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Reduction of the Chromium(III)–Neptunium(V) Complex by Neptunium(III)

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The empirical rate law for the reaction $Np^{III} + Cr^{III}{\cdot}Np^{V} = 2Np^{IV} + Cr^{III}$ in acid perchlorate solution is $-d[Np^{III}]/dt = k[Cr^{III}{\cdot}Np^{V}][Np^{III}][H^+]^0$. Values of $k = (1.6 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$, $\Delta H^* = 2.6 \pm 0.1$ kcal/mol, and $\Delta S^* = -35.3 \pm 0.4$ cal mol^{-1} deg^{-1} were determined at 25°, $I = 0.50\ M$ ($LiClO_4$). A comparison with the Np^{III}–Np^{V} reaction suggests that the coordinated Cr^{III} is much more effective than H^+ at promoting reduction of Np^{V}. The rate law implies an activated complex with a formal charge of 7+, a rarity in ionic reactions. The $S^*(CrONpONp^{7+})$ is estimated to be −144 cal mol^{-1} deg^{-1}, a value in harmony with an extension of the previously noted approximate correlation between the formal charge and entropy of activated complexes.

Introduction

The complex between Cr^{III} and Np^{V} is weak in a thermodynamic sense but undergoes dissociation slowly.[1] The effect of the coordinated Cr^{III} on the oxidation of Np^{V} by Co^{III} has been tested previously.[2] A comparative kinetic study of the reduction of the $Cr^{III}{\cdot}Np^{V}$ complex and hydrated Np^{V} by the common reagent Np^{III} is the topic of this article. The rate law for the latter system included a positive hydrogen ion dependence.[3-5] This result suggests that the $Cr^{III}{\cdot}Np^{V}$–Np^{III} reaction may proceed through an activated complex with a formal charge as high as 7+, a rarity in ion reactions.[6] The activation entropy and medium effects of a system with such high ionic charges are additional features of interest.

Experimental Section

Reagents. The preparation and standardization of the Np^{V},[7] chromium(III) perchlorate,[8] and sodium and lithium perchlorate[9] solutions have been described elsewhere. Fresh stock solutions of the $Cr^{III}{\cdot}Np^{V}$ complex were isolated from an equilibrated solution by ion-exchange techniques.[10] Np^{III} solutions were freshly prepared for each experiment by reduction of Np^{V} over a granular zinc–mercury pool in a carbon dioxide atmosphere. Np^{IV} solutions were obtained by allowing equivalent amounts of Np^{V} and Np^{III} to react in the absence of oxygen. Triply distilled water, once each from acid, chromium trioxide, and permanganate, was used. The $[H^+]$ of the reaction solutions was determined by titration of the spent reaction mixtures.

Procedures. The stoichiometry of the reaction

$$Np^{III} + Cr^{III}{\cdot}Np^{V} = 2Np^{IV} + Cr^{III} \tag{1}$$

was established by spectrophotometry. The Cr^{III} product was found to be hexaaquochromium(III) rather than a polynuclear species by ion-exchange techniques. The $Cr^{III}{\cdot}Np^{V}$ stock solutions were assayed at 9930 Å after extinction coefficients were determined for the complex at the various ionic strengths used in this study (ε 168, 184, and 223 M^{-1} cm^{-1} at $I = 8.0$, 4.0, and 1.0 M, respectively). The reaction was monitored by following the disappearance of Np^{III} at 2670 Å (ε 1596 M^{-1} cm^{-1}). Small corrections were applied for absorbance of the complex; the Cr^{III} and Np^{IV} products were essentially transparent under the experimental conditions at this wavelength. The major experimental problems in this study were the very rapid rate of reaction 1, even at low concentrations of reactants, ionic strength, and temperatures, and the necessity to maintain a very low available oxygen concentration to prevent the rapid Np^{3+}–O_2 reaction.[11] The entire sample compartment of the Zeiss PMQ-11 spectrophotometer was continuously flushed with tank CO_2. The 2-cm^2 quartz reaction vessel was fitted with a special cover with two thin polyethylene tubes extending into the cell; CO_2 purified by bubbling through a Cr^{II} trap was passed through the solution containing all the reagents except Np^{III} for 50 min prior to initiation of the reaction. The reaction vessel was thermostated to ±0.1° and was fitted with a magnetic stirring device that allowed rapid mixing (<1 sec) of the reactants. The reaction was initiated by addition of Np^{III} from a syringe that had been thoroughly flushed with CO_2. Blank experiments demonstrated that the Np^{III} was quantitatively added and mixed with no detectable loss and that less than 4% O_2 oxidation occurred over a 10-min period ($[Np^{III}] = (5–18) \times 10^{-5}\ M$). This loss is probably negligible in the kinetic experiments, since data were seldom taken after 1 min. The transmittance–time data were collected on a strip chart recorder at a maximum chart speed of 24 cm/min. The time of half-reaction of many of the reactions was <20 sec. Unfortunately, radiation safety regulations prohibited the use of stopped-flow techniques with the α emitter Np. Values of the second-order rate parameter k were estimated from a least-squares adjustment of the data (10–20 data points per experiment).

