

# Kinetics of the Neptunium(V)–Chromium(VI) Reaction in Perchlorate Solutions<sup>1</sup>

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The empirical form of the rate law determined for the oxidation of Np(V), by Cr(VI) in a perchloric acid–lithium perchlorate media is  $-d[\text{NpO}_2^{+}]/dt = k[\text{NpO}_2^{+}][\text{Cr(VI)}]/(1 + k'[\text{NpO}_2^{+}]/[\text{NpO}_2^{+}])$  at constant hydrogen ion concentration. The hydrogen ion and temperature dependencies of  $k$  and  $k'$  are presented.

## Introduction

In the oxidation of Np(V) to Np(VI) the linear O–M–O structure is preserved and we may formally describe the process as the transfer of one of the two 5f electrons from Np(V) to the oxidant. Other changes concomitant with this electron removal, such as reorganization of the equatorial water molecules and variation in the O–M bond lengths, should not influence the empirical form of the rate law.

A study of the oxidation of Np(V) by Cr(VI) should provide information relevant to the hypothesis previously advanced<sup>2</sup> that the Cr(V)–Cr(IV) transformation is the rate-determining step in the reaction of Cr(VI) with many one-equivalent reducing agents.

## Experimental

**Procedures.** The preparation and standardization of the Np(V) and Np(VI) stock solutions, as well as the perchloric acid and lithium perchlorate solutions, have been described in a previous publication.<sup>3</sup> Stock solutions of Np(V) and Np(VI) were prepared and standardized immediately before a kinetic experiment to minimize the amount of H<sub>2</sub>O<sub>2</sub> formed by the radiolysis of the solutions due to the  $\alpha$ -particles from the decay of Np<sup>237</sup>.<sup>4</sup> Reagent grade sodium dichromate (Baker) was recrystallized and centrifugally washed with and dissolved in triply distilled water. A second source of Cr(VI) was prepared by dissolving potassium dichromate (oxidimetric standard NBS) in triply distilled water.

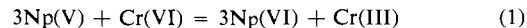
The reaction vessels were 2- or 5-cm. cylindrical silica absorption cells. The cell compartment of the Cary Model 14 spectrophotometer used in this study was thermostated to  $\pm 0.1^\circ$  of the working temperature.

Weighed amounts of Cr(VI) solutions containing the appropriate concentrations of perchloric acid, lithium perchlorate, and, when applicable, Np(VI) perchlorate were added to the cells at room temperature. After attainment of temperature equilibrium an aliquot of Np(V) (from a stock solution maintained at the work-

ing temperature) was rapidly injected into the cell and the change of optical density with time at 9800 or 3500 Å. was recorded. Concentrations were calculated for approximately forty different values of the recorded optical density in each kinetic experiment. Time intervals ranged from 15 sec. to 10 min. The first observation usually corresponded to a time interval of 30 sec.

## Results

**Stoichiometry.** In a series of preliminary experiments the stoichiometry of the reaction was found to correspond to



The Cr(III) species produced at perchloric acid concentrations of 2.0 *M* and concentrations of initial Np(V) =  $1.28 \times 10^{-3}$  *M* and Cr(VI) =  $6.91 \times 10^{-4}$  *M* was characterized by ion-exchange separation of the equilibrium reaction mixture<sup>5</sup> and spectrophotometric observation of the hexaaquochromium(III) absorption bands.

In the series of equilibrium experiments, weighed amounts of Cr(VI) and Np(V) solutions, with initial concentrations of  $1.75 \times 10^{-4}$ – $6.91 \times 10^{-4}$  *M* and  $5.22 \times 10^{-4}$ – $1.28 \times 10^{-3}$  *M*, respectively, in a medium of 2.0 *M* perchloric acid were allowed to reach equilibrium. From the known initial concentrations and the final absorbance values at 3500 or 9800 Å., the ratio (moles of Np(V) consumed)/(moles of Cr(VI) consumed) was  $2.96 \pm 0.05$ .

In these experiments at 3500 Å. the pertinent molar extinction coefficients (l. mole<sup>-1</sup> cm.<sup>-1</sup>) are  $1345 \pm 21$  for Cr(VI) and  $102.7 \pm 4.5$  for Np(VI), while the values for Np(V) of 3.2 and Cr(III) of 2.5 are small enough to be ignored. At 9800 Å. the molar extinction coefficient of Np(V) in 2.0 *M* HClO<sub>4</sub> is 386.9<sup>6</sup> while Cr(VI), Cr(III), and Np(VI) are essentially transparent. These values, but not the relevant orders of magnitude, changed slightly with temperature and solution composition.

