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Kinetics of the Oxidation of Selenium(IV) by Neptunium(VII) in Aqueous Acidic Perchlorate Media[1a]

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The Np(VII) oxidation of Se(IV) proceeds with two-to-one stoichiometry to yield Np(VI) and Se(VI) according to the empirical rate law $-d(\ln [\mathrm{Np(VII)}])/dt = k_1[\mathrm{Se(IV)}] + k_2[\mathrm{Se(IV)}]^2$ with no detectable acid dependence. The apparent activation parameters are $\Delta H_1^* = 7.43 \pm 0.14$ and $\Delta H_2^* = 3.70 \pm 0.65$ kcal/mol and $\Delta S_1^* = -19.7 \pm 0.5$ and $\Delta S_2^* = -28.9 \pm 2.2$ eu. This rate law is accounted for by a mechanism involving the known dimerization of Se(IV) in acidic media and parallel paths for oxidation of both monomeric and dimeric forms. At 25° and $\mu = 1.00$ M, the specific rate constants for oxidation of the monomer (k_M) and dimer (k_D) are $(1.07 \pm 0.02) \times 10^3$ and $(4.37 \pm 0.17) \times 10^3$ M^{-1} s^{-1}, respectively. The observed rate law and rate parameters are discussed in terms of, and are found to be consistent with, the established reactivity pattern exhibited by Np(VII) when oxidizing aquometal ions.

Introduction

Selenious acid is a well-known and widely used oxidizing agent in organic synthesis[2,3] ($E°_{H_2SeO_3} = 0.74$ V[4]) but it has received much less attention as a mild reducing agent ($E°_{H_2SeO_4} = 1.15$ V[4]). Recent renewed interest in the inorganic and bioinorganic chemistry of selenium[5] has prompted us partly to fill this void and investigate the detailed kinetics of the oxidation of Se(IV) by the potent 1-equiv oxidant Np(VII) ($E°_{Np(VII)} > 2.0$ V[6]). Neptunium(VII) provides a significantly larger thermodynamic driving force for the conversion of selenium(IV) to selenium(VI) than do the two oxidants previously investigated in any detail (MnO_4^- [7] and H_2O_2[8], both in acid media). This work comprises the most complete study to date on the oxidation of selenious acid and further serves to delineate the dynamic chemical behavior of neptunium(VII) in acidic media.[6,9-13]

Experimental Section

Reagents and Analyses. The preparation and standardization of Np(VII), $LiClO_4$, and $HClO_4$ solutions have been described previously.[9,13] Fisher Certified selenious acid was dissolved in triply distilled water, and a duplicate preparation was made from material which had been recrystallized two times from triply distilled water. Since these preparations yielded consistent kinetic results, they were used interchangeably. Stock solutions of selenious acid were standardized by titration with permanganate.[14] Sodium selenate was prepared by neutralization of selenic acid followed by two recrystallizations of the resulting salt from triply distilled water.

Equipment and Procedures. The computer-interfaced, stopped-flow instrumentation, as well as the basic procedures and techniques used in this work, have been detailed previously.[12] The title reaction was monitored at 440 nm where the molar extinction coefficient of Np(VII) (ca. 410 M^{-1} cm^{-1}) is much larger than that of any other species present in solution. The slow oxidation of water by Np(VII)[6] in the storage syringe results in decreasing $[\mathrm{Np(VII)}]_0$, and concomitant increasing $[\mathrm{Np(VI)}]_0$, as repetitive experiments are performed; the range of $[\mathrm{Np(VII)}]_0$ encountered in this work was $(6-60) \times 10^{-5}$ M. All kinetic data were obtained with $[H^+]_0$ and $[\mathrm{Se(IV)}]_0$ in at least 10-fold equivalent excess over $[\mathrm{Np}]_{tot}$ (i.e., the total concentration of neptunium which is equal to the maximum possible value of $[\mathrm{Np(VII)}]_0$). Within a series of consecutive, repetitive experiments the continuously varying $[\mathrm{Np(VII)}]_0$ and $[\mathrm{Np(VI)}]_0$ had no effect on the observed rate parameters. Unless otherwise noted, all kinetic data were obtained at $\mu = 1.00$ M ($LiClO_4$).