Table I. Effect of Metal Ion Concentration and Temperature on the Np^{III}–$Cr^{III}{\cdot}Np^{V}$ Reaction[a]

T, °C	$10^5[Cr^{III}{\cdot}Np^{V}]_0$, M	$10^5[Np^{III}]_0$, M		k, M^{-1} sec^{-1}
0.0	4.65	5.71		867 ± 35
	5.46	12.7		1036 ± 15
	6.81	5.71		992 ± 47
	6.81	7.12		835 ± 5
	16.5	6.52		1057 ± 10
	16.4	12.7		1049 ± 25
			Av	973 ± 81
10.0	5.46	5.53		1266 ± 15
	5.46	10.5		1008 ± 11
	5.46	10.8		1136 ± 3
	8.43	6.52		1223 ± 38
	8.43	12.7		1151 ± 44
	8.43	17.3		1055 ± 24
	11.9	6.52		1335 ± 9
	11.9	12.7		1172 ± 30
	11.9	17.3		1124 ± 7
	16.5	6.52		1248 ± 29
	16.5	12.7		1246 ± 34
	16.5	17.3		1148 ± 14
			Av	1176 ± 73
17.0	8.48	6.52		1421 ± 26
	8.48	12.7		1319 ± 4
			Av	1370 ± 51
25.0	11.9	6.52		1696 ± 43
	11.9	12.7		1475 ± 37
				1586 ± 110

[a] $[HClO_4] = 0.26\ M$, $I = 0.50\ M$ ($LiClO_4$). Uncertainties are average deviations of triplicate experiments.

Results

The kinetic data were correlated fairly well by the integrated form of the expression

$$-d[Np^{III}]/dt = k[Cr^{III}{\cdot}Np^{V}][Np^{III}] \tag{2}$$

Standard deviations in the rate parameter k usually ranged from 1 to 6% over 1–3 half-lives but were occasionally as high as 20%. The rate data invariably were fit better when a stoichiometric excess of the complex was employed; it is not clear why this should be the case unless trace amounts of the inadvertent oxidation of Np^{III} by oxygen is a serious problem.[12] The reproducibility of triplicate determinations of the rate parameter was usually better than 6%, but there is considerable scatter in the value of k over a moderate range of reactant concentrations (Table I). This scatter appears to be random, and we conclude that rate law (2) adequately describes the

Table II. Hydrogen Ion Dependence of k^a

Salt	$[H^+]$, M	No. of determins	k(av), M^{-1} sec^{-1}
$LiClO_4$	0.050	9	950 ± 67
	0.13	9	995 ± 58
	0.26	18	973 ± 81
	0.51	9	942 ± 36
$NaClO_4$	0.060	6	790 ± 17
	0.13	6	897 ± 27
	0.26	6	955 ± 59
	0.51	6	995 ± 47

[a] $[Cr^{III}\cdot Np^{V}]_0 = (4.35–16.6) \times 10^{-5}\ M$, $[Np^{III}]_0 = (3.43–12.7) \times 10^{-5}\ M$, $T = 0.0°$, $I = 0.51\ M$. Uncertainties are average deviations.

major reaction path under the stated experimental restraints. The initial presence of either product, Np^{IV} or Cr^{III}, at a concentration twice that subsequently produced during the reaction was without effect within the experimental uncertainty. An appropriate blank experiment demonstrated that Np^{IV} does not catalyze the dissociation of the $Cr^{III}\cdot Np^{V}$ complex over times much longer than required for the complete reduction by Np^{III}. Catalytic impurities were apparently not introduced in the preparation of Np^{III}; Np^{III} that had been air oxidized and reduced three times did not alter the value of the rate parameter.

