulting values of log ($[NpO_2L]/[Np]_T$) are plotted as solid lines in Figure 1.

The calculated curves were scaled to match approximately the maximum values of k_{obs}. The agreement of the curves with the data points is good for oxalic and malonic acids but somewhat poorer for methylmalonic and dimethylmalonic acids at higher $[H^+]$, possibly because of the formation of the NpO_2HL species. For all four dicarboxylic acids, the maximum values of the experimental log k_{obs} do occur at the

α activity of ^{237}Np on a Packard Tri-Carb 4000 Series liquid scintillation counter.

A computer-interfaced Cary-14 spectrophotometer (rebuilt by On-Line Instrument System) was used for measuring the absorbance of NpO_2^+ at 980.5 nm in the spectrophotometric experiments on the micelle effect.

GC–MS measurements of the organic oxidation products were performed on a Finnegan 4510 GC–MS spectrometer.

Procedures

The procedures for the solvent-extraction experiments and for counting the radioactivity were described in a previous publication (1). Duplicate or triplicate experiments were performed to check the reproducibility of the results.

same $[H^+]$ as for the calculated curves. This agreement supports the model that the NpO_2L complex is, indeed, involved in the redox reaction.

Taube (13) explained that a similar observation for $MnC_2O_4^+$ and $Mn(C_2O_4)_2^-$ was due to a higher activation energy for the decomposition of the 1:2 complex. The second ligand probably increases the average metal–donor distance for both ligands. The great sensitivity of the electron transfer to this distance accounts for the observed reduction inhibition by the formation of $NpO_2L_2^{2-}$.

On the basis of this model the rate constant, k_1, should be calculated from k_{obs} (7) for the dissociation:

$$NpO_2L \xrightarrow{k_1} NpO_2{}^+ + \cdot L^- \qquad (1)$$

where $\cdot L^-$ is the dicarboxylate free radical anion. The equations are (7):

$$\text{rate} = k_1[NpO_2L] \qquad (2)$$

$$k_1 = k_{obs}\frac{Y^2 + \beta_1 C_T Y + \beta_2 C_T{}^2}{\beta_1 C_T Y} \qquad (3)$$

where β_1 and β_2 are the stability constants for the formation of NpO_2L and $NpO_2L_2^{2-}$, respectively. C_T is the total concentration of the dicarboxylic acid and

$$Y = 1 + K_{2a}{}^{-1}[H^+] +$$
$$(K_{1a}K_{2a})^{-1}[H^+]^2 \qquad (4)$$

in which K_{1a} and K_{2a} are the acid dissociation constants of H_2L. Table I lists the values of k_1 and the activation parameters $\Delta H^{\ddagger}$ (enthalpy of activation), $\Delta G^{\ddagger}$ (activation free energy), and $\Delta S^{\ddagger}$ (entropy of activation) from the variation of $\ln k_1$ with temperature.

Studies of Ce^{4+} reduction by malonic acid and alkylmalonic acids indicated that the unpaired electron in $\cdot CR(CO_2H)_2$ (R

is alkyl) was located on the methylene carbon and that the rate-determining step involved loss of a methylene proton (14). This model was supported by the studies in reference 15, which found that the rate decreased successively as a methyl and an ethyl group replaced one of the methylene protons of malonic acid. Moreover, complexation of Ce^{4+} by dimethylmalonic acid (no methylene proton) did not result in a redox reaction (15). Our data (Table I) showed a sequence in reaction rates of malonate > methylmalonate ~ succinate > dimethylmalonate, which would support the model proposed in references 14 and 15. Moreover, our observed sequence of oxalate < malonate > succinate indicates that the stability of the NpO_2L complex is also a factor because that is the pattern of the $\log \beta_1$ values (16).

Reduction by Hydroxyl Compounds

The kinetics of reduction of $NpO_2{}^{2+}$ to $NpO_2{}^+$ by two nonaromatic cyclic compounds with a hydroxyl and a carbonyl group in the α and β ring positions, respectively, were studied. The two compounds were 5-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one (kojic acid, **1**) (9) and 2-hydroxycyclohepta-2,4,6-triene-1-one (tropolone, **2**) (10). The rate constants and activation parameters at 298 K are given in Table II.