Data Analysis. The observed OD–t data from individual kinetic experiments were treated by standard nonlinear least-squares techniques[15] within the first-order rate expression

$$\mathrm{OD}_t = (\mathrm{OD}_0 - \mathrm{OD}_\infty) \exp(-k_{obsd}t) + \mathrm{OD}_\infty \qquad (1)$$

allowing k_{obsd}, OD_0, and OD_∞ to be adjustable parameters. Each kinetic experiment was monitored to at least 90% completion, 800–950 OD_t–t data points being collected during this period. Previously described criteria[12] were applied to show that eq 1 adequately describes the observed OD_t–t data, and optimized values of OD_0 and OD_∞ always agreed with observed OD_0 and OD_∞ values to within experimental error. A minimum of seven experimental determinations of k_{obsd} were made for each set of reaction conditions, and we report here the mean of these determinations, $\bar{k}_{obsd}$, as well as the standard deviation of that mean, σ_m. Unless otherwise noted, all uncertainties reported in this work are standard deviations.

Results

Stoichiometry. Determination of the excess Se(IV) remaining after oxidation by insufficient Np(VII) in excess perchloric acid leads to the ratio $\Delta[\mathrm{Np(VII)}]/\Delta[\mathrm{Se(IV)}] = 1.97 \pm 0.03$. Spectrophotometric analysis of the product mixture shows no detectable Np(V). Thus the stoichiometry of the title reaction may be taken to be

$$2\mathrm{Np(VII)} + \mathrm{Se(IV)} \rightarrow 2\mathrm{Np(VI)} + \mathrm{Se(VI)} \qquad (2)$$

Kinetics. The $\bar{k}_{obsd}$ independence of $[\mathrm{Np(VII)}]_0$ and $[\mathrm{Np(VI)}]_0$ and the successful fit of the OD_t–t data to eq 1 show that the rate law governing the Se(IV)–Np(VII) reaction (when Se(IV) is present in pseudo-first-order excess) is first order in Np(VII) and zero order in Np(VI). Sodium selenate, initially in fourfold excess over that produced during the reaction, has a negligible effect on $\bar{k}_{obsd}$; varying $[H^+]$ over the range 0.0605–0.588 M changes $\bar{k}_{obsd}$ by less than 4%. Therefore the net rate law is also zero order in both [Se(VI)] and $[H^+]$. The data illustrated in Table I show that $\bar{k}_{obsd}$ is strongly dependent upon the total concentration of Se(IV), this dependence being best expressed as a sum of first-order and second-order terms. Linear least-squares adjustment of the $\bar{k}_{obsd}$–[Se(IV)] data to the polynomial expression

$$\bar{k}_{obsd} = k_0' + k_1'[\mathrm{Se(IV)}] + k_2'[\mathrm{Se(IV)}]^2 \qquad (3)$$

with a minimum of six different [Se(IV)] values for each temperature leads to the coefficients listed in Table II. For all temperatures the k_0 term is statistically insignificant at the 95% confidence level and thus the net rate law governing the Se(IV)–Np(VII) reaction may be expressed as

$$-d(\ln [\mathrm{Np(VII)}])/dt = \bar{k}_{obsd} = k_1[\mathrm{Se(IV)}] + k_2[\mathrm{Se(IV)}]^2 \qquad (4)$$

Nonlinear least-squares analysis[16] of all 26 data points in Table I (each value of $\bar{k}_{obsd}$ weighted as $1/\sigma_m^2$) within the Eyring formalism

$$\bar{k}_{obsd} = 2(k_BT/h)\Sigma_m[\mathrm{Se(IV)}]^m \exp(\Delta S_m^*/R) \times \exp(-\Delta H_m^*/RT) \qquad (5)$$

with $m = 1$ and 2, leads to the following apparent activation parameters: $\Delta H_1^* = 7.43 \pm 0.14$ and $\Delta H_2^* = 3.70 \pm 0.65$

Table I. Dependence of $\bar{k}_{obsd}$ on [Se(IV)][a]

$T = 1.2\ °C$[b]		$T = 12.7\ °C$[c]		$T = 25.0\ °C$[d]			
10^2[Se(IV)], M	$\bar{k}_{obsd}$, s^{-1}	10^2[Se(IV)], M	$\bar{k}_{obsd}$, s^{-1}	10^2[Se(IV)], M	$\bar{k}_{obsd}$, s^{-1}	10^2[Se(IV)], M	$\bar{k}_{obsd}$, s^{-1}
0.654	4.97 ± 0.12	0.327	4.04 ± 0.07	0.127	2.76 ± 0.04	2.05	51.78 ± 0.83
1.31	10.01 ± 0.09	0.654	8.17 ± 0.07	0.254	5.49 ± 0.05	3.19	80.90 ± 0.67
1.31	10.36 ± 0.16	1.31	17.08 ± 0.27	0.512	11.65 ± 0.15	3.58	94.63 ± 0.90
3.27	28.69 ± 0.61	3.27	49.68 ± 0.40	0.640	14.79 ± 0.20	4.76	130.4 ± 1.9
4.91	49.47 ± 0.66	4.91	80.33 ± 0.88	1.02	24.69 ± 0.49	6.38	183.8 ± 6.5
6.54	70.14 ± 1.7	6.54	115.5 ± 1.7	1.02[e]	25.45 ± 0.51	6.38	184.6 ± 3.6
9.81	124.9 ± 2.2			1.02[f]	25.69 ± 0.45	8.89	288.4 ± 9.1
				1.92	47.73 ± 1.4	9.53	319.8 ± 8.0

