tem employing $NiCl_2[P(n\text{-}C_4H_9)_3]_2$ and $(i\text{-}C_4H_9)_2AlCl$, where nickel hydrides are presumed to be involved.[25] Carbon skeleton rearrangements in that system have also been observed.[26]

The definitive experiment to prove the origin of the high isomerization/deuteration ratio we observed is to show that the ratio decreases on addition of L. Increasing the free ligand concentration should increase the rate of capture of $HNiL_3^+$, thus decreasing the number of cycles of isomerization without deuteration.[27] Unfortunately, the dealkylation of $P(OEt)_3$ is much faster in CH_3OD, and we were unable to obtain appreciable inhibition of olefin isomerization in deuterated solvent even on adding 0.25 M $P(OEt)_3$ and reducing the temperature to 10°. Apparently, dealkylation of $P(OEt)_3$ has a large isotope effect. That the $P(OEt)_3$ was rapidly and completely destroyed was indicated by the disappearance of both its characteristic odor and its resonance in the ^{31}P nmr spectrum.

The rate of 1-butene isomerization, in the absence of added ligand, was about eight times as fast in CH_3OD at 10° as in CH_3OH at the same temperature. This is in the direction expected if olefin insertion into the Ni–H bond to give an alkyl is the rate-determining step in the loop. This kinetic isotope effect is probably, however, a composite effect, also involving higher concentrations of loop species in CH_3OD as a consequence of more rapid $P(OEt)_3$ dealkylation.

The utility of this catalyst system for olefin isomerization depends on the ratio of the loop cycle rate to the alkane formation rate. The number of catalytic cycles, defined as the moles of product per mole of catalyst lost, must be ~300 at 25° and ~3000 at 10°, based on the 2-butene:butane ratio. The larger temperature dependence of butane formation suggests that catalyst life can be greatly prolonged by operation at reduced temperature.

The electron configurations and coordination numbers are indicated near each nickel complex in Scheme II. It can be seen that the catalytic reaction involves only complexes with 16 or 18 valence electrons. This is believed to be a general feature of homogeneous catalytic reactions.[28]

Acknowledgments. The author is indebted to R. Cramer for helpful discussions and to W. C. Drinkard, Plastics Department, for providing the initial sample of $Ni[P(OEt)_3]_4$. Special thanks are owed to Mrs. Adah B. Richmond for the many gc analyses and separations required in this work.

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Association of Chromium(VI) with Neptunium(IV) and Thorium(IV) in Perchlorate Solution

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Abstract: The association of chromium(VI) with the cations Np(IV), Th(IV), and Fe(III) in perchlorate solution has been studied by a spectrophotometric procedure. Values of the formation constant $K_{eq} = (M\text{–}CrO_4)^{n-2}(H^+)/(M^{n+})(HCrO_4^-)$ at 25° and $I = 0.20\ M$ are 63.6 ± 6.1 (Np(IV)–Cr(VI)), 4.70 ± 0.14 (Th(IV)–Cr(VI)), and 1.93 ± 0.13 (Fe(III)–Cr(IV)). Values of $\Delta H°$ are 1.17, 3.67, and 3.09 kcal, respectively. The greater stability of the Np(IV) complex compared to that of Th(IV) is interpreted in terms of donation of 5f electron density from the cation to the chromium(VI). The spectra of the complexes are presented.

A limited amount of data has been reported for the association between chromium(VI) and tri- and tetravalent cations cerium(IV)[1], iron(III),[2] arsenic(III),[3] chromium(III),[4] plutonium(IV),[5] and aquopentaamminecobalt(III)[6] in aqueous solution. The factors that influence the magnitude of the formation constants are not well understood. Further work in this area seems warranted, especially in view of the detailed attention that has been devoted to sulfur(VI)–metal ion complexation. The absorption spectrum of chromium(VI) is altered sufficiently upon association with cations to allow spectrophotometric determination of the formation constants. This paper reports on the equilibria in perchlorate solutions of chromium (VI) with neptunium(IV) and thorium(IV). The choice of these cations was governed in part by their similar charge to radius ratios and their electronic configurations ($5f^0$ for thorium(IV) and $5f^3$ for neptunium(IV)). In addition, thermodynamic parameters for the formation of the chromium(VI)–iron(III) complex were determined during the course of this investigation.