Data at various hydrogen ion concentrations are summarized in Table II. The rate parameter k is essentially independent of hydrogen ion concentration when lithium perchlorate is used to maintain constant ionic strength; with sodium perchlorate there is an apparent, but small, positive dependence.

The ionic strength has a marked effect on the reaction rate. The values of k were 1032 ± 84, 1168 ± 2, 1967 ± 125, and 4229 ± 70 M^{-1} sec^{-1} at I = 0.49, 0.74, 1.20, and 1.80 M ($LiClO_4$), respectively (0.0°, $[H^+] = 0.13\ M$, $[Cr^{III}\cdot Np^{V}]_0 = (4.37–7.77) \times 10^{-5}\ M$ and $[Np^{III}]_0 = (3.43–5.48) \times 10^{-5}\ M$).

Activation parameters for the net activation process[13]

$$Np^{3+} + Cr\cdot NpO_2^{4+} = [CrONpONp^{7+}]^* \tag{3}$$

were calculated from the temperature dependence data in Table I. Values of $\Delta H^* = 2.59 \pm 0.12$ kcal/mol and $\Delta S^* = -35.3 \pm 0.4$ cal mol^{-1} deg^{-1} were obtained.

Discussion

The present results coupled with previous data on the Np^{III}–Np^{V} reaction are sufficient to provide an insight as to the effect of coordinated Cr^{III} on the reduction of Np^{V} by Np^{III}. The net activation process

$$Np^{3+} + NpO_2^{+} + H^+ = [HONpONp^{5+}]^* \tag{4}$$

has been proposed as the dominant pathway in the Np^{III}–Np^{V} reaction.[3] Debate has arisen concerning the importance of a parallel path independent of hydrogen ion,[4,5] but the results in ref 3 will be used in this discussion since that study is the most comprehensive. A convenient way to compare the relative effectiveness of Cr^{3+} and H^+ in promoting reduction of NpO_2^+ by Np^{3+} is to consider the formal process[14]

$$[HONpONp^{5+}]^* + Cr^{3+} = [CrONpONp^{7+}]^* + H^+ \tag{5}$$

The value of the formal equilibrium constant for this process (Q^*) is

$$Q^* = k_1Q/k_2 \tag{6}$$

where k_1 is the rate constant for the hydrogen ion independent $Cr^{III}\cdot Np^{V}$–Np^{III} reaction (*ca.* 5700 M^{-1} sec^{-1} at 25° and I = 2 M), Q is the formation constant for the $Cr^{III}\cdot Np^{V}$ complex (2.6 M^{-1} at 25° and I = 8 M),[1] and k_2 is the rate constant for the hydrogen ion dependent Np^{V}–Np^{III} reaction (43 M^{-2} sec^{-1} at 25°, I = 2 M).[3] The value of Q^* is about 3.5×10^2 using these data. This result suggests that Cr^{3+} is much more effective than H^+ in promoting reduction of NpO_2^+, at least when Np^{3+} is the reductant. Cr^{3+} was also concluded to be more effective than H^+ in the reduction of PuO_2^+ by either Pu^{3+} or Fe^{2+}.[6c] The suggestion that Cr^{3+} weakens and lengthens the actinide metal–oxygen bond that is broken on reduction to a greater extent than H^+ is an appealing one.[6c] Absorption spectra data are consistent with a variation in the Np–O Bond when NpO_2^+ is complexed, particularly with Rh^{3+} and Cr^{3+}, although the infrared data are not so convincing.[10,15] A perplexing question that has existed since the discovery of the $Cr^{III}\cdot Np^{V}$ complex[15] and is relevant to the above is why the complex dissociates so slowly.

The hydrogen ion dependence and ionic strength effects observed in this study are strikingly similar to those reported under comparable conditions in the $Cr^{III}\cdot Pu^{V}$–Pu^{III} system.[6d] The apparent slight hydrogen ion dependence in sodium perchlorate is probably due to a medium effect, as it is unlikely that a reaction pathway is available in these solutions that is not also available in lithium perchlorate. The marked ionic strength effect is consistent with the extended form of the Debye–Hückel equation when the large $\Delta Z^2 = 24$ for this system is considered. The faster rate of the present reaction compared to the corresponding plutonium system ($\Delta H^* = 3.98 \pm 0.13$ kcal/mol and $\Delta S^* = -39.2 \pm 0.4$ cal mol^{-1} deg^{-1} in 0.50 M $HClO_4$)[6d] is due to a more favorable enthalpy and entropy of activation.