The empirical rate expression for reduction by kojic acid (HK) was found to be

$$\text{rate} = k[NpO_2{}^{2+}][HK]_{total}[H^+]^{-1} \quad (5)$$

The result of the study of the primary salt effect provided further support for this rate equation. According to Espenson (17), the slope of the correlation of $\log k$ and $I^{1/2}/(1 + I^{1/2})$ (where I denotes the ionic strength) can be assigned as

Table I. Rate Constants and Activation Parameters
for Reduction of Np(VI) by Dicarboxylic Acids

Reductant	pH	T (K)	$k_1 (s^{-1})$	$\Delta H^\ddagger$ $(kJ \cdot mol^{-1})$	$\Delta S^\ddagger$ $(J \cdot K^{-1} \cdot mol^{-1})$	$\Delta G^\ddagger (298\ K)$ $(kJ \cdot mol^{-1})$
Oxalic acid	1.1	306.7	1.30×10^{-3}	90 ± 7	-7 ± 21	92 ± 13
Malonic acid	2.2	307.2	2.70×10^{-3}	70 ± 10	-64 ± 25	89 ± 17
Methylmalonic acid	2.4	307.7	1.06×10^{-4}	88 ± 9	-16 ± 29	93 ± 17
Dimethylmalonic acid	3.0	308.2	3.10×10^{-5}	43 ± 13	-183 ± 33	98 ± 22
Succinic acid	4.0	307.0	1.50×10^{-4}	66 ± 9	-103 ± 42	97 ± 22
Maleic acid	3.0	308.9	1.00×10^{-4}	87 ± 12	-43 ± 42	100 ± 16
Phthalic acid	3.0	307.1	5.20×10^{-5}	38 ± 8	-209 ± 25	100 ± 16
Fumaric acid	3.0	296.2	1.80×10^{-5}	37 ± 23	-209 ± 84	99 ± 41

NOTE: $I = 0.1$ M NaCl.

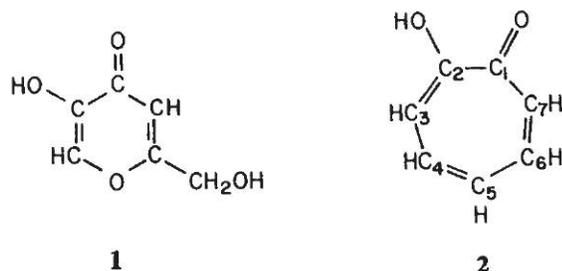SOURCE: Reproduced from reference 7. Copyright 1984 American Chemical Society.

1

2

Table II. Rate Constants and Activation Parameters for Reduction of Np(VI) by Kojic Acid and Tropolone

Reductant	k	$\Delta H^{\ddagger}$ $(kJ \cdot mol^{-1})$	$\Delta S^{\ddagger}$ $(J \cdot K^{-1} mol^{-1})$
Kojic acid[a]	1.47 s^{-1}	82.7 ± 3.4	34 ± 11
Tropolone[b]	70.8 M s^{-1}	67.2 ± 3.4	15 ± 12

NOTE: $I = 1.0$ M (NaCl); $T = 298$ K.

[a]Data taken from reference 9.

