

Bohr and nuclear magnetons, respectively, and g_N is the nuclear g factor. N_{π_2} and λ_{π_2} are related by the normalization requirement $N_{\pi_2}^2 = [1 - 4\pi_{\pi_2}S_{b2} + \lambda_{\pi_2}^2]^{-1}$.

In order to solve for $N_{\pi_2}^2$, $N_{\sigma_2}^2$, and $N_{\pi_1}^2$ in the above equations, values must be obtained for ξ , P , $T(n)$, S_{b2} , S_{b1} , and S_e . The values of ξ and P depend on the formal charge which is assigned to the vanadium atom. In calculations involving the VO^{2+} group, most authors⁵ feel the formal charge on the vanadium is reduced to approximately 2+. It would seem reasonable to assume the charge on the vanadium in the $V(OR)^{3+}$ group is approximately 3+. Thus⁴ P is $1.50 \times 10^{-2} \text{ cm}^{-1}$. ξ is taken from Dunn's tables as 210 cm^{-1} . $T(n)$ depends on the ligand σ -orbital hybridization. In our case where we have used sp hybrids for the σ bonding, $T(n)$ is estimated as 0.25.²⁶ The overlap terms were not determined but those values calculated for $VOCl_5^{2-}$ by Gutowsky should be very near the values for the alkoxides. Thus, S_{b2} , S_{b1} , and S_e were taken as 0.099, 0.165, and 0.139, respectively. The assumption was made that little charge occurs in the overlap terms in going from the methoxide to the butoxide. We also assumed $\lambda_{\pi_1}^a \approx \lambda_{\pi_1}^e$.

The values obtained by an iterative treatment of eq 8-10 are given in Table IV. A decrease in $N_{\pi_2}^2$ and $N_{\sigma_2}^2$ is observed in going from the methoxide to the butoxide ion and an increase is observed in $N_{\pi_1}^2$. The decrease in $N_{\pi_2}^2$ and $N_{\sigma_2}^2$ indicates that the B_2 and B_1 molecular orbitals become more covalent through the

TABLE IV
MOLECULAR ORBITAL COEFFICIENTS AND SPIN DENSITIES

	$N_{\pi_2}^2$	$N_{\pi_1}^2$	$N_{\sigma_2}^2$	λ_{π_2}	% f_{π}
II	0.947	0.882	0.794	0.506	4.87
III	0.934	0.910	0.767	0.529	5.31
IV	0.921	0.924	0.751	0.552	5.75
V	0.919	0.924	0.739	0.555	5.81
VII	0.982	0.914	0.811	0.438	3.64
VIII	0.961	0.949	0.767	0.481	4.41
IX	0.944	0.955	0.765	0.512	4.99

series. The increase in $N_{\pi_1}^2$ indicates the E molecular orbital becomes more ionic from $^-OCH_3$ to $^-OC_4H_9$.

The unpaired electron density in the four equatorial $3p_{\pi}$ orbitals of Cl^- is given by the Mulliken population analysis²⁷

$$\left(\begin{array}{c} \text{unpaired electron density in} \\ \text{each ligand } 3p_{\pi} \text{ orbital} \end{array} \right) = \frac{\lambda_{\pi_2}^2 N_{\pi_2}^2 - N_{\pi_2}^2 \lambda_{\pi_2} S_{b2}}{4}$$

The values obtained from this treatment are also given in Table IV. Manoharan and Rogers¹ and we, in our previous work,² have found excellent agreement between spin densities calculated in this manner and those calculated from ligand hyperfine splittings.

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Kinetics of Reduction of Neptunium(VI) with Disodium Ethylenediaminetetraacetate in Aqueous Perchloric Acid

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The kinetics for the reduction of neptunium(VI) with disodium ethylenediaminetetraacetate has been studied in aqueous perchlorate media. Stoichiometry, specific velocity constants, enthalpy of activation, and entropy of activation have been determined. A possible mechanism has been suggested which explains the observed kinetics and the stoichiometry of the reaction.

Introduction

Ethylenediaminetetraacetic acid (EDTA) has been reported to react with MnO_4^- , H_2O_2 , Ce^{4+} , V^{5+} , and Cr^{6+} .¹⁻³ Disodium ethylenediaminetetraacetate ($Na_2 \cdot H_2Y \cdot 2H_2O$) has been found to reduce plutonium(VI) as $PuO_2(ClO_4)_2$ to plutonium(V).⁴ Further reduction is reported to take place slowly in a large excess

of disodium EDTA. The following paper presents a kinetic study of the reaction of neptunium(VI) with disodium EDTA. This reaction was deemed important to the authors because of the similarity in behavior of Np(VI) and Pu(VI) as oxidizing agents.