[a] $\mu = 1.00$ M ($LiClO_4$), $[Np(VII)]_0 = (0.006\text{-}0.06) \times 10^{-2}$ M. [b] $[H^+] = 0.0601$ M. [c] $[H^+] = 0.0586$ M. [d] $[H^+] = 0.0608$ M. [e] $[H^+] = 0.260$ M. [f] $[H^+] = 0.558$ M.

Table II. Nonlinear Least-Squares Optimized Parameters Describing the Dependence of $\bar{k}_{obsd}$ on [Se(IV)] in Terms of Eq 3[a]

T, °C	k_0', s^{-1}	$10^{-3}k_1'$, $M^{-1}\ s^{-1}$	$10^{-3}k_2'$, $M^{-2}\ s^{-1}$
1.2[b]	0.4 ± 0.6	0.70 ± 0.03	5.8 ± 0.3
12.7[c]	−0.5 ± 0.3	1.28 ± 0.03	7.6 ± 0.4
25.0[d]	1.5 ± 1.7	2.12 ± 0.11	12.1 ± 1.1

[a] $\mu = 1.00$ M ($LiClO_4$). [b] $[H^+] = 0.0607$ M. [c] $[H^+] = 0.0558$ M. [d] $[H^+] = 0.0608$ M.

Table III. Ionic Strength Dependence of the Se(IV)-Np(VII) Reaction[a]

μ, M	$\bar{k}_{obsd}$, s^{-1}	μ, M	$\bar{k}_{obsd}$, s^{-1}
0.358	13.86 ± 0.07	1.00	14.8 ± 0.2
0.598	14.49 ± 0.07	2.00	16.4 ± 0.3
0.798	14.4 ± 0.1		

[a] Ionic strength maintained with $LiClO_4$; $[H^+] = 0.060$ M; [Se(VI)] = 0.006 40 M; 25.0 °C.

kcal/mol; $\Delta S_1^* = -19.7 \pm 0.5$ and $\Delta S_2^* = -28.9 \pm 2.2$ eu. The average difference between $\bar{k}_{obsd}$ and the rate constant calculated from these optimized parameters by eq 5 is 2.4%, and the maximum difference is 8.1%. The data of Table III show that under conditions where more than 95% of the reaction proceeds by the k_1 path, $\bar{k}_{obsd}$ exhibits a slight positive salt effect over the ionic strength range 0.36–2.00 M ($LiClO_4$).

Discussion

The Se(IV)–Np(VII) reaction is noncomplementary, and as is usual for this type of reaction, the available data are not sufficient to distinguish between a mechanism involving successive 1-equiv oxidations of the selenium moiety and a 2-equiv mechanism involving Np(V) as a transient intermediate. However, it should be noted that a Se(V) species has been observed[17] in the pulse radiolytic oxidation of selenite solutions, and to date no evidence has been obtained to indicate that Np(VII) oxidations proceed by anything but 1-equiv processes.[9-13] Therefore we tentatively favor the successive 1-equiv oxidation scheme for the Se(IV)–Np(VII) reaction.

The appearance of a $[Se(IV)]^2$ term in the rate law is presumably due to the well-established[18] dimerization of Se(IV) in aqueous acidic media

$$Q = \frac{[H_4Se_2O_6]}{[H_2SeO_3]^2} = 5.6 \pm 1.0\ M^{-1}$$

(25 °C, $\mu = 1.00$ M ($NaClO_4$)[18]). In the concentration range investigated ([Se(IV)] = 0.010–0.100 M) the percent monomeric form varies from 92 to 62% and therefore the observation of mixed-order kinetics is consistent with both the monomer, H_2SeO_3, and the dimer, formulated as $H_4Se_2O_6$,[18] being kinetically reactive. This interpretation is in accord with the two previously reported studies on the oxidation of selenious acid: oxidation by MnO_4^- in sulfuric acid[7] is reported to be first order in [Se(IV)] over the much lower concentration range 10^{-4}–10^{-3} M where the percent monomer is always greater than 99%; oxidation by H_2O_2 in perchloric acid[8] is reported to be second order in [Se(IV)] over the higher concentration range 0.2–0.5 M where the percent monomer ranges from 50 to 36%. A mechanism based on parallel paths for oxidation of the monomer and dimer