**Form of the Rate Law.** In preliminary kinetic experiments it was found that treatment of the rate data in terms of a simple second-order reaction did not adequately describe the results. When, in addition, it was found that the integrated form of a rate law analo-

(5) (a) J. L. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959); (b) The Np(VI) is rapidly reduced by Dowex-50 cation-exchange resin to Np(V), which is readily eluted in 2.0 *M* HClO<sub>4</sub>; see J. C. Sullivan, D. Cohen, and J. C. Hindman, *ibid.*, **77**, 6203 (1955).

(6) This value is based on observations of the author and Dr. A. J. Zielen of this laboratory over a period of some 5 years, and we believe it is accurate to within 2%. The uncertainties listed for the other values presented are a measure of the precision in this particular study and are based on a much smaller set of observations.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

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

(4) A. J. Zielen, J. C. Sullivan, and D. Cohen, *J. Inorg. Nucl. Chem.*, **7**, 378 (1958).

gous to that determined for the reactions of Cr(VI) with Fe(II)<sup>7</sup> or V(IV)<sup>8</sup> did not describe the data, recourse was had to a program which approximates the first derivative of an unknown function from a given set of experimental data points.<sup>9</sup> This treatment of the data indicated<sup>10</sup> that the appropriate differential form of the rate law at constant acidity is

$$-d[\text{NpO}_2^+]/dt = \frac{k[\text{NpO}_2^+][\text{Cr(VI)}]}{1 + k'[\text{NpO}_2^{2+}]/[\text{NpO}_2^+]} \quad (2)$$

The indefinite integral of (2) is

$$t = A \log \frac{[\text{NpO}_2^+]}{[\text{Cr(VI)}]^0 - \frac{[\text{NpO}_2^+]^0}{3} + \frac{[\text{NpO}_2^+]}{3}} + \frac{B}{[\text{NpO}_2^+]} + C \quad (3)$$

The parameter  $C$  is dependent upon the parameters  $A$  and  $B$  which are mutually independent. In terms of initial stoichiometric concentrations and the rate constants previously defined

$$A = \frac{[\text{Cr(VI)}]^0(1 - k') - [\text{Np(V)}]^0/3 - k'[\text{NpO}_2^{2+}]^0/3}{k\{[\text{Cr(VI)}]^0 - [\text{NpO}_2^+]^0/3\}^2} \quad (4)$$

$$B = \frac{k'\{[\text{NpO}_2^+]^0 + [\text{NpO}_2^{2+}]^0\}}{k\{[\text{Cr(VI)}]^0 - [\text{NpO}_2^+]^0/3\}}$$

A program was prepared<sup>11</sup> which determined values for  $A$ ,  $B$ , and  $C$  (eq. 3) given values of  $\text{Np(V)}$  and  $t$ . From these computed values of  $A$  and  $B$  the set of eq. 4 were solved to obtain values of  $k$  and  $k'$ .

In terms of the usual criteria, eq. 3 adequately adjusts all the kinetic data (with an average standard deviation corresponding to  $\pm 0.003$  in the optical density) for the 80 independent experiments reported in this study. In addition values obtained for  $k$  and  $k'$  from eq. 4 agreed with the values obtained from eq. 2.

Sets of duplicate experiments, 2.0  $M$  in  $\text{HClO}_4$ , with initial concentrations of  $\text{Cr(VI)} = 3.43 \times 10^{-4}$  and  $\text{Np(V)} = 1.26 \times 10^{-3} M$ , were monitored at 9800 Å. (by following the disappearance of the  $\text{Np(V)}$ ) and 3500 Å. where the disappearance of the  $\text{Cr(VI)}$  was observed. Values obtained for  $k$  were 11.09 and 11.13 l. mole<sup>-1</sup> sec.<sup>-1</sup>, while values obtained for  $k'$  were 0.267 and 0.268, respectively. This very close agreement is in part fortuitous since average values obtained in another set, with the same concentrations of reactants but using entirely different sources of

reagents, were 11.66 and 0.281, respectively. In addition the uncertainty in  $k'$  is *ca.* 10% based on all the kinetic results. In all of the kinetic experiments (which were followed to at least 95% of completion) the final value of the absorbance at either 3500 or 9800 Å. was within 1–2% of that calculated on the basis of the demonstrated stoichiometry.