[b]Data taken from reference 10.

$$slope = 0.5[Z_X{}^2 + Z_Y{}^2 - Z_A{}^2 - Z_B{}^2] \quad (6)$$
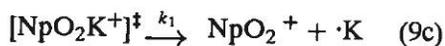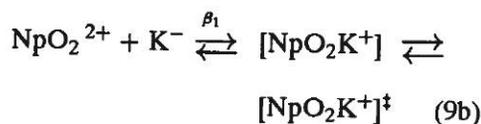
for a hypothetical net activation reaction

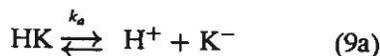$$A + B \rightarrow X^{\ddagger} + Y \quad (7)$$
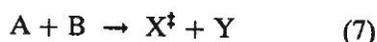
where A and B denote the reactants, $X^{\ddagger}$ the activated complex, and Y the product; Z_A, Z_B, Z_X, and Z_Y are their charges, respectively. The simplest reaction that fits the rate expression is

$$NpO_2{}^{2+} + HK = (NpO_2K^+)^{\ddagger} + H^+ \quad (8)$$
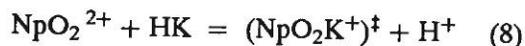
for which the predicted slope of the correlation of $\log k$ and $I^{1/2}/(1 + I^{1/2})$ would be expected to be -1 (eq 6). For the $NpO_2{}^{2+}$–HK system, measurement of the rate constant as a function of ionic strength of the solution showed a slope of -0.97 for

$\log k$ vs. $I^{1/2}/(1 + I^{1/2})$, which is consistent with the expected value. The inverse [H$^+$] dependence in the empirical rate expression suggests a mechanism with an equilibrium (which produces a hydrogen ion) preceding the rate-determining step. These data are consistent with the following mechanism:

$$HK \xrightleftharpoons{k_a} H^+ + K^- \quad (9a)$$

$$NpO_2{}^{2+} + K^- \xrightleftharpoons{\beta_1} [NpO_2K^+] \rightleftharpoons$$
$$[NpO_2K^+]^{\ddagger} \quad (9b)$$

$$[NpO_2K^+]^{\ddagger} \xrightarrow{k_1} NpO_2{}^+ + \cdot K \quad (9c)$$

$$\cdot K \rightarrow products \quad (9d)$$

The rate equation derived from this mechanism is

$$\text{rate} = k_1\beta_1 \frac{[\text{Np(VI)}][\text{HK}]_T}{1 + K_a[\text{H}^+] + \beta_1[\text{HK}]} \quad (10)$$

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 $\log \beta_1 = 7.1$ (the value for formation of $[\text{UO}_2\text{K}^+]$ (18)), the rate equation, for the experimental conditions, could be reduced to

$$\text{rate} = \frac{k_1\beta_1}{K_a} \frac{[\text{Np(VI)}][\text{HK}]_T}{[\text{H}^+]} \quad (11)$$

From equations 5 and 11, the relationship $k = k_1\beta_1/K_a$ was derived. This relationship resulted in a value of $k_1 = 6.06 \pm 0.30$ s^{-1} at 25 °C and $I = 1.0$ M (NaCl).

The empirical rate expression for the reduction by tropolone (HTr) was

$$\text{rate} = k[\text{NpO}_2{}^{2+}][\text{HTr}]_T[\text{H}^+]^{-2} \quad (12)$$

This expression led to a mechanism identical to that for the kojic acid system, except for an initial fast equilibrium

$$\text{H}_2\text{Tr}^+ \rightleftharpoons \text{HTr} + \text{H}^+ \quad (13)$$

C-13 NMR spectroscopy confirmed the presence of H_2Tr^+ at the pH of the experiments. The values of $pK_1 = 1.0$, $pK_2 = 6.75$, and $\log \beta_1 = 8.18$ give a value of the specific rate constant of $k_1 = 28.5 \pm 0.1$ s^{-1}, which is larger than the corresponding value for reduction by kojic acid. This comparison reflects the lower value of $\Delta H^{\ddagger}$ for the tropolone system.