Experimental Section

Reagents. Thorium(IV) oxalate was precipitated from a solution of reagent grade thorium(IV) nitrate. The perchlorate salt was ob-

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tained by repeated fuming in perchloric acid followed by recrystallization. The Th(IV) solutions were assayed by converting an aliquot to the oxalate and firing to the oxide, which was weighed.[7] The ^{237}Np was obtained as the dioxide from Oak Ridge National Laboratory. This material was converted to Np(V), and trace amounts of plutonium were removed by ion-exchange procedures. Stock solutions of neptunium(V) perchlorate solutions were prepared as previously described.[8] Solutions of Np(IV) in perchloric acid were prepared by mixing equivalent amounts of Np(III) and Np(V) in the absence of oxygen. Neptunium(III) perchlorate solutions were obtained by reduction of an Np(V) solution over amalgamated zinc in the absence of oxygen. The extinction coefficient of Np(V) is 400 M^{-1} cm^{-1} at 9805 Å. The Np(IV) solutions were assayed at 9600 Å on the Cary 14 (ϵ 213 M^{-1} cm^{-1} in 0.05 M perchloric acid) and by conversion to Np(V). A molar absorptivity coefficient of 124 M^{-1} cm^{-1} was determined for Np(IV) in 0.05–0.20 M perchloric acid at 7270 Å on the Zeiss (only partial resolution of the peak is achieved on this instrument). Iron(III) perchlorate was prepared by repeated fuming of reagent grade iron(III) chloride in perchloric acid. The Fe(III) concentrations were determined spectrophotometrically at 2400 Å (ϵ 4160 M^{-1} cm^{-1} in 0.5 M perchloric acid).[9] Chromium(VI) solutions were prepared from reagent grade potassium dichromate. Assays were made at 3500 Å (ϵ-($HCrO_4^-$) 1556 M^{-1} cm^{-1} in 0.05 M perchloric acid at I = 0.20). Lithium perchlorate was prepared by neutralization of the reagent grade carbonate followed by three recrystallizations. Triply distilled water, once each from acid chromium trioxide and permanganate, was used.

Stoichiometry of the Np(IV)–Cr(VI) Redox Reaction. Neptunium(IV) and chromium(VI) undergo an oxidation–reduction reaction at a rate considerably slower than that ascribed to complex formation. The former reaction is quite complicated and will be reported elsewhere. The products of the reaction were shown to be neptunium(V), hexaaquochromium(III), and Np(V)–Cr(III) complex.[10] The latter product was obtained in up to 30% yield based on the Np(IV) reacted. This result strongly suggests the importance of a Cr(IV) intermediate. The product identification was made by ion-exchange procedures using short columns of Dowex 50W-X2 resin in the hydrogen ion form.

Procedures. The Fe(III) and Th(IV) complexes of Cr(VI) were prepared by mixing both reactants, acid, and salt in a volumetric flask. Aliquots of each solution were pipetted into appropriate 1- or 2-cm stoppered cells and were used for all temperatures at which the formation was studied. Both complexes were observed at 3800 Å. Since Fe(III) exhibited absorbance at 3800 Å, suitable blanks were run. The absorption maximum of the Th(IV)–Cr(VI) complex is at 3600 Å and the maximum of the Fe(III)–Cr(VI) is at 3800 Å.

This procedure was modified for the Np(IV) system owing to the subsequent redox reaction. Neptunium(IV) and chromium(VI) were mixed directly in a square 2-cm spectrophotometer cell containing acid, salt, and one of the reactants. The reaction was initiated by injecting the second reactant into the rapidly stirred cell using a λ pipet. Mixing was complete in 1 sec. The order of mixing was varied and all experiments were run in duplicate. Most of the complex formation studies were performed at 3700 Å and kinetic runs were followed at 3310 and 7270 Å. The absorption maximum of the Np(IV)–Cr(VI) complex is 3650 Å, and at 3310 Å an isosbestic occurs between the complex and uncomplexed Cr(VI).