*Test of the Rate Law.* Values calculated for  $k$  and  $k'$  from experiments with varying initial concentrations of  $\text{Cr(VI)}$ ,  $\text{Np(V)}$ , and  $\text{Np(VI)}$  at constant hydrogen ion concentration and ionic strength are presented in Table I.

Table I. Test of the Rate Law<sup>a</sup>

$$\frac{-d[\text{Np(V)}]}{dt} = k_1[\text{Np(V)}][\text{Cr(VI)}] / \left(1 + k' \frac{[\text{Np(VI)}]}{[\text{Np(V)}]}\right)$$

10 <sup>4</sup> [Cr(VI)], moles/l.	10 <sup>4</sup> [Np(V)], moles/l.	$k$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	$k'$
3.49	13.21	8.41	0.463
3.51	5.59	7.92	0.415
3.54	13.20	8.12 <sup>b</sup>	0.476
14.14 <sup>c</sup>	13.35	8.27	0.429
3.40	13.23	8.68 <sup>d</sup>	0.432
3.45	13.62	9.00 <sup>e</sup>	0.365
3.51	13.73	7.99 <sup>f</sup>	0.379
3.50	32.00	7.94	0.473
1.42	9.93	7.61	0.422
1.42	10.06	7.99	0.374
Av.		8.26 ± 0.42	0.42 ± 0.04

<sup>a</sup> All values are averages of two to four independent determinations.  $[\text{H}^+] = 1.51$  moles/l.,  $\mu = 2.00$  (with  $\text{LiClO}_4$ ), 25°. <sup>b</sup> Initial  $\text{Cr(III)}$  concentration =  $2.18 \times 10^{-2}$  mole/l. <sup>c</sup> Maximum  $[\text{Cr}_2\text{O}_7^{2-}]_0 \sim 5\%$  of total initial  $\text{Cr(VI)}$ . <sup>d</sup> Initial concentration of  $10^4[\text{Np(VI)}] = 38.50$  moles/l. <sup>e</sup> Initial concentration of  $10^4[\text{Np(VI)}] = 19.58$  moles/l. <sup>f</sup> Initial concentration of  $10^4[\text{Np(VI)}] = 9.51$  moles/l.

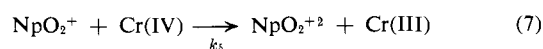
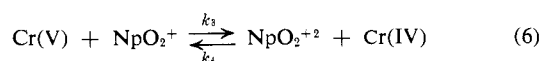
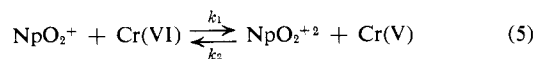
*Hydrogen Ion and Temperature Dependence.* The variation of the empirical rate constants as a function of hydrogen ion concentration and temperature are presented in Table II.

$k'$  exhibits an apparent inverse second-order hydrogen ion dependence at the three temperatures. Values of  $k'[\text{H}^+]^2$  calculated from the data at 15, 25, and 35° are  $0.76 \pm 0.10$ ,  $0.99 \pm 0.14$ , and  $0.84 \pm 0.16$ , respectively.

At 15, 25, and 35° the apparent dependencies of  $k$  upon hydrogen ion concentration are  $1.45 \pm 0.03$ ,  $1.51 \pm 0.05$ , and  $1.35 \pm 0.03$ , respectively.

## Discussion

The following set of one-equivalent steps (eq. 5–7)



provides a reasonable mechanism for this reaction. The empirical form of the rate law is consistent with

(7) J. H. Espenson and E. L. King, *J. Am. Chem. Soc.*, **85**, 3328 (1963).

(8) J. H. Espenson, *ibid.*, **86**, 1883 (1964).

(9) Argonne National Laboratory Applied Mathematics Division Program 1967/SSS 143.

(10) While this program has incorporated techniques to eliminate sharp discontinuities in the first derivatives obtained, the numerical procedure only approximates the first derivative. Consequently, treatment of the data in terms of eq. 2 superimposes the errors of this computational procedure upon the experimental errors. Therefore, values of  $k$  and  $k'$  determined by this treatment will not be reported.

(11) J. Varley, CHM 195, Applied Mathematics Division, Argonne National Laboratory.

the assumption that Cr(V) is the only intermediate of kinetic importance. In terms of this proposed mechanism, the empirical rate constants are identified as  $k = 3k_1$  and  $k' = k_2/k_3$ .