Reduction by Hydroxybenzoic Acids

Rate Constants

The kinetics of reduction of $\text{NpO}_2{}^{2+}$ were studied with o-, m-, and p-HBA (1, 8); 3-, 4-, and 5-MSA (methylsalicylic acids) (11), and p-hydroxybenzoic acid methyl ester (p-HBAME) (12). The reactions were followed at tracer concentrations of neptunium by solvent extraction and at macroscopic concentrations by spectroscopy at higher pH values where the rate was too rapid for the solvent extraction method. In all systems, the product of the $\text{NpO}_2{}^{2+}$ reduction was $\text{NpO}_2{}^+$. The empirical kinetic rate expression for all the reductants was the same:

$$\text{rate} = k[\text{NpO}_2{}^{2+}][\text{HOLH}][\text{H}^+]^{-1} \quad (14)$$

where HOLH represents the acid form of the hydroxyl reducing agents (e.g., $o-\text{HO}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ for o-HBA). The inverse dependence on the hydrogen ion concentration is most simply interpreted as indicating release of a proton in the redox process.

The values of k in eq 14 for the ligands studied, as well as for phenol (19) and p-hydroxybenzenesulfonic acid (p-HBSA) (1), are listed in Table III. The reduction rate expression for the latter two ligands is the same as eq 14. Figure 2 shows the correlation of the values of $\log k$ with the pK_a values for the ionization of the hydroxyl proton. The pK_a measures the electronic density on the hydroxyl oxygen, so the correlation of $\log k$ and pK_a indicates that the rate constants are sensitive to that charge density. Such sensitivity, as well as the observation that the reduction by the methyl ester fits the correlation, suggests that the $\text{NpO}_2{}^{2+}$ reacts with the hydroxyl group. Any interaction with the carboxylic (or sulfonic) group must be secondary.

The data fit two separate correlations, one for the salicylic acids (N.B., o-HBA is

Table III. Rate Constants and Activation Parameters
for the Reduction of Np(VI) by Phenolic Compounds

Reductant	k (s^{-1})	$\Delta H^{\ddagger}$ $(kJ \cdot mol^{-1})$	$\Delta S^{\ddagger}$ $(J \cdot K^{-1} mol^{-1})$	Ref.
o-HBA	$(3.03 \pm 0.12) \times 10^{-1}$	96 ± 3	67 ± 7	a
p-HBA	$(9.12 \pm 0.67) \times 10^{-2}$	104 ± 5	83 ± 13	a
m-HBA	$(6.47 \pm 0.37) \times 10^{-1}$	89 ± 4	50 ± 9	a
3-MSA	(5.15 ± 0.48)	87 ± 3	62 ± 7	11
4-MSA	$(5.36 \pm 0.57) \times 10^{-1}$	102 ± 1	93 ± 2	11
5-MSA	$(1.05 \pm 0.10) \times 10$	83 ± 4	54 ± 8	11
p-HBAME	$(3.94 \pm 0.10) \times 10^{-2}$	94 ± 4	43 ± 3	12
p-HBSA	$(7.94 \pm 0.52) \times 10^{-2}$			1
Phenol	(2.45)			19

NOTE: $I = 0.1$ M (NaCl); $T = 298$ K.
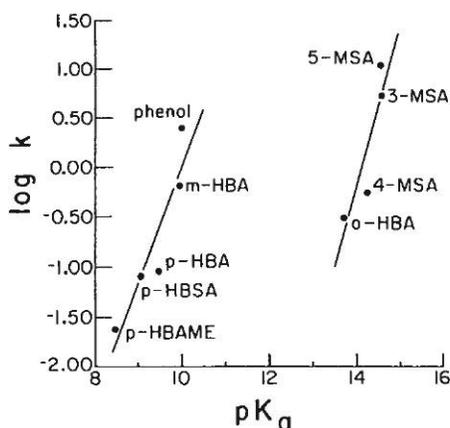
[a]Present work.

Figure 2. Correlation of log k and pK_a for the reduction of NpO_2^{2+} by phenolic compounds.

salicylic acid) and a second for the other ligands. This difference may be related to the intramolecular hydrogen bonding between the phenolic and carboxylic groups in the salicylic acids, which makes the second pK_a values high as they reflect not only the electron density on the phenolic group but also the degree of intramolecular hydrogen bonding. As a result, this pK_a value is not a good measure for the elec-

tron density on the phenolic group of the salicylic acids. Furthermore, the rate constants for the salicylic acids could be lower than predicted from the pK_a's if the intramolecular hydrogen bonding decreases the probability of formation of an intermediate complex between NpO_2^{2+} and the phenolic group.