The [H$^+$] in the stock solutions and some of the equilibrium solutions was determined by placing suitable aliquots on a column of Dowex 50W-X8 resin in the hydrogen ion form and titrating the eluent with standard base. Suitable corrections were made for the hydrogen ion released by the metal ions originally present.

Determination of Equilibrium Constants. The absorbance of all the solutions used in the equilibrium studies showed considerable enhancement from 3000–4000 Å over that calculated from the individual contributions from Cr(VI) and the metal ion. This enhanced absorbance is ascribed to the formation of a complex

$$M^{n+} + HCrO_4^- = (M\text{-}CrO_4)^{n-2} + H^+ \qquad (1)$$

The reactants are written in terms of the predominant species, and justification for the hydrogen ion dependence will be given later. The method used to calculate the equilibrium constant, K_{eq} (eq 2) and the extinction coefficient of the complex was essentially that of Tong and King.[1]

$$K_{eq} = [(M\text{-}CrO_4)^{n-2}][H^+]/[(M^{n+})][(HCrO_4^-)] \qquad (2)$$

A computer program was written which calculated the value of K_{eq} for a given complex extinction coefficient for a series of absorbances obtained from solutions of varying concentrations of reactants and hydrogen ion. The best value of K_{eq} was taken as corresponding to the extinction coefficient that resulted in the smallest average deviation in K_{eq} for that series of experiments.

Results

Formation constants for the systems Np(IV), Th(IV), and Fe(III) with Cr(VI) were studied in aqueous perchloric acid with lithium perchlorate used to maintain constant ionic strength. The formation of each complex was studied as a function of metal ion concentration, hydrogen ion concentration, ionic strength, and temperature. The temperature was varied in the range from 1.0 to 25.0° for Fe(III) and from 10.0 to 25.0° for Th(IV) and Np(IV). The formation constants were obtained at hydrogen ion concentrations of 0.024–0.20 M for Fe(III) and 0.05–0.20 M for Np(IV) and Th(IV).

The narrow range of hydrogen ion concentration employed was dictated primarily by the Np(IV) system. At [H$^+$] much less than 0.05 M, hydrolysis and polymerization become significant.[11] Above 0.20 M [H$^+$], the absorbance enhancement becomes too small for accurate work. This limit could not be circumvented by resorting to high Np(IV) concentrations because of the redox reaction with Cr(VI).

The molar extinction coefficient for the Np(IV)–Cr(VI) complex was independent of ionic strength, hydrogen ion concentration, and temperature under the experimental conditions employed. The same invariance was assumed to hold for the Th(IV) and Fe(III) systems.

For the Np(IV) system the determinations of the formation constant were done in duplicate. Only a

Table I.[a] Equilibrium Constant Determinations at I = 0.20 M

Complex	Temp, °C	K_{eq}	No. of determinations
Np(IV)–Cr(VI)[b]	25.0	63.6 ± 6.1	24
	17.0	59.6 ± 3.5	8
	10.0	57.3 ± 3.3	11
Th(IV)–Cr(VI)[c]	25.7	4.70 ± 0.14	10
	17.3	3.91 ± 0.14	10
	11.0	3.42 ± 0.12	10
Fe(III)–Cr(VI)[d]	25.0	1.93 ± 0.13	6
	17.2	1.68 ± 0.02	6
	9.3	1.47 ± 0.04	5
	1.0	1.22 ± 0.02	5

[a] Tables listing further details of these results will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-2999. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche. [b] $[Np(IV)]_0 = 0.24 - 1.91 \times 10^{-3}$ M, $[Cr(VI)]_0 = 1.03 \times 10^{-3}$ M. [c] $[Th(IV)]_0 = 0.77\text{–}1.48 \times 10^{-2}$ M, $[C(VI)]_0 = 1.05\text{–}3.31 \times 10^{-4}$ M. [d] $[Fe(III)]_0 = 0.39\text{–}2.56 \times 10^{-2}$ M, $[Cr(VI)]_0 = 1.62\text{–}4.04 \times 10^{-4}$ M.