Experimental Section

Stock solution of neptunium(VI) was prepared by electrolytic oxidation of a pure neptunium(V) solution in standard aqueous perchloric acid.⁵ The course of oxidation was followed spectrophotometrically. Complete oxidation was ascertained by

(1) P. N. Palei and N. I. Udaltsova, *Zh. Anal. Khim.*, **15**, 668 (1960).
(2) P. N. Palei and N. I. Udaltsova, *ibid.*, **16**, 649 (1961).
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(4) O. L. Kabanova, M. A. Danushenkova, and P. N. Palei, *Anal. Chim. Acta*, **22**, 66 (1960).

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observing the neptunium(VI) peaks at 1230, 557, and 476 $m\mu$ to the exclusion of all others on a Beckman DK-1 recording spectrophotometer.^{5,6} The neptunium concentration was determined by α -particle counting on the basis of 790 α counts min^{-1} μg^{-1} specific counting yield on a Nuclear Chicago gas flow counter.

All solutions were prepared with deionized distilled water. A standard stock solution of disodium ethylenediaminetetraacetate was prepared by weight. The reagent used was a Fisher Certified reagent and was used without further purification. Stock solution of perchloric acid was prepared by diluting the concentrated acid obtained from the Mallinckrodt Chemical Works. This solution was standardized against standard sodium hydroxide solution using phenolphthalein as an indicator. Stock solution of sodium perchlorate used to adjust the ionic strength was prepared by direct weighing.

Appropriate amounts of all solutions except neptunium(VI) were mixed and placed in a thermostated bath. Neptunium(VI) solution was also placed separately in the bath and the two solutions were allowed to attain thermal equilibrium. The temperature of the bath was maintained within $\pm 0.1^\circ$. The thermometer used was calibrated against an NBS thermometer. The reaction was started by adding neptunium(VI) solution and the start of the reaction was timed when half of the solution drained out of the pipet. A thorough mixing of the reactants was ensured before the sample was transferred to a stoppered silica spectrophotometer cell. The cell was placed in the thermostated cell compartment of a Beckman DU spectrophotometer maintained within $\pm 0.1^\circ$. The reaction was followed by making absorption measurements at the 983- $m\mu$ absorption band of neptunium(V) at constant slit width using matched silica cells of 10.00 ± 0.01 mm light path. The molar extinction coefficient was $325 M^{-1} \text{cm}^{-1}$. The course of reduction was also followed by observing the decrease in the neptunium(VI) peak at 1230 $m\mu$ using the tungsten lamp. The molar extinction coefficient was $21.69 M^{-1} \text{cm}^{-1}$. This was done to check the rate data as well as the analytical uses of this band which is in the near-infrared region. In all runs the reference used was a mixture of perchloric acid and sodium perchlorate of the same acid concentration and ionic strength as the sample. The time taken from mixing the reactants to the first observation was between 2 and 3 min.

Results

Disodium ethylenediaminetetraacetate was found to reduce neptunium(VI) to neptunium(V). An interesting feature of the reaction was the color changes of the reaction mixture. Neptunium(VI) has a pink color in perchloric acid. Upon mixing the reactants, the color changed to yellow. After completion of the reaction the color once again changed to the blue-green of the neptunium(V) in perchloric acid.

One mole of disodium ethylenediaminetetraacetate was found to react with 6 mol of neptunium(VI) and one of the products was identified as CO_2 . The stoichiometry was determined by making triplicate runs with a large excess of Np(VI) and taking the final spectrophotometric reading of the Np(V) peak after the completion of the reaction. The results of the three runs presented in Table I are in good agreement. Data for a typical run are presented in Table II.

At constant ionic strength, the kinetics were found to be consistently of second order, first order with respect to neptunium(VI) and first order with respect to disodium ethylenediaminetetraacetate.