Mechanism

The correlation of log k and $I^{1/2}/(1 + I^{1/2})$ was linear with a slope of -0.8 ± 0.2 for the NpO_2^{2+}–hydroxybenzoic acids. This finding is in fair agreement with the value of -1 predicted by eq 6 for the reaction

$$NpO_2^{2+} + HBA \rightarrow$$
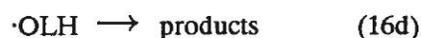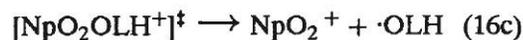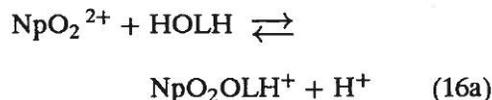$$[NpO_2BA^+]^{\ddagger} + H^+ \qquad (15)$$
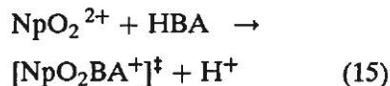
Additional evidence for reaction of the NpO_2^{2+} directly with the hydroxyl groups was obtained in a measurement of the kinetic solvent isotope effect in reduction by p-HBAME. A kinetic solvent isotope effect (20) may arise from the substitution of H_2O with D_2O if there is a fast

exchange of hydrogen between the solvent and the reactant molecules. In an aqueous solution of p-HBAME, there is such fast exchange of the hydrogen of the phenolic group with water. The study of the kinetic solvent isotope effect gave k_H/k_D ratios from 3.56 to 2.90 as the temperature increases from 5.5 to 25.0 °C. The ratio of the dissociation constants, K_A^H/K_A^D, of various phenolic compounds in H_2O and in D_2O varies from 3.1 to 5.0 (21), in agreement with the values of k_H/k_D. Such agreement is consistent with a model in which the kinetic isotope effect arises from the difference in the strengths of the O–H and the O–D bonds of the phenolic group in p-HBAME.

The slope of log k_H vs. $I^{1/2}/(1 + I^{1/2})$ for the NpO_2^{2+} + p-HBAME was -0.81 ± 0.20. This is the same slope observed for the hydroxybenzoic acid system. Thus, it is strong evidence that the $[H^+]^{-1}$ dependence of eq 14 and the H^+ released in the reaction of eq 15 are associated with the hydroxyl proton and not the proton of the carboxylic acid group of the HBAs.

In the spectrophotometric study (8) of the reduction of NpO_2^{2+} by HBAs, a yellow color formed rapidly when solutions of NpO_2^{2+} and the HBAs were mixed, and then decayed gradually. This observation suggested that intermediates are formed in the course of the reaction. Kinetic experiments by the stopped-flow technique in the 400–450-nm wavelength region provided evidence for the rapid formation of intermediate complex followed by its gradual decomposition (8).

On the basis of the preceding data, a mechanism was proposed for the reduction of NpO_2^{2+} to NpO_2^+ by hydroxyl compounds (represented as HOLH). This mechanism is

$$NpO_2^{2+} + HOLH \rightleftharpoons$$

$$NpO_2OLH^+ + H^+ \quad (16a)$$

$$NpO_2OLH^+ \rightleftharpoons [NpO_2OLH^+]^\ddagger \quad (16b)$$

$$[NpO_2OLH^+]^\ddagger \longrightarrow NpO_2^+ + \cdot OLH \quad (16c)$$

$$\cdot OLH \longrightarrow products \quad (16d)$$

Oxidation Products

The products formed from the oxidation of the organic reagent could not be determined in the neptunium studies, as the total amount of reactants was always very small. Reduction of Ce(IV) to Ce(III), which is a one-electron reaction of reduction potential similar to that of the Np(VI)–Np(V) couple, would be expected to follow a similar mechanism. Therefore, this system was studied for products after reaction of macroconcentrations.

