

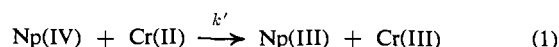
A Kinetic Study of the Reaction between Neptunium(IV) and Chromium(II)¹

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Contribution from the Department of Chemistry, Argonne National Laboratory, Argonne, Illinois 60439. Received September 1, 1966

Abstract: The empirical form of the rate law for the reaction $\text{Np(IV)} + \text{Cr(II)} \rightarrow \text{Np(III)} + \text{Cr(III)}$, in perchloric acid–lithium perchlorate media, is $-\text{d}[\text{Np(IV)}]/\text{d}t = k'[\text{Np(IV)}][\text{Cr(II)}][\text{H}^+]^{-1.27 \pm 0.02}$ at 25°. The variation of k' with temperature is presented.

Preliminary experiments had indicated that the reaction between Np(V) and Cr(II) can be described in terms of three consecutive second-order reactions.³ The second of these is the reaction



To minimize computational uncertainties in the first-mentioned system, it became apparent that the kinetic parameters characteristic of reaction 1 should be determined independently. This communication presents the values obtained for the relevant kinetic parameters.

Experimental Section

Reagents. Cr(II) stock solutions in perchloric acid were prepared by the dissolution of pure Cr metal⁴ and standardized spectrophotometrically with Cr(VI). The Np(IV) solutions were prepared by electrolytic reduction of Np(V). The Np(V) solutions were prepared by oxidation of a stock solution with NaBrO₃, reduction with NaNO₂, and precipitation of neptunium(V) hydroxide which was extensively washed with triple distilled water and then dissolved in ca. 2 M perchloric acid. The Np(IV) stock solutions were prepared and all measurements made within a period of 48–72 hr. If the Np(IV) solutions were allowed to stand for longer periods, the kinetic results became irreproducible. This is very probably due to the increasing concentration of peroxide from the α radiolysis of the solution. The Np(IV) solutions were standardized spectrophotometrically at 7230 Å using the value of $A = 144 \text{ M}^{-1} \text{ cm}^{-1}$ or at 9800 Å (after oxidation to Np(V)) using the value of $A = 403 \text{ M}^{-1} \text{ cm}^{-1}$. The LiClO₄ and perchloric acid solutions were prepared and standardized as described in a previous publication.⁸

Procedures. All the reagents, except the Cr(II), were pipetted into 2- or 5-cm absorption cells. The cells were then stoppered with a rubber serum cap, placed in a water bath, and deoxygenated for at least 1 hr⁷ using either CO₂ or argon. The cell was then placed in the compartment of a Cary Model 14 MR spectrophotometer, which was thermostated at the working temperature, and an aliquot of the Cr(II) solution was introduced through the serum

cap using a glass syringe fitted with a Pt needle. The absorptivity at 7230 Å was recorded as a function of time. The [H⁺] of the reaction mixture was determined by titration with standard base after completion of the reaction.

Data Treatment. The initial estimate of the rate parameter k' was obtained graphically from the usual integrated form of the second-order rate law

$$\frac{1}{[\text{Np(IV)}]_0 - [\text{Cr(II)}]_0} \ln \frac{[\text{Cr(II)}]}{[\text{Np(IV)}]} = -k't + I \quad (2)$$

The first observation was made within 10 sec after mixing, and the reaction was observed to within 99% of completion.

The values reported for k' were obtained from a least-squares adjustment of the data (20–30 OD, t data points per experiment) for the functional form⁸

$$\text{OD} = E([\text{Np(IV)}]_0 - [\text{Cr(II)}]_0) \times [1 - I'e^{k't/([\text{Np(IV)}]_0 - [\text{Cr(II)}]_0)}]^{-1} \quad (3)$$

where E = path length \times molar absorptivity and $I' = E[\text{Cr(II)}]_0/(\text{OD})_0$.

Results

Form of the Rate Law. As pointed out earlier, the integrated form of the second-order rate law was found adequate to correlate the data. The information presented in Table I corroborates that statement.

Two points should be noted in conjunction with these data. (1) The two parameters, k' and I' , reproduced the observed optical densities to ≤ 0.003 unit. (2) The standard deviations assigned the values of k' based on the least-squares adjustment of the data were 0.5–1.0%. The scatter observed in the data presented in Table I therefore very probably reflects the uncertainties in the constant term.

Table I. Effect of Metal Ion Concentration on the Np(IV)–Cr(II) Reaction^a

$[\text{Np(IV)}] \times 10^3, M$	$[\text{Cr(II)}] \times 10^4, M$	$k', M^{-1} \text{ sec}^{-1}$
1.18	8.78	4.55
1.18	9.06	4.40
1.18	9.14	4.32
2.87	8.58	4.21
2.87	22.5	4.00
2.88	21.3	4.08
2.88	21.8	4.11
5.63	49.7	4.53
5.72	50.5	4.38
		$\langle k \rangle = 4.29 \pm 0.20$

^a At 25°, $\mu = 1.00$, $[\text{HClO}_4] = 1.00 \text{ M}$.