The variation of  $k$  with hydrogen ion concentration can be interpreted in terms of the usual power series approximation,  $k = a[\text{H}^+] + b[\text{H}^+]^2$ . For the present system the condition of restraint that the order of the reaction should always be integral can be satisfied as well by the mechanism outlined below.

When the data are treated in this manner, the values obtained for  $k_0K_2$  ( $\text{l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ ) are  $3.49 \pm 0.09$ ,  $9.95 \pm 0.68$ , and  $11.5 \pm 0.6$  at 15, 25, and 35°, respectively. The uncertainties listed are standard deviations based on external consistency. The difference in the standard deviations computed for the value of  $k_0K_2$  at 25° is simply a reflection of the difference in the two arithmetical procedures.

The mechanism proposed to account for the variation of  $k$  with hydrogen ion concentration does not depend

Table II.  $[\text{H}^+]$  and Temperature Dependencies of  $k$  and  $k'$ <sup>a</sup>

15°			25°			35°		
$[\text{H}^+]$ , moles/l.	$k$ , l. $\text{mole}^{-1}$ $\text{sec.}^{-1}$	$k'$	$[\text{H}^+]$ , moles/l.	$k$ , l. $\text{mole}^{-1}$ $\text{sec.}^{-1}$	$k'$	$[\text{H}^+]$ , moles/l.	$k$ , l. $\text{mole}^{-1}$ $\text{sec.}^{-1}$	$k'$
0.42	0.551	5.01	0.51	1.31	3.34	0.42	2.24	4.50
0.58	0.921	2.24	0.76	2.84	1.78	0.60	3.78	2.14
0.83	1.58	0.988	1.01	4.32	0.76	0.81	5.75	1.82
0.99	2.08	0.702	1.51 <sup>b</sup>	8.26	0.42	1.00	7.83	0.778
1.17	2.56	0.53	1.75	9.93	0.39	1.20	9.49	0.485
1.40	3.21	0.367	1.97	11.38	0.274	1.40	12.8	0.387
1.64	3.97	0.355				1.60	14.2	0.304
1.80	4.57	0.21				1.80	15.9	0.295

<sup>a</sup> All values are averages of from two to four independent determinations.  $\mu = 2.00$  ( $\text{LiClO}_4$ ),  $[\text{NpO}_2^{+}]^0 \sim 1.3 \times 10^{-3} \text{ mole/l.}$ ,  $[\text{Cr(VI)}]^0 \sim 3.5 \times 10^{-4} \text{ mole/l.}$  <sup>b</sup> Average values from Table I.

Over the range 0.4–2.0  $M$   $\text{HClO}_4$  covered in these experiments at the low ( $10^{-3}$ – $10^{-4} M$ ) Cr(VI) concentrations used, the principal species of Cr(VI) are  $\text{HCrO}_4^-$  and  $\text{H}_2\text{CrO}_4$ . Based on the assumption that the first step in the reaction sequence is between  $\text{NpO}_2^+$  and  $\text{H}_3\text{CrO}_4^+$ ,<sup>12</sup> the empirical rate coefficient can be expressed as

$$k = \frac{k_0 K_1 K_2 [\text{H}^+]^2}{1 + K_1 [\text{H}^+]} \quad (8)$$

(with  $k_0 = 3k_1$ ) where

$$K_1 = \frac{[\text{H}_2\text{CrO}_4]}{[\text{H}^+][\text{HCrO}_4^-]} \quad (9)$$

and

$$K_2 = \frac{[\text{H}_3\text{CrO}_4^+]}{[\text{H}_2\text{CrO}_4][\text{H}^+]} \quad (10)$$

When the values of  $k$  at 25° in Table II are used in eq. 8 along with the known value of  $K_1 = 0.77$ ,<sup>13</sup> the average value obtained for  $k_0K_2$  is  $9.83 \pm 0.35 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ .

A similar test of the proposed mechanism (with respect to hydrogen ion dependencies) cannot be made at the other temperatures since data are not available for  $K_1$ . The data at 15 and 35° can, however, be correlated by eq. 8 after a simple transformation into a linear form where  $K_1$  is incorporated in the value obtained for the intercept.

(12) This proposed interpretation is equivalent to considering the rate law term  $[\text{H}^+][\text{NpO}_2^+][\text{H}_2\text{CrO}_4]$  since the product  $k_0K_2$  is never resolved. The formulation presented facilitates the comparison to be made later between the Cr(VI)– $\text{NpO}_2^+$  and Cr(VI)– $\text{Fe(Phen)}_3^{+2}$  systems.