The oxidation products of the reaction were expected to provide useful data for evaluation of the relative roles of the carboxylic and of the phenolic groups. Redox reactions involving the phenolic group would result in the formation of phenoxy radicals, which would react further via redox reaction or by undergoing an oxidative radical combination involving either carbon–carbon or carbon–oxygen coupling (22). Simple phenoxy radicals link at positions ortho or para to the phenoxy group to yield dimers, trimers, and polymers.

An electron spin resonance study of phenoxy radicals, using a flow technique (23), found that a large fraction of the unpaired spin density in the radicals is distributed over the π-electron system of the aromatic ring; in monohydroxyl radicals the spin density is nearly 50% higher in the para than in the ortho position. These data agree with the observation that para coupling seems to predominate in competition with ortho coupling (24).

Two samples of the reaction mixture of Ce(IV) + o-HBA were analyzed by mass spectrometry (Figure 3). Three major peaks were observed in each spectrum. In the spectrum of sample I, the m/e ratios of the peaks were 138.1, 120.1, and 92.1; no peaks at higher m/e ratios were detected. In the spectrum of sample II, the ratios
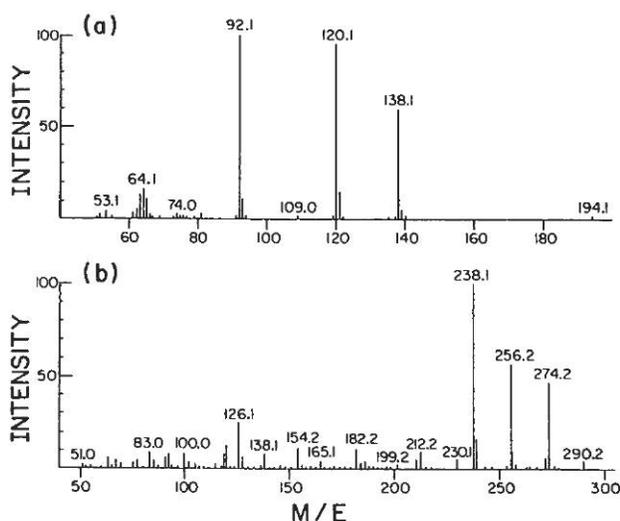
Figure 3. Mass spectra of the reaction products between Ce(IV) and o-HBA: a, sample I; and b, sample II.

were 274.2, 256.2, and 238.1. The yield (weight percent) of sample II was about 50%.

The scheme of radical coupling (Scheme I) is consistent with the mass spectra of the organic products of the reaction between Ce(IV) and o-hydroxybenzoic acid (Figure 3). The MS spectrum of sample I shows mainly unreacted o-HBA (mol wt is 138) and larger molecules are not detected. For sample II, the peak at 274.2 corresponds to the dimeric species of o-HBA. The peaks at 256.2 and 238.1 (m/e) could be assigned to the dimer species that have lost one and two water molecules, respectively, at the high temperature and under the electron bombardment in the mass spectrometer.

The presence of the dimeric species of o-HBA in the reaction products was strong evidence for the formation of phenoxy radicals. This observation supports the model in which the reaction occurs through the interaction between NpO_2^{2+} and the phenolic group. The mass spectra provide no evidence for products resulting from redox reaction involving the carboxylic group.

Activation Parameters

The activation parameters were obtained by measuring k over a range of temperatures (0–50 °C). The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are listed in Table III. The values are plotted in Figure 4, where the methylsalicylic acids show an isokinetic correlation parallel to that of the simple hydroxybenzoic acids. An isokinetic correlation is taken to reflect that the correlating systems proceed by the same mechanism.

The fact that the two groups of organic reductants do not fall on the same correlation line would not seem to be evidence for different mechanisms because reaction by o-HBA should exhibit the same mechanism as the other three salicylic acids. The slopes are, within error limits, the same; the error bars of each value are large, and the two series were done some time apart. Some experimental effect may be responsible for the observed offset of the two lines.