(8) The program, C150, was developed by C. Chamot, Applied Mathematics Division of this laboratory. The computations were carried out on the CDC 3600 in that division.

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) A preliminary account of this investigation was presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

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(3) R. C. Thompson and J. C. Sullivan, *J. Am. Chem. Soc.*, **89**, 1098 (1967).

(4) The metal was in the form of Cr pellets purchased from United Mineral and Chemical Corp., New York, N. Y. The quoted purity was 99.999%. Dissolution was achieved by treating one or two pellets with 6 M HCl, washing thoroughly with triple distilled water, and placing these activated pellets in contact with the bulk of the metal.

(5) R. Sjöblom and J. C. Hindman, *J. Am. Chem. Soc.*, **73**, 1744 (1951).

(6) J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *ibid.*, **82**, 5288 (1960).

(7) Preliminary experiments indicated that shorter periods of deoxygenation (10–20 min) were not sufficient, while longer periods (2–4 hr) produced no observable increase in precision.

Table II. $[H^+]$ and Temperature Dependencies of k'^a

5°		10°		17°		25°	
$[H^+]$, M	k' , $M^{-1} \text{sec}^{-1}$	$[H^+]$, M	k' , $M^{-1} \text{sec}^{-1}$	$[H^+]$, M	k' , $M^{-1} \text{sec}^{-1}$	$[H^+]$, M	k' , $M^{-1} \text{sec}^{-1}$
0.166	5.08 ± 0.09	0.168	8.95 ± 0.13	0.128	27.4 ± 0.1	0.214	32.0 ± 0.2
0.262	2.54 ± 0.03	0.262	4.61 ± 0.03	0.264	9.54 ± 0.4	0.412	12.3 ± 0.1
0.450	1.35 ± 0.03	0.451	2.38 ± 0.15	0.449	4.88 ± 0.03	0.612	8.33 ± 0.40
0.651	0.921 ± 0.051	0.652	1.71 ± 0.21	0.652	3.24 ± 0.05	0.812	5.77 ± 0.05
0.851	0.658 ± 0.016	0.841	1.10 ± 0.02	0.842	2.38 ± 0.02	1.00	4.29 ± 0.20^b
1.00	0.557 ± 0.046	1.00	0.930 ± 0.004	1.00	1.91 ± 0.04		

^a $\mu = 1.00$ maintained with LiClO_4 . $[\text{Np(IV)}]_0 = 2.77\text{--}1.16 \times 10^{-3} M$. $[\text{Cr(II)}]_0 = 1.00\text{--}2.55 \times 10^{-3} M$. All values are averages of at least two independent determinations and the uncertainties are the standard deviations based on the average. ^b Average value from Table I.

Values of $k' = 5.66 \pm 0.11 M^{-1} \text{sec}^{-1}$ and $4.33 \pm 0.25 M^{-1} \text{sec}^{-1}$ were obtained in experiments in $1.0 M$ perchloric acid with 1.0×10^{-2} and $1.0 \times 10^{-3} M$ added HCl, respectively. This suggests that catalysis of the reaction by chloride ion inadvertently introduced by the preparation of the Cr(II) stock solutions is not significant.

Small amounts of HSO_4^- markedly influence the reaction rate. At $1.0 \times 10^{-3} M \text{HSO}_4^-$, $1.0 M \text{HClO}_4$, and 25° , the average value determined for $k' = 6.26 \pm 0.05 M^{-1} \text{sec}^{-1}$.

Not unexpectedly the product, Cr(III), does not influence the reaction rate.⁹ Under the same conditions as described for the previous experiments with the exception that the initial concentration of Cr(III) was $1.0 \times 10^{-3} M$, the average value determined for $k' = 4.47 \pm 0.07 M^{-1} \text{sec}^{-1}$.

Effects of $[H^+]$ and Temperature. Table II contains a summary of the variation of k' as a function of hydrogen ion concentration and temperature.

An empirical form of the rate expression that summarizes the variation in k' with change in the hydrogen ion concentration is

$$k' = k'' [H^+]^n \quad (4)$$

Values determined for n , from a least-squares adjustment of the data,¹⁰ are -1.21 ± 0.03 , -1.23 ± 0.03 , -1.25 ± 0.03 , and -1.27 ± 0.02 at 5, 10, 17, and 25° , respectively.

