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A Kinetic Study of the Oxidation of Vanadium(IV) by Americium(V)[1]

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For the reaction Am(V) + 2V(IV) = Am(III) + 2V(V) the empirical form of the rate law is $d[V(V)]/dt = k[Am(V)][V(IV)]$. At 25 °C in 1.0 M perchloric acid the value of $k = 4.58 \pm 0.17\ M^{-1}\ s^{-1}$. The values calculated from the variation of k with temperature are $\Delta H^* = 12.7 \pm 0.3$ kcal/mol and $\Delta S^* = -12.7 \pm 1$ cal deg^{-1} mol^{-1}. Mechanistic considerations are presented for this reaction and the present results are compared to those of other oxidation studies of V(IV).

A previous study designed to characterize the dynamic reaction patterns of Am(V) used the hydrated electron[3] to reduce this dioxocation. The product of such a 1 equiv reduction, Am(IV), was not stable in dilute perchlorate media, a feature consistent with the estimated[4] potentials. This investigation provides an opportunity to determine the effect of a much smaller thermodynamic driving force on the dynamic parameters that govern the reduction of Am(V) by a reagent constrained to a one equivalent change. The results of this investigation will also provide an opportunity to determine the effect of an intermediate value of the thermodynamic driving force[5] on the dynamic parameters that describe the oxidations of V(IV).

Experimental Section

Reagents. Stock solutions of vanadyl perchlorate were prepared from vanadyl sulfate by using an ion-exchange procedure similar to one previoulsy described.[6] These solutions were standardized by using the molar extinction coefficient for V(IV) at 7650 Å of 17.19 M^{-1} cm^{-1} [7] and by standard redox titrimetry. The preparation and standardization of Am(V), $LiClO_4$, and $HClO_4$ solutions have been described previously.[8] Am(III) solutions were prepared by dissolving americium(III) hydroxide in perchloric acid and standardized by measurement of the absorbance at 5032 Å where $\epsilon = 450\ M^{-1}\ cm^{-1}$.[9] All solutions were prepared in triply distilled water.

Equipment and Procedures. The computer-interfaced stopped-flow instrumentation and the basic procedures and techniques have been detailed previously.[5] The reaction was followed by measuring the increase in absorbance at 350 nm where the molar extinction coefficients of Am(V) and Am(III) are quite similar (10.6 and 11.4 M^{-1} cm^{-1}, respectively) and that of V(V) (136 M^{-1} cm^{-1}) is larger than those of all other species present. All the kinetic determinations were carried out under pseudo-first-order constraints, $[Am(V)]_0 = (3.1–4.5) \times 10^{-4}$ M and $[V(IV)]_0 = 0.02–0.16$ M. All kinetic data were obtained at an ionic strength of 2.0 M (maintained with lithium perchlorate).

Results and Discussion

Stoichiometry. The estimated values for the relevant Am couples[4] along with that of the V(V)/(IV) couple[10] (+1.00 V) provide assurance that the reaction

$$Am(V) + V(IV) \rightarrow Am(IV) + V(V) \qquad (1)$$

should go to completion. The subsequent reaction

$$Am(IV) + V(IV) \rightarrow Am(III) + V(V) \qquad (2)$$

is also thermodynamically feasible but is apparently too rapid to be of dynamic significance on the time scales involved in this study. The stoichiometry was determined by adding aliquots of a standardized $VO(ClO_4)_2$ solution to an excess of standardized Am(V) in perchloric acid. The concentration of Am(V) was monitored at 718 nm (ϵ 66 M^{-1} cm^{-1}) and a stoichiometric ratio $\delta[VO^{2+}]/\Delta[Am(V)] = 1.98 \pm 0.08$ was determined from four determinations. The product Am(III) was qualitatively identified by the band at 503 nm. The experimentally determined stoichiometry is therefore

$$Am(V) + 2V(IV) = Am(III) + 2V(V) \qquad (3)$$

Table I. Summary of Rate Data[a]