The $\Delta H^{\ddagger}$ values are comparable to those of the kojic acid and tropolone systems, whereas the $\Delta S^{\ddagger}$ values are larger. This difference may be due to the ionic
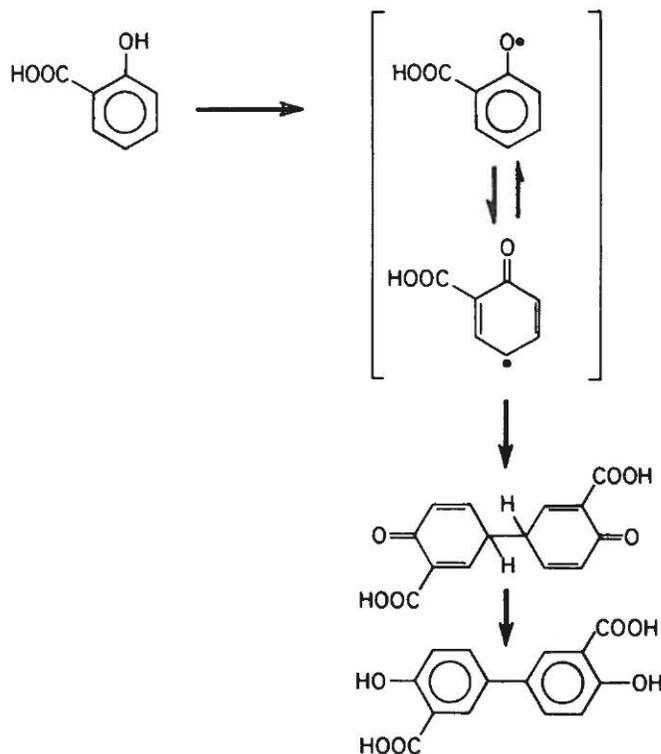
Scheme I. Formation of dimer due to phenolic oxidative coupling.

strengths of the solution (0.1 M for the hydroxybenzoic acids and 1.0 M for the kojic–tropolone system).

Effect of Micelles

The reduction of NpO_2^{2+} by *o*-HBA was also studied in the presence of micelle-forming agents to investigate the effect of the interaction between the reactants and the micellar aggregates on the reaction kinetics. In natural aquatic systems that have neutral pH values, metal cations react not only by complexation, hydrolysis, etc.; the complexed species can further interact with colloids. An understanding of the role colloids can play in the environmental behavior of actinides is essential to developing satisfactory geochemical models.

The rate of the reduction of NpO_2^{2+} was measured in solutions in which the pH was 1.0 and the concentration of *o*-HBA constant while the concentration of the

anionic micelle sodium dodecyl sulfate, SDS, was varied. The results are shown in Figure 5. [SDS] is defined as the concentration of SDS in moles of monomeric species.
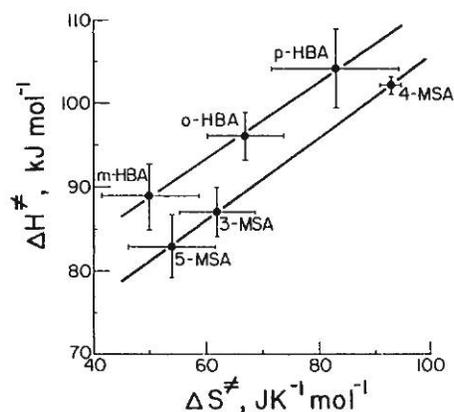

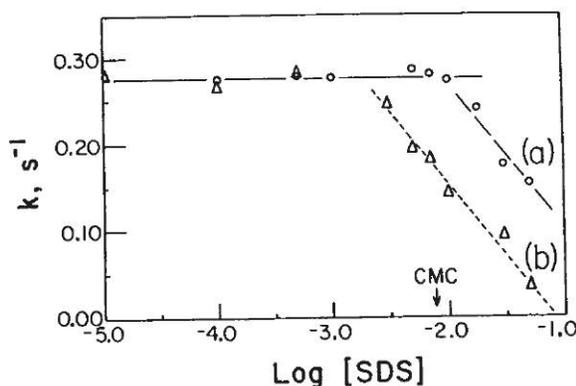*Figure 4. Isokinetic relationship for the reduction of NpO_2^{2+} and hydroxybenzoic acids.*