In the case of the runs made at the same concentra-

TABLE I
INITIAL CONCENTRATIONS OF NEPTUNIUM(VI) AND DISODIUM ETHYLENEDIAMINETETRAACETATE AND THE RATIO OF NEPTUNIUM(V) TO EDTA AT 25°

$10^2[\text{Np(VI)}], M$	$10[\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}], M$	Np(V) produced/EDTA
2.72	0.40	5.9
4.84	0.48	5.8
4.84	0.50	5.7

TABLE II
THE CONCENTRATION OF Np(V) AS A FUNCTION OF TIME FOR THE REDUCTION OF Np(VI) WITH DISODIUM ETHYLENEDIAMINETETRAACETATE AT 25° ^a

Time	$10^2[\text{Np(V)}], M$	Time	$10^2[\text{Np(V)}], M$
2 min	0.3	60 min	0.99
5 min	0.36	120 min	1.22
10 min	0.45	180 min	1.45
21 min	0.62	36 hr	2.39
30 min	0.72	60 hr	2.39
52 min	0.85		

^a $[\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}] = 0.4 \times 10^{-3} M$; $[\text{Np(VI)}] = 2.72 \times 10^{-3} M$; $[\text{H}^+] = 0.5 M$.

tions of neptunium(VI) and disodium ethylenediaminetetraacetate a plot of $\log k'$ against $\log [\text{H}^+]$ gives a straight line with a negative slope of 1.5. The data at 25° and $\mu = 1$ are summarized in Table III.

Effect of Ionic Strength.—To observe the effect of a neutral electrolyte on the reaction rate, runs were made with the addition of sodium perchlorate. Data in Table IV indicate a small decrease in the value of k with increasing ionic strength.

Energy of Activation.—The energy of activation was determined by carrying out the reaction at five temperatures. From the data presented in Table V, the energy of activation is calculated to be 23,000 cal mol^{-1} , and the entropy of activation ΔS^* is 12.28 eu.

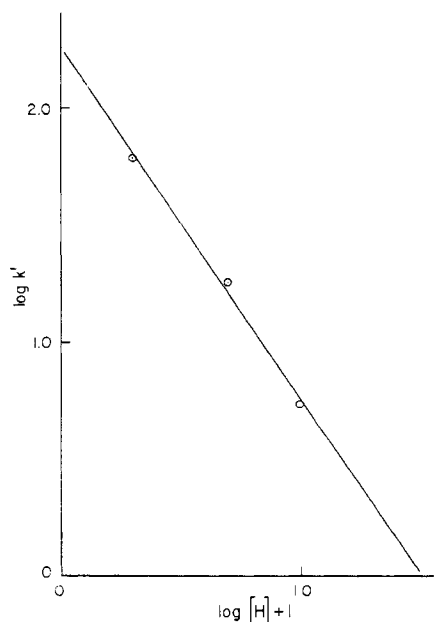


Figure 1. Effect of hydrogen ion concentration on the apparent rate constant k' at 25° and $\mu = 1$ in the reduction of neptunium(VI) with disodium ethylenediaminetetraacetate.

TABLE III
SPECIFIC VELOCITY CONSTANTS AT 25° AND $\mu = 1$ IN THE
REDUCTION OF NEPTUNIUM(VI) WITH DISODIUM
ETHYLENEDIAMINETETRAACETATE

$10^3 [\text{Np(VI)}], M$	$10^3 \times [\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}], M$	$[\text{H}^+], M$	$k',^a M^{-1} \text{sec}^{-1}$	$k, M^{1/2} \text{sec}^{-1}$
2.72	0.4	0.5	0.260	0.092
2.72	20.0	0.4	0.452	0.114
2.72	20.0	0.8	0.131	0.094
2.72	5.0	0.5	0.303	0.107
2.72	5.0	1.0	0.091	0.092
2.72	5.0	0.2	1.04	0.093
10.9	5.0	0.5	0.307	0.108
1.36	5.0	0.5	0.283	0.102
4.84 ^b	25.0	0.5	0.282	0.100
7.09 ^b	25.0	0.375	0.470	0.108
3.457 ^b	5.0	0.125	2.08	0.092
4.84 ^b	0.5	0.5	0.262	0.093
				Av 0.100 \pm 0.002

^a The apparent rate constant k' was calculated using the equation

$$k't = \frac{(2.303)(6)}{a - 6b} \log \frac{6b(a - x)}{a(6b - x)}$$

where a and b are the initial concentrations of neptunium(VI) and disodium ethylenediaminetetraacetate, respectively, and x is the concentration of neptunium(V) produced in time t . ^b Data observed at the Np(VI) peak at 1230 m μ .