An approximate correlation between the formal charge (Z^*) and entropy (S^*) of many activated complexes has been noted.[16-18] Values of S^* have been tabulated for activated complexes with Z^* up to 6+; in the latter case the range is −118 to −133 cal mol^{-1} deg^{-1}. For the present system $S^*(CrONpONp^{7+}) = \Delta S^* + S°(Np^{3+}) + S°(CrO_2Np^{4+}) = -35 - 37 - 72 = -144$ cal mol^{-1} deg^{-1}.[19] This is a reasonable value, and may represent an upper limit on the charge and corresponding entropy of viable activated complexes. It will be interesting in the future to see if a value of $Z^* = 8+$ or higher is observed.

Registry No. Np(III), 21377-65-1; Cr(III), 16065-83-1; NpO_2^+, 21057-99-8; H^+, 12408-02-5.

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(12) The Np^{3+}–O_2 reaction produces Np^{4+}, NpO_2^+, and H_2O_2.[11] Other investigators have admitted difficulty in obtaining reproducible results in studies involving Np^{III}. (See ref 3–5, for example.) Other metal ions that reduce O_2 more than H_2O_2 include the following: (a) $Ru(NH_3)_6^{2+}$ [J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, **12**, 639 (1973)]; (b) Pu^{3+} [T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **60**, 1417 (1956)] and Eu^{2+} [R. C. Thompson, unpublished observations; T. W. Newton, private communication].

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(14) This procedure is quite analogous to that used in ref 6c and utilizes absolute reaction rate theory. See S. Glasstone, R. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N.Y., 1941.

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(18) A striking exception to this correlation has been reported:

$S^*(\mathrm{Np^{VII}{\cdot}Hg_2}^{2+}) - S^*(\mathrm{Np^{VII}{\cdot}VO}^{2+}) = 61$ cal mol^{-1} deg^{-1}; the two activated complexes presumably have the same formal charge. See K. D. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **13**, 1712 (1974).

(19) $S°(\mathrm{CrO_2Np^{4+}})$ can be estimated from data on the activation process[2] $\mathrm{Co^{3+} + CrO_2Np^{4+} + H_2O = [CrONpOCoOH^{6+}] + H^+}$: $S°(\mathrm{CrO_2Np^{4+}}) - \Delta S^* - S°(\mathrm{Co^{3+}}) - S°\mathrm{H_2O} = -125 - 2 + 72 - 17 = -72$ cal mol^{-1} deg^{-1}.

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Formation Constants of 2,3-Dihydroxy-2-methylpropanoato and 2,3-Dihydroxy-2-methylbutanoato Rare Earth Chelate Species

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The consecutive step formation constants of the 1:1, 2:1, and 3:1 chelate species formed by interaction of 2,3-dihydroxy-2-methylpropanoate and 2,3-dihydroxy-2-methylbutanoate anions (separately) with the tripositive lanthanon and yttrium cations were determined potentiometrically at an ionic strength of 0.100 ($\mathrm{KNO_3}$) and 25.0°. The results indicate that these dihydroxycarboxylate ligands exhibit a tridentate character in bonding to the lighter (larger) lanthanons (La–Sm) but bond only bidentately to the heavier (smaller) lanthanons (Ho–Lu) and to yttrium. The dentate character appears to change gradually from tridentate to bidentate as the lanthanon radius diminishes from that of samarium to that of holmium.

Introduction

Various investigators have measured the formation constants of consecutive chelate species formed by yttrium and the tripositive rare earth cations with the presumably bidentate ligand anions derived from various α-hydroxycarboxylic acids (glycolate and lactate,[1-6] α-hydroxyisobutyrate,[2-4,7-9] and other homologs of the hydroxyacetate anion[8,10-14]).

Grenthe[15] has determined the structures of solid heavy rare earth glycolates (hydroxyacetates) of the composition $\mathrm{Ln(HOCH_2COO)_3{\cdot}2H_2O}$ (where Ln = Tb, Dy, Ho, Er, Tm, Yb, or Lu) from X-ray intensity data. He reported two nonequivalent eight-coordinated metal atoms in the structure, located on twofold axes. One metal ion is coordinated to eight O atoms furnished by four hydroxyacetate ligands, forming a discrete (distorted dodecahedral) anionic complex; the other is coordinated to eight O atoms furnished by two hydroxyacetate anions and four water molecules, forming a discrete (distorted dodecahedral) cationic complex. The anionic and cationic entities are joined by hydrogen bonds.