The condition of restraint that the order of the reaction should be integral may be satisfied by the usual power series development¹¹

$$k' = a + b[H^+]^{-1} + c[H^+]^{-2} \quad (5)$$

The results of the least-squares adjustment of the data in terms of eq 5 are for a $(7.8 \pm 8.3) \times 10^{-2}$, $(9.7 \pm 12.0) \times 10^{-2}$, 0.18 ± 0.89 , and -0.33 ± 0.58 ; for b , $(43.1 \pm 8.0) \times 10^{-2}$, 0.74 ± 0.13 , 1.58 ± 0.09 , and 4.17 ± 0.71 ; for c $(6.2 \pm 1.4) \times 10^{-2}$, 0.122 ± 0.026 , 0.237 ± 0.015 , and 0.57 ± 0.15 at 5, 10, 17, and 25° , respectively.

(9) The product $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was not identified directly. However, in the reaction between Np(V) and Cr(II), under conditions where the Cr(II)-Np(IV) reaction is of kinetic significance, the chromium product was identified as hexaquo chromium(III) by conventional ion-exchange techniques.

(10) The computations used the results of the individual experiment, not the summary presented in Table II.

(11) The hydrolysis of Np(IV) can be neglected over the acid range used in these experiments since the first hydrolysis constant of Np^{4+} is 5×10^{-3} as determined by J. C. Sullivan and J. C. Hindman, *J. Phys. Chem.*, **63**, 1332 (1959).

The value for a is spanned by one standard deviation in all cases. It is therefore only necessary to consider parameters b and c , and the interpretation advanced is that these parameters are rate coefficients for parallel reaction paths. Such an interpretation is not unique because of the functional form employed in eq 5.

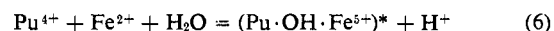
The interpretation advanced is consistent with the following observations. On the assumption of a single path plus activity coefficient changes, $k'[H^+]$ varies by about 60% (25° data) over a fivefold variation of hydrogen ion concentration at constant ionic strength. This variation is somewhat greater than that usually considered as "medium" effect. In addition, the value for $k' = 29.2 \pm 0.5 M^{-1} \text{sec}^{-1}$, determined at 25° and at $0.213 M$ perchloric acid, is within ca. 10% of the value determined at the same acidity and ionic strength of 1.0 maintained with lithium perchlorate.

The energies of activation calculated from the temperature variation of the rate parameters b and c are 18.4 ± 1.0 and 17.5 ± 0.8 kcal/mole.

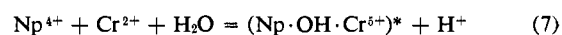
Discussion

Quantitative *a priori* calculation of rate constants for redox reactions of the type studied in this investigation is not feasible within the framework of existing theories. Comparisons of similar reactions, based on the qualitative considerations suggested by Halpern,¹² do, however, provide an *a posteriori* rationale of the observations.

In a kinetic study of the reaction between Pu(IV) and Fe(II), Newton and Cowan¹³ describe a net activation process



which is similar, in charge and stoichiometry of the activated complex,¹⁴ to the process



The kinetic parameters characteristic of (6) and (7) are $k = 50.8 M^{-1} \text{sec}^{-1}$, $E_A = 19.7 \pm 0.6$ kcal/mole, and $k = 4.29 \pm 0.20 M^{-1} \text{sec}^{-1}$, $E_A = 18.4 \pm 1.0$ kcal/mole at 25° .

In the reactions under comparison, the explicit assumption is made that both complexes are of the same type, *i.e.*, either both inner or outer sphere. Then the contribution to the free energy of activation due to

(12) J. Halpern, *Quart. Rev. (London)*, **15**, 223 (1961).

(13) T. H. Newton and H. D. Cowan, *J. Phys. Chem.*, **64**, 244 (1960).

(14) The molecules of water in the first coordination sphere of the reactant cations and the activated complexes are not depicted in this formalism since the empirical form of the rate law provides no information as to the degree of hydration of the activated complex.

electrostatic repulsion and electron conductivity should be quite similar.

From the available potentials,¹⁵ $\Delta F^\circ = -5.6$ kcal for (6) and $\Delta F^\circ = -13.0$ kcal for (7). This contribu-

(15) Fe(II)-Fe(III) and Cr(II)-Cr(III) couples are from W. H. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938. The neptunium and plutonium couples are from J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957.

tion to the free energy of activation would make the rate of (7) greater than that of (6).

The fact that the specific rate constants under consideration are of the opposite order may very well reflect the importance of the reorganization free energy of activation in the two examples. A considerable portion of this difference would arise from the fact that the d electron being transferred to a 5f orbital is e_g in the case of Cr^{2+} and t_{2g} in the case of Fe^{2+} .