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few experiments were performed at ionic strengths other than 0.20 *M*. For each set of concentration conditions, the formation constant, extinction coefficient of the complex, and the resulting concentrations at equilibrium were evaluated using the previously described computer program. The initial concentrations and the formation constant K_{eq}, as defined in eq 2, are listed in Table I. The calculated absorbance based on these results deviated from the observed absorbance by ≤ 0.003OD for all the experiments. At other ionic strengths used, for an initial Cr(VI) concentration of 1.03×10^{-4} *M* and initial Np(IV) concentration of 9.90×10^{-4} *M* at 25.0° and 0.07 *M* hydrogen ion, K_{eq} was 96.4 at $I = 0.073$ *M*, 55.9 at $I = 0.20$ *M*, 26.0 at $I = 1.00$ *M*, and 16.9 at $I = 3.80$ *M*.

For the Th(IV) and Fe(III) system, concentrations were chosen such that the observed absorbance enhancement upon formation of the complex was at least 0.20 absorbance unit. The hydrogen ion was not varied at $I = 0.20$ *M* because the thorium concentrations used contributed almost all of the balance of the ionic strength. Concentrations and K_{eq} at an ionic strength of 0.20 *M* are listed in Table I. At an ionic strength of 1.00 *M* with a Cr(VI) concentration of 2.4×10^{-4} *M* and a Th(IV) concentration of $1\text{-}7 \times 10^{-2}$ *M*, K_{eq} was 1.96 ± 0.17 at 25.0°, 1.54 ± 0.10 at 16.7°, and 1.37 ± 0.09 at 9.6°.

Part of the concentrations for the Fe(III) study were chosen to correspond closely to those used by Espenson and Helzer[2b] in their preliminary investigation of the Fe(III)–Cr(VI) complex. Initial concentrations and K_{eq} for Fe(III)–Cr(VI) at an ionic strength of 0.20 *M* are listed in Table I. At an ionic strength of 0.084 *M* with a Cr(VI) concentration of 2.02×10^{-4} *M* and an Fe(III) concentration of $3\text{-}10 \times 10^{-3}$ *M*, K_{eq} was 2.84 ± 0.20 at 25.0° and 1.85 ± 0.10 at 1.0°. At an ionic strength of 1.00 *M* with a Cr(VI) concentration of $2\text{-}3 \times 10^{-4}$ *M* and an Fe(III) concentration of $0.1\text{-}3.5 \times 10^{-2}$ *M*, K_{eq} was 1.28 ± 0.11 at 25.0° and 0.94 ± 0.09 at 1.0°.

Table II. Thermodynamic Parameters at 25.0°

$\Delta H°$, kcal	$\Delta S°$, eu	$\Delta G°$, kcal
	Np(IV)–Cr(VI) at $I = 0.20$ *M*	
1.17 ± 0.14	12.2 ± 0.5	−2.47
	Fe(III)–Cr(VI) at $I = 0.084$ *M*	
2.88	11.7	−0.62
	Fe(III)–Cr(VI) at $I = 0.20$ *M*	
3.09 ± 0.14	11.7 ± 0.5	−0.40
	Fe(III)–Cr(VI) at $I = 1.00$ *M*	
2.09	7.5	−0.15
	Th(IV)–Cr(VI) at $I = 0.20$ *M*	
3.67 ± 0.04	15.4 ± 0.3	−0.92
	Th(IV)–Cr(VI) at $I = 1.00$ *M*	
3.91 ± 0.36	14.4 ± 2.4	−0.38