The anhydrous $\mathrm{Gd(HOCH_2COO)_3}$ and $\mathrm{Eu(HOCH_2COO)_3}$ species,[16] on the other hand, involve nine-coordinated metal ions.[17,18] The coordination polyhedra are of the tricapped trigonal-prism type. All three ligands are bonded as chelates, with the hydroxy O atoms in the equatorial (tricapped) positions and one of the carboxyl O atoms of each ligand at a corner position of the trigonal prism (two at one end and one at the other). The three remaining corners of the trigonal prism are occupied by (unchelated) O atoms furnished by glycolate ligands which are chelated to neighboring lanthanons.

From the above-determined structures in crystalline materials and stability data,[3] it may be inferred that the hydroxyacetate ligand exhibits predominantly bidentate character in bonding to lanthanons in aqueous media as well. It also appears safe to presume that the hydroxyl O atoms of homologous (alkyl-substituted hydroxyacetate) ligands are generally involved in five-membered ring formation with rare earth metal ions. In solution, the various $\mathrm{Ln(HOCH_2COO)_3{\cdot}}n\mathrm{H_2O}$ species probably exist in monomeric form with two to four molecules of water in the coordination sphere, depending on the radius of the particular $\mathrm{Ln^{3+}}$ ion. However, Grenthe[19] and Larson[20] earlier suggested that the glycolate chelate ring might be formed *via* a water molecule between the hydroxyl O atom and the cation. The latter suggestion should not be taken too seriously, since it involves a seven-membered ring not indicated by subsequent crystallographic studies. Jones and Choppin,[21] on the basis of formation constants and thermodynamic data, concluded that the conceivable six-membered chelate ring does not form in the case of β-hydroxypropionate lanthanon complexes, although the strain involved in forming a six-membered ring ought not to exceed by much that involved in forming five-membered ring systems.

Two striking effects are observed in complex formation constants reported for species formed between rare earth cations and simple carboxylic acid anions (*e.g.*, acetate,[22] propionate,[23] and isobutyrate[7]), as well as with β-hydroxypropionate,[21] methoxyacetate,[23] and most (not too sterically hindered) α-hydroxycarboxylate homologs.[3,8,13] They are the "gadolinium break" and a rather abrupt decline in K_1/K_2 ratios as the lanthanon radius decreases beyond that of $\mathrm{Sm^{3+}}$. In the case of acetate[22] and propionate[23] chelate species, the K_1/K_2 ratio gradually decreases from about 5 to *ca.* 2.5 (from $\mathrm{Eu^{3+}}$ to $\mathrm{Dy^{3+}}$). In the case of 1-hydroxycyclopentanecarboxylate (HCPC) complexes,[14] the K_1/K_2 ratio changes from about 4.9 to 3.3, and with 2-hydroxy-2-methylbutanoate (HMB) species,[13] the change is from about 6.0 to 4.0. Powell and coworkers[13,14] have cited the statistical ratio theory of Bjerrum.[24] They have concluded that such changes in the K_1/K_2 ratios correspond to a change from tridentate to bidentate ligancy in the case of α-hydroxycarboxylate anions combining with a nine-coordinate (tricapped trigonal prism) hydrated lanthanon. It is just as possible that such ratio changes signal a change from tridentate ligancy on more highly coordinated lanthanons (say 10 or 9) to bidentate ligancy on cations of lower coordination number (say 9 or 8).

The statistical ratio argument immediately raises the question as to how a simple carboxylate anion such as acetate can function bidentately (or how α-hydroxycarboxylates can function tridentately) in bonding to the larger rare earth cations. It has been suggested that the second carboxyl oxygen of the ligand is simply hydrogen bonded to a water molecule that occupies a coordination site, rather than occupying a coordination site itself.[13] A tenuous bond of this kind would affect the statistical ratio by blocking access to an additional site without causing any large anomaly in the overall chelate stability trend.

It occurred to us that introduction of an alternate donor atom, as in 2,3-dihydroxycarboxylate anions, should permit