$$2H_2SeO_3 \overset{Q}{=} H_4Se_2O_6 \tag{6}$$

$$Np(VII) + H_2SeO_3 \xrightarrow{k_M} \text{products} \tag{7}$$

$$Np(VII) + H_4Se_2O_6 \xrightarrow{k_D} \text{products} \tag{8}$$

leads to the rate expression

$$\bar{k}_{obsd} = 2k_M[(-1 + (1 + 8Q[Se(IV)])^{1/2})/4Q] + 2k_DQ[(-1 + (1 + 8Q[Se(IV)])^{1/2})/4Q]^2 \tag{9}$$

where

$$[Se(IV)] = [H_2SeO_3] + 2[H_4Se_2O_6] \tag{10}$$

represents the total concentration of Se(IV) in both monomeric and dimeric forms. Nonlinear least-squares adjustment[16] of the appropriate 17 $\bar{k}_{obsd}$ data points in Table I (taken at 25 °C, $\mu = 1.00$ M, the only conditions under which Q is known;[18] each value of $\bar{k}_{obsd}$ weighted as $1/\sigma_m^2$) within eq 9 with Q held constant at 5.6 M^{-1} [18] leads to optimized values of $k_M = (1.07 \pm 0.02) \times 10^3\ M^{-1}\ s^{-1}$ and $k_D = (4.37 \pm 0.17) \times 10^3\ M^{-1}\ s^{-1}$. The average difference between $\bar{k}_{obsd}$ and the rate constant calculated from these optimized parameters by eq 9 is 3.0%, and the maximum difference is 7.9%. From the data of Table I it is seen that the value of k_1 determined from eq 3 (25 °C, $\mu = 1.00$ M) is equal within the assigned uncertainties to this directly calculated value of k_M and thus the empirical parameter k_1' may be identified with the specific rate constant governing oxidation of the monomeric form at 25 °C. The empirical parameter k_2' of eq 3 cannot be identified with any simple combination of rate and equilibrium parameters. It is interesting that k_M and k_D are similar in magnitude, indicating that the net activation process for Np(VII) oxidation of Se(IV) is not very sensitive to whether the Se(IV) is in the monomeric or dimeric form.

The lack of a first-order acid-dependent path in the Se(IV)–Np(VII) reaction is in harmony with the previously noted[13] correlation between the acidity of an aquometal ion and its oxidation by Np(VII) via an acid-independent path. Nonacidic aquometal ions ($pK_a > 9$) are oxidized predominantly by paths first order in $[H^+]$, but acidic aquometal ions ($pK_a < 5$) exhibit paths independent of $[H^+]$. This observation is rationalized[13] by invoking a "tautomeric" transition state in which the proton required by Np(VII) in the activated complex originates on the acidic reductant, i.e.

reductant–H + Np(VII) = H–O=NP=O–reductant resulting in no net observed $[H^+]$ dependence. Since H_2SeO_3 is a reasonably strong acid (pK_a = 2.51 at 25 °C, μ = 1.00 M ($NaClO_4$)[18]) and since Se(IV) can readily expand its coordination shell to accept the neptunium "yl" oxygen as a ligand, all the requirements of the "tautomeric" transition state are satisfied by the Se(IV)–Np(VII) system.

The lack of an inverse acid-dependent path in the Se(IV)–Np(VII) reaction is in marked contrast to the presence of this path in the HCOOH–Np(VII) reaction.[11] However, the HCOOH–Np(VII) system is distinct from all of the Np(VII) oxidations of aquometal ions (including H_2SeO_3) studied to date [9–13] in that HCOOH cannot readily function as a Lewis acid toward the neptunium "yl" oxygen. It is therefore not unreasonable to expect that the HCOOH–Np(VII) reaction proceeds by an entirely different mechanism, and indeed strong evidence has been presented[11] indicating that C–H bond fission is predominant in the rate-determining step of this reaction. The disparate nature of the mechanisms of the H_2SeO_3–Np(VII) and HCOOH–Np(VII) reactions is further reflected in the considerably different entropies of the two activated complexes. The standard entropy of the activated complex, relative to that of Np(VII), can be calculated as $S^* - S°_{Np(VII)} = \Delta S^* + S°_{reductant}$;[13,19] using ΔS^* values of $[H^+]$-independent terms for HCOOH and H_2SeO_3, $S°_{HCOOH}$ = 39.0 eu and $S°_{H_2SeO_3}$ = 49.7 eu,[20] the relative entropies of the activated complexes for H_2SeO_3 and HCOOH oxidation are respectively +30 and –2.5 eu (no account has been taken of the moles of water involved in these activated complexes). These values for neutral reductants are greater than or equal to those observed for Np(VII) oxidation of positively charged reductants,[13] consistent with the proposition that Np(VII) bears a formal positive charge in aqueous acidic media.[13,19] The relatively small enthalpies of activation for both the HCOOH–Np(VII) and H_2SeO_3–Np(VII) reactions (5.8 and 7.4 kcal/mol, respectively) are characteristic of Np(VII) oxidations in acidic media.[9–13]

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Registry No. H_2SeO_3, 7783-00-8; Np(VII), 20826-07-7.