Figure 5. Effect of SDS micelles on the reduction of NpO_2^{2+} by o-HBA: a, set I; and b, set II.
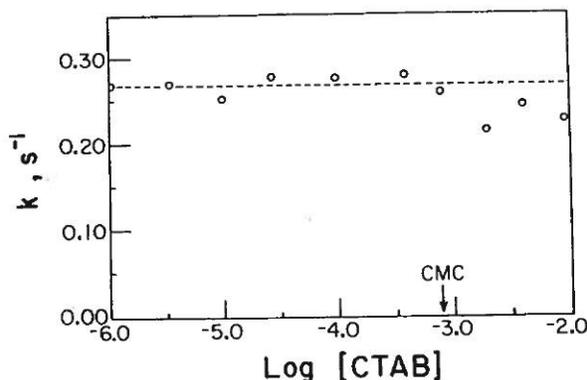

Figure 6. Effect of CTAB micelles on the reduction of NpO_2^{2+} by o-HBA.

Two sets of experiments were conducted in which the sequence of mixing the two reactants with the micelle was reversed. In I, *o*-HBA was mixed with SDS, then NpO_2^{2+} tracer was added. In II, NpO_2^{2+} tracer was mixed with SDS, then *o*-HBA was added. The time interval between the initial mixing of SDS and a reactant and the addition of the second reactant was about half an hour. In both cases, at higher concentrations of SDS, the rate constant decreased with increasing [SDS]. This effect was greater in II than in I and was present for II even when [SDS] was lower than the critical micelle concentration (CMC). For both I and II, no effect on the reduction rate was observable at [SDS] < 0.001 M.

Figure 6 shows the absence of an effect by the cationic micelle, cetyltrimethylammonium bromide (CTAB), on the redox reaction between NpO_2^{2+} and *o*-HBA. Even when the CTAB concentration ([CTAB] is defined as the concentration of CTAB in moles of monomeric species) was higher than the CMC, the variation of the rate constant fell within the error limits of the experimental value of the rate constant in the absence of the CTAB.

The two micellar agents studied, SDS and CTAB, have anionic sulfate and cationic alkylammonium as their head groups. The decrease in rate constants for the reduction of NpO_2^{2+} by *o*-HBA in the presence of SDS micelles (both Set I and Set II shown in Figure 5) indicates that the

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interaction between NpO_2^{2+} and the SDS micelle inhibits the reduction of NpO_2^{2+} by o-HBA. This pattern can be explained as follows.

In the presence of SDS micelles, the NpO_2^{2+} cations are attracted by the negatively charged SDS micelles. As a result, the rate of the reduction should be expected to decrease because the negative potential field of the SDS micelles repels the o-hydroxybenzoate anion, thereby reducing the availability of o-HBA for reaction with NpO_2^{2+} bound to the micelles. This latter effect has been used to explain the decreased reduction of UO_2^{2+} by viologen radical anions in the presence of poly(vinyl sulfate) (25). The enhanced decrease in the rate when the NpO_2^{2+} tracer was mixed with SDS followed by addition of o-HBA (Set II, Figure 5) probably reflects diffusion of NpO_2^{2+} farther into the Stern layer of the micelle, which causes the NpO_2^{2+} to be more shielded from reaction with o-HBA. For Set II, the decrease in rate constant was present even for SDS concentrations below the CMC. This decreased rate constant may mean that the interaction of the SDS with NpO_2^{2+} promotes aggregation of the SDS even below the CMC.

In the CTAB system, the cationic head groups of the micelles would attract neither the NpO_2^{2+} cations nor the un-ionized HBA molecules present at pH 1.0. These expectations are consistent with the observation of no significant effect by CTAB micelles on the reaction between NpO_2^{2+} and HBA (Figure 6).

Acknowledgment

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