TABLE IV
EFFECT OF IONIC STRENGTH ON THE REDUCTION
OF NEPTUNIUM(VI) WITH DISODIUM
ETHYLENEDIAMINETETRAACETATE AT 25°^a

μ	$k, M^{1/2} \text{sec}^{-1}$	μ	$k, M^{1/2} \text{sec}^{-1}$
0.5	0.100	1.5	0.077
1.0	0.092	2.0	0.070

^a $[\text{Np(VI)}] = 2.72 \times 10^{-3} M$; $[\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}] = 5.0 \times 10^{-3} M$; $[\text{H}^+] = 1.0 M$.

TABLE V
EFFECT OF TEMPERATURE UPON THE SPECIFIC VELOCITY
CONSTANTS IN THE REDUCTION OF NEPTUNIUM(VI)
WITH DISODIUM ETHYLENEDIAMINETETRAACETATE^a

Temp, °C	$k, M^{1/2} \text{sec}^{-1}$	Temp, °C	$k, M^{1/2} \text{sec}^{-1}$
20	0.046	30	0.173
23	0.069	35	0.322
25	0.091		

^a $[\text{Np(VI)}] = 2.72 \times 10^{-3} M$; $[\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}] = 5 \times 10^{-3} M$; $[\text{H}^+] = 1.0 M$.

Discussion and Mechanism

The reaction between neptunium(VI) and disodium ethylenediaminetetraacetate is very similar to the reduction of plutonium(VI) to plutonium(V) by disodium ethylenediaminetetraacetate in perchlorate media studied by Kabanova, Danushenkova, and Palei.⁴ They found that the reaction was first order with respect to the PuO_2^{2+} ion concentration and first order with respect to the disodium ethylenediamine-

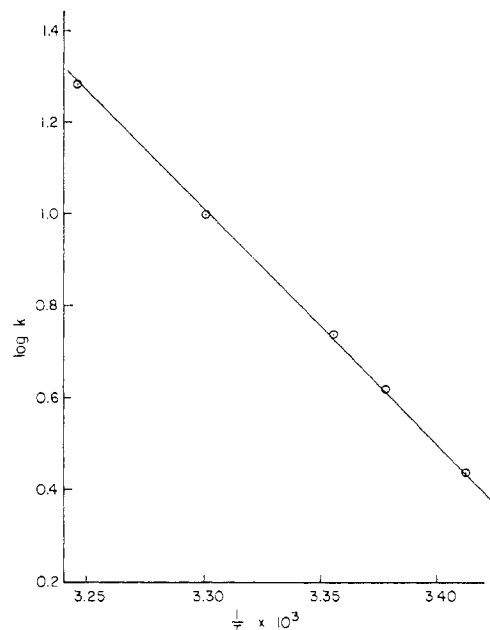
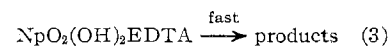


Figure 2.—Plot of $\log k$ against $(1/T) \times 10^3$ to determine the energy of activation in the reduction of neptunium(VI) with disodium ethylenediaminetetraacetate.

tetraacetate concentration. They also observed that 6 equiv of PuO_2^{2+} was reduced to PuO_2^+ by 1 mol of disodium ethylenediaminetetraacetate with the formation of hydrogen ions. No reaction mechanism was proposed to account for these observations though the over-all reaction given was similar to eq 3. If the oxidation product of the disodium ethylenediaminetetraacetate be assumed to be the same in both of the reactions, the following mechanism will satisfy the stoichiometry of the over-all reaction and the order for each reactant in the reduction of neptunium(VI). It

$$\text{NpO}_2^{2+} + \text{EDTA} + \text{H}_2\text{O} \longrightarrow \text{NpO}_2(\text{OH})\text{EDTA}^+ + \text{H}^+ \quad (1)$$

$$\text{NpO}_2^{2+} + \text{EDTA} + 2\text{H}_2\text{O} \longrightarrow \text{NpO}_2(\text{OH})_2\text{EDTA} + 2\text{H}^+ \quad (2)$$

$$10\text{NpO}_2^{2+} + \text{NpO}_2(\text{OH})\text{EDTA}^+ +$$


is assumed that at the concentrations of perchloric acid used the ethylenediaminetetraacetate is in the form of the slightly ionized ethylenediaminetetraacetic acid.

The fractional dependence upon the hydrogen ion concentration probably arises from simultaneous reactions 1 and 2 which are about equally influential in controlling the rate. Formation of the initial complex between NpO_2^{2+} ion and disodium ethylenediaminetetraacetate is supported by the observed color changes which take place during the reaction. Subsequently reaction 3 which has the required stoichiometry of 6 equiv of NpO_2^{2+} reacting per mole of the disodium ethylenediaminetetraacetate must occur.