References and Notes

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(2) T. A. Turney, "Oxidation Mechanisms", Butterworths, London, 1965.

(3) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 992.

(4) Standard reduction potentials taken from G. Charlot "Selected Constants: Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution", Butterworths (IUPAC), London, 1971.

(5) See, for example, R. A. Zingaro and W. C. Cooper, "Selenium", Van Nostrand, New York, N.Y., 1974.

(6) J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Lett.*, **5**, 927 (1969).

(7) K. Keshava and B. C. Haldar, *Nature (London)*, **207**, 187 (1965).

(8) F. J. Hughes and D. S. Martin, Jr., *J. Phys. Chem.*, **59**, 410 (1955).

(9) R. C. Thompson and J. C. Sullivan, *J. Am. Chem. Soc.*, **92**, 3028 (1970).

(10) M. A. Thompson, J. C. Sullivan, and E. Deutsch, *J. Am. Chem. Soc.*, **93**, 5667 (1971).

(11) M. Thompson and J. C. Sullivan, *Inorg. Chem.*, **11**, 1707 (1972).

(12) K. O. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **13**, 1712 (1974).

(13) E. Deutsch, J. C. Sullivan, and K. O. Watkins, *Inorg. Chem.*, **14**, 550 (1975).

(14) I. M. Kolthoff and P. J. Elving, Ed., "Treatise on Analytical Chemistry", Part II, Vol. 7, Interscience, New York, N.Y. 1959, p 178.

(15) The programs for the on-line operation of the equipment and the least-squares adjustment of the data were written by Mr. John Hines and Dr. A. J. Zielen of the Chemistry Division, Argonne National Laboratory.

(16) R. H. Moore and R. K. Zeigler, Report No. LA-2367, plus addenda, Los Alamos Scientific Laboratory, Los Alamos, N.Mex., 1959.

(17) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1417 (1965).

(18) L. Barcza and L. G. Sillen, *Acta Chem. Scand.*, **25**, 1250 (1971).

(19) (a) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959); (b) T. W. Newton, "The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions", Publication No. TID-26506, U.S. Energy Research and Development Administration Technical Information Center, Oak Ridge, Tenn., 1975.

(20) M. Kh. Karapet'yants and M. L. Karapet'yants, "Thermodynamic Constants of Inorganic and Organic Compounds", Humphrey Science Publishers, Ann Arbor, Mich., 1970.

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Pulse Radiolysis Studies on the OH-Induced Oxidation of Thiolatometal Complexes[1]

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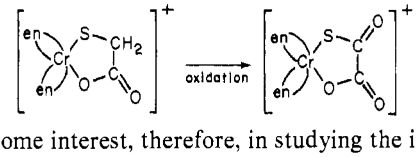
Pulse radiolysis of an N_2O-saturated solution of (mercaptoacetato-*O,S*)bis(ethylenediamine)chromium(III) perchlorate using the streak-camera method shows two intense transient absorption bands centered at 345 and 410 nm. The absorption bands are due to the oxidation of the compound by OH radicals, the absorption at 345 nm being due to attack at the S atom and the one at 410 nm being due to reaction at the α-carbon atom. The results differ from those obtained by the use of strong chemical one-electron oxidants such as neptunium(VI) and cerium(IV). An explanation is offered for this difference.

Introduction

Several enzymes such as hepatic aldehyde dehydrogenase and xanthine oxidase are capable of catalyzing the dehydrogenation of aldehyde to carboxylic acids. A new class of thiolato–transition metal complexes may represent useful models for the active sites of these enzymes.[3] The oxidation of one of these compounds, (mercaptoacetato-*O,S*)bis(ethylenediamine)chromium(III) perchlorate, by one-electron oxidants such as neptunium(VI) and cerium(IV), has been studied by both conventional and stopped-flow methods.[4] These studies showed an unexpected result in that the α-carbon atom was oxidized rather than the sulfur atom, i.e.



There is some interest, therefore, in studying the initial steps