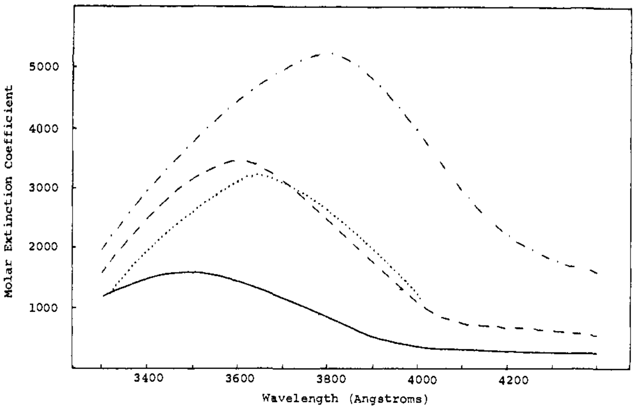

Figure 1. Absorption spectra of $HCrO_4^-$ (—), Np(IV)·Cr(VI) (· · ·), Th(IV)·Cr(VI) (---), and Fe(III)·Cr(VI) (-·-·).

Figure 1 displays spectra of the complexes of Np(IV), Th(IV), and Fe(III) with Cr(VI) as well as the spectrum of $HCrO_4^-$. The Np(IV), Fe(III), and $HCrO_4^-$ spectra were taken in an ionic strength of 0.20 *M* at a hydrogen ion concentration of 0.06 *M*, while the Th(IV) spectrum was taken in a medium of ionic strength 1.00 *M* and hydrogen ion concentration of 0.06 *M*. A spectrum of the Fe(III)–Cr(VI) complex was also run at 1.0° to determine if the position of the maximum was dependent upon temperature. No shift was observed.

The thermodynamic parameters, $\Delta H°$ and $\Delta S°$, for the various formation constants were obtained by a least-squares treatment of the functional form $\ln (K_{eq}) = -\Delta H°/RT + \Delta S°/R$. The values obtained are summarized in Table II. The errors represent one standard deviation, and the values listed without uncertainties are based on two points only.

Discussion

The justification for the hydrogen ion dependence given in eq 1 and incorporated into the equilibrium constant definition in eq 2 rests in the constancy of the K_{eq} values for the systems studied. A small increase in K_{eq} with increasing hydrogen ion concentration was observed. This trend probably reflects an additional equilibrium involving a protonated form of the complex. However, the effect could be due to a variation in the activity coefficients as the $[HClO_4]$ and $[LiClO_4]$ are varied.

The major equilibrium under the conditions of our experiments can be rewritten as

$$M^{n+} + CrO_4^{2-} = M\text{-}CrO_4^{n-2} \qquad K_I \qquad (3)$$

Values of K_{eq} and K_I for both Cr(VI) and S(VI) are tabulated in Table III for various cations. The entries for K_{eq} for the sulfate systems are taken from the literature,[12-17] and values of K_I are calculated in all cases by using the acid dissociation constants reported for $HCrO_4^-$[16] and HSO_4^-.[15] The U(IV)–Cr(VI) system has been studied,[18] but owing to the rapid redox reaction, only very dilute solutions were used and no complex formation was detected. It is apparent that the chromate complexes are considerably more stable than the corresponding sulfate complexes. This result is no doubt related to the much stronger basicity of the chromate ion.

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Table III. Association Constants of Complex Chromates and Sulfates[a] at 25.0°

Ion	K_{eq}[b]	K_I,[c] M^{-1}	K_{eq}[d]	K_I,[e] M^{-1}
Np(IV)	26 $I = 1.0\ M$	8.1×10^7 $I = 1.0\ M$	2.7×10^2 [f] $I = 2.0\ M$	3.6×10^3 $I = 2.0\ M$
Th(IV)	1.96 $I = 1.0\ M$	6.1×10^6 $I = 1.0\ M$	1.6×10^2 [g] $I = 2.0\ M$	2.1×10^3 $I = 2.0\ M$
U(IV)			1.3×10^2 [h] $I = 3.5\ M$	1.7×10^3 $I = 3.5\ M$
Fe(III)	1.28 $I = 1.0\ M$	4.0×10^6 $I = 1.0\ M$	8.0[i] $I = 1.0\ M$	1.1×10^2 $I = 1.0\ M$