(13) J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

very critically upon the exact value assigned to  $K_1$ . This point is demonstrated by the fact that the value calculated from the linearized form of eq. 8,  $K_1$ , is equal to  $0.75 \pm 0.08$ .

The result that  $k'(\text{H}^+)^2$  is essentially independent of temperature is not inconsistent with the identification of  $k' = k_2/k_3$ . Consideration of the temperature variation of  $k_0K_2$  adds no insight into the proposed mechanism.

The interpretation of the empirical form of the rate law presented here is consistent with the ideas previously advanced of the importance of unstable tetra- and pentavalent oxidation states of chromium in oxidation–reduction reactions<sup>14</sup> and the hypothesis advanced by Tong and King<sup>2</sup> of the kinetic significance of the Cr(V)–Cr(IV) transformation.

Because of the difference between the empirical rate law presented here and those determined for the one-equivalent acceptors,  $\text{Fe(II)}$ <sup>7</sup> and  $\text{V(IV)}$ ,<sup>8</sup> it is not feasible to make detailed intercomparisons between these systems. However, it is possible to abstract information from the data presented for the reaction between Cr(VI) and  $\text{Fe(Phen)}_3^{+2}$  that can be compared with the present study.

Use of eq. 8 with a value of  $K_1 = 1.0$  results in a value of  $37.5 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$  (from the data in ref. 7, Table II at 30°) for a coefficient which can be compared to  $k_0K_2 = 5.6$ . From these calculations the rate constant for the oxidation of  $\text{Fe(Phen)}_3^{+2}$  by  $\text{H}_3\text{CrO}_4^+$  is *ca.* seven times as large as that for the oxidation of  $\text{NpO}_2^+$  by the same species.<sup>15</sup>

An important difference in the two reductants compared is that the  $\text{Fe(Phen)}_3^{+2}$  reacts with the Cr(VI)

(14) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

(15) Differences in ionic strength cannot account for this result since at ionic strength 1.51 the empirical rate coefficient for the present system was determined as 7.15 (in 1.51  $M$  perchloric acid), a value to be compared with 8.26 determined at ionic strength 2.0 and the same acidity.

solely by outer-sphere transition states,<sup>16</sup> but it is possible for the Np(V) to form bridged-activated complexes. One plausible method would be by substitution on the Cr(VI) *via* one of the collinear oxygen atoms or through one of the equatorial water molecules. Since we cannot entirely eliminate the possibility of an outer-sphere-activated complex in this latter case, a comparison of the two reactions in terms of the Marcus<sup>17</sup> theory is of some interest.

All of the data necessary for a quantitative comparison of the two rates are not available. However, it is possible to calculate the ratio of the rate constants for the comparable steps using the reduced equation presented by Dulz and Sutin.<sup>18</sup> The pertinent values used are<sup>19</sup>:  $k = 457 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  for the Np(V)-

Np(VI) exchange reaction;  $k > 1 \times 10^5 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  for the  $\text{Fe(Phen)}_3^{+2}$ - $\text{Fe(Phen)}_3^{+3}$  exchange reaction; and  $E^\circ$  values of 1.13 v. for the Np(V)-Np(VI) couple and 1.04 v. for the  $\text{Fe(Phen)}_3^{+2}$ - $\text{Fe(Phen)}_3^{+3}$  couple. These calculations indicated that the rate constant for the oxidation of the iron compound should be greater than four times that for the oxidation of Np(V).

This result reflects the importance of the electron-transfer rate term in the comparison of two reactions in which the appropriate free energy changes are of the same order of magnitude. The idea presented by Sebera and Taube<sup>20</sup> of electron conduction through a conjugated system provides an appealing explanation of the relative rate with which an electron can be transferred from the tris(1,10-phenanthroline)iron(II) compared to a similar transfer from the  $\text{NpO}_2^+$  ion to a common acceptor.

(16) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(17) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(18) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(19) Np(V)-Np(VI) exchange: D. Cohen, J. C. Sullivan, and J. C. Hindman, *J. Am. Chem. Soc.*, **77**, 4964 (1955);  $\text{Fe(Phen)}_3^{+2}$ - $\text{Fe(Phen)}_3^{+3}$  exchange: M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591

(1963); Np(V)-Np(VI)  $E$  value: A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962).

(20) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).