The Reaction between Excess Neptunium(V) and Chromium(II) in Perchlorate Solution¹

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Abstract: The kinetics of the reaction $\text{Np(V)} + \text{Cr(II)} = \text{Np(IV)} + \text{Cr(III)}$ have been studied in acid perchlorate solutions from 0.02 to 0.20 M HClO_4 . The reaction is complicated by a competitive consecutive reaction between the Cr(II) reactant and the Np(IV) product. The rate law for the 1-equiv reduction of Np(V) by Cr(II) is $-d[\text{Np(V)}]/dt = k_1[\text{Np(V)}][\text{Cr(II)}][\text{H}^+]^{0.78}$, where $k_1[\text{H}^+]^{0.78}$ is interpreted to equal $k_0[\text{H}^+]e^{\beta[\text{H}^+]}$. Values of ΔH^\ddagger and ΔS^\ddagger appropriate to the k_0 term were found to be 1.85 kcal/mole and -38.4 eu. Oxygen-18 tracer results indicate the formation of an inner-sphere activated complex.

The reduction of the oxyocations NpO_2^{2+} and NpO_2^+ by chromium(II) is complicated by the existence of competitive and perhaps parallel paths. The reduction of excess neptunium(VI) by chromium(II) in 1 M perchloric acid is reported to yield predominantly neptunium(IV) along with smaller amounts of neptunium(V) and neptunium(V)-chromium(III) complex.³ Preliminary experiments revealed the presence of a neptunium(III) intermediate in the reduction of excess Np(V) by Cr(II) at hydrogen ion concentrations ≤ 0.2 M. Appelman and Sullivan⁴ also report a Np(III) intermediate in the V(III)-Np(V) reaction at low acidities. Kinetic, stoichiometric, and oxygen-18 tracer results for the Np(V)-Cr(II) reaction are reported in this communication.

Experimental Section

Reagents. The neptunium(V), chromium(II), and lithium perchlorate and perchloric acid solutions were prepared and standardized as described previously.^{5,6} Neptunium(III) perchlorate solutions were prepared by reduction of a Np(V) solution over amalga-

mated zinc in the absence of oxygen. The extinction coefficients for Np(V) at 9800 Å were determined at each solution composition and temperature, but the variations from the reported value⁷ of $A = 403 \text{ M}^{-1} \text{ cm}^{-1}$ were small.

Kinetic Experiments. The procedures used were essentially the same as previously reported.⁵ Since up to 10 hr was required for completion of the Np(V)-Np(III) reaction in some experiments, the serum caps were covered with Apiezon T grease approximately 5 min after initiation of the reaction to prevent entry of oxygen gas. The Np(III) intermediate was monitored at 2670 Å and the formation of Np(IV) at 7230 Å; the absorbance by the other reactants or products is small at these wavelengths. The hydrogen ion concentration of the reaction mixture was determined by titration with standard base after completion of the reaction.

Stoichiometry and Tracer Experiments. In the stoichiometry experiments, the hexaquo-chromium(III) product was separated from the other species in a spent reaction mixture by ion-exchange techniques employing BiO-Rad AG 50W-X8 resin in the hydrogen ion form. The excess Np(V) was eluted with 1 M perchloric acid, and the Cr(OH)_2^{3+} was eluted from the Np(IV) and any possible dimeric chromium(III) with 3 M perchloric acid. The hexaquo-chromium(III) eluent was analyzed spectrophotometrically at 4075 and 5750 Å, where values of $A = 15.9$ and $13.6 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, were used.

For the tracer experiments, oxygen-18 enriched Np(V) was prepared by removing the solvent water from a neptunium(V) perchlorate solution under reduced pressure until the green solid began crystallizing and then equilibrating with a large excess of 1.5% H_2O^{18} (YEDA). The enriched water was then distilled from the enriched Np(V) solution and collected for analysis. The dry, enriched neptunium(V) perchlorate (~ 0.4 mmole) was dissolved in ca. 1 ml of unenriched triply distilled water and quickly injected with vigorous stirring into less than the stoichiometric amount of Cr(II) in unenriched, oxygen-free perchloric acid solution adjusted to the desired hydrogen ion concentration. The O^{18} enrichment of the Np(V) used in these experiments was taken to be that of the removed, equilibrated water. This assumption will only be correct

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) A preliminary account of this investigation was presented before the Inorganic Chemistry Division, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(2) Resident Research Associate.

(3) J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).

(4) E. H. Appelman and J. C. Sullivan, *J. Phys. Chem.*, **66**, 442 (1962).

(5) R. C. Thompson and J. C. Sullivan, *J. Am. Chem. Soc.*, **89**, 1096 (1967).

(6) J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *ibid.*, **82**, 5488 (1960).

(7) R. Sjöblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).