[a] $K_{HCrO_4^-} = 3.2 \times 10^{-7}$ (ref 16). $K_{HSO_4^-} = 0.075$ (ref 15) was used in all of the studies above. However, Kerker[17] has recently determined the value as 0.365 at $I = 1.00\ M$. [b] $(MCrO_4)(H^+)/(M)(HCrO_4^-)$. [c] $(MCrO_4)/(M)(CrO_4^{2-})$. [d] $(MSO_4)(H^+)/(M)(HSO_4^-)$. [e] $(MSO_4)/(M)(SO_4)^{2-})$. [f] Reference 12. [g] Reference 13. [h] Reference 14. [i] Reference 15.

The Np(IV) and Th(IV) systems provide the best data for a consideration of the factors that influence the stability constants, in that the charge to radius ratios of these two ions are quite similar.

It has been suggested that complexes of the actinide ions are largely electrostatic in character.[19] This presumably arises from shielding effects on the 5f electrons which limit their participation in chemical bonding. Ligand-field effects are roughly one order of magnitude smaller than for the transition-series ions.[20] It is noted, however, that the chromate complex of Np(IV) is significantly more stable than that of Th(IV), whereas the stabilities of the corresponding sulfate complexes are about equal. Wolfsberg and Helmholz[21] have suggested that all available orbitals of chromium participate in the bonding in the chromate ion. Conversely, by analogy to the perchlorate ion,[21] there is little participation of the orbitals in the bonding of the sulfate ion. We suggest that the electrostatic contribution to the bonding in the chromate complexes of Np(IV) and Th(IV) is about equal. This conclusion is consistent with the similar stabilities of the sulfate complexes, where the bonding should be almost exclusively electrostatic. We further suggest that the enhanced stability of the chromate complex of Np(IV) compared to that of Th(IV) is due to limited donation of the 5f electron density of Np(IV) to d orbitals of chromium in the chromate ion. This additional, nonelectrostatic contribution does not appear in the sulfate complexes, as discussed above.

The spectral data in Figure 1 are not inconsistent with this proposal. The shift in the absorption maximum for Np(IV)–Cr(VI) toward longer wavelengths is more pronounced than for Th(IV)–Cr(IV) (both relative to the position for the hydrogen chromate ion). It should be noted that the shift in the position of the absorption maximum for Fe(III)–Cr(VI) is the greatest for the systems studied. It is unfortunate that data for Sc(III)–Cr(VI) are not available. Ignoring differences in ionic radii, our bonding scheme would predict a greater stability for Fe(III)–Cr(VI), and an absorption maximum for Sc(III)–Cr(VI) at around 3600 Å.

The thermodynamic data indicate that the enthalpy of formation is the important term resulting in a greater stability of Np(IV)–Cr(VI) relative to Th(IV)–Cr(VI). This again suggests differences in the mode of bonding in the two complexes. The thermodynamic data alone do not distinguish whether these complexes are of the inner-sphere or outer-sphere type. However, it is likely that our results refer to inner-sphere complexes in that the mode of detection involved spectral changes in the chromate ion upon complexation.

A limited amount of data is available for the formation of the chromate complex of Fe(III). Espenson and King[2a] report a value of 1.4 ± 0.2 for K_{eq} at $I = 0.084\ M$ and 0°. This result is in satisfactory agreement with our value of 1.85 ± 0.10 under the same conditions. Espenson and Helzer[2b] report a value of $K_{eq} = 0.43 \pm 0.05$ at $I = 1.00\ M$ and 25°. Our value of 1.28 ± 0.11 under identical conditions is in poor agreement with this result. The reason for the discrepancy in the latter case is not known.

It is disturbing that the ability to predict even relative association constants for simple ligands with similar cations is so limited, especially in light of the vast amount of equilibrium data in the literature. Thermodynamic data coupled with spectral data for complexes with ligands such as Cr(IV) would seem to be a promising area of investigation.

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