T, °C	$[VO^{2+}]$, M	$[H^+]$, M	$\bar{k}_{obsd}$,[b] s^{-1}	no. of independent determns
25.0[c]	0.0217[d]	0.10	0.101 ± 0.001	10
	0.0303	0.10	0.168 ± 0.001	9
	0.0304[d]	1.82	0.157 ± 0.004	10
	0.0395[d]	0.10	0.185 ± 0.002	9
	0.087[d]	0.12	0.406 ± 0.004	10
	0.087[d]	0.12	0.439 ± 0.008	10
	0.087	0.22	0.415 ± 0.002	9
	0.087	0.22	0.450 ± 0.009	8
	0.130[d]	0.17	0.598 ± 0.005	10
	0.174[d]	0.23	0.795 ± 0.012	10
	0.235[d]	0.35	1.047 ± 0.013	10
35.1[e]	0.0303	0.10	0.307 ± 0.002	
	0.087[d]	0.12	0.897 ± 0.012	9
	0.087	0.22	0.842 ± 0.008	10
	0.087	0.22	0.868 ± 0.008	9
	0.133	0.34	1.297 ± 0.006	8
	0.159	0.41	1.554 ± 0.025	9
	0.159	1.19	1.595 ± 0.008[f]	10
	0.217[d]	0.29	2.202 ± 0.019	7
45.2[g]	0.0266	0.07	0.550 ± 0.008	8
	0.0798	0.20	1.601 ± 0.022	8
	0.133	0.33	2.495 ± 0.034	8
	0.159	0.40	2.905 ± 0.056	8
	0.217[d]	0.28	4.271 ± 0.14	8

[a] $\mu = 2.0$ ($LiClO_4$), reaction monitored at 350 nm, stock $[VO^{2+}] = 0.532$ M. [b] $\bar{k}_{obsd}$ is the average value of the first-order rate parameter for the number of independent determinations listed. Uncertainties are standard deviations from the mean. [c] $[Am(V)]_0 = (3.10–3.60) \times 10^{-4}$ M. [d] Stock $[VO^{2+}] = 0.868$ M. [e] $[Am(V)]_0 = (3.25–4.48) \times 10^{-4}$ M. [f] $[Am(III)]_0 = 4.53 \times 10^{-4}$ M. [g] $[Am(V)]_0 = 4.02 \times 10^{-4}$ M.

Kinetics. The integrated form of the first-order rate law provided an adequate description of the data for all experiments. The values determined for the rate parameters were invariant (within the noted error limits) with change in source solutions of VO^{2+} or Am(V).[11] The dependence of $\bar{k}_{obsd}$ on the variation in concentration of V(IV), initial hydrogen ion concentration, and temperature is summarized in Table I. From these data we conclude that there is no identifiable kinetic path that is dependent on the hydrogen ion concentration.

The data that describe the variation of $\bar{k}_{obsd}$ with change in V(IV) concentration may be adjusted in terms of the linear expression

$$\bar{k}_{obsd} = a + b[V(IV)] \qquad (4)$$

The least-squares values (and standard deviations calculated on the basis of external consistency) that were calculated from the data at 25, 35, and 45 °C for a are 0.015 ± 0.008, 0.007 ± 0.008, and 0.061 ± 0.026 s^{-1} and for b are 4.58 ± 0.17, 9.85 ± 0.11 and 18.6 ± 0.5 M^{-1} s^{-1}, respectively. On the basis of

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the above, the empirical form of the rate law is

$$d[V(V)]/dt = k[Am(V)][V(IV)] \qquad (5)$$

From the variation of the second-order rate parameter with change in temperature the values calculated by a nonlinear least-squares adjustment of the data with the Eyring formalism resulted in values of $\Delta H^* = 12.7 \pm 0.3$ kcal/mol and $\Delta S^* = -12.7 \pm 1.0$ cal deg^{-1} mol^{-1}. The empirical formula of the activated complex for the title reaction is one molecule of Am(V) and one of V(IV). The absence of any discernible hydrogen ion dependence on the rate of the reaction may well be a fortuitous cancellation of the expected positive hydrogen ion dependence for the transformation of the dioxoamericium(V) and the inverse dependence to be expected in the formation of V(V) from V(IV). Alternatively, the absence of a hydrogen ion dependent term in the rate law could be interpreted in a reaction scheme where an oxygen of the linear $O\text{–}Am\text{–}O^+$ replaces the water molecule trans to the "yl" oxygen of the V(IV)[12] with subsequent atom transfer.

Consistency between the demonstrated stoichiometry and the empirical form of the rate law requires that the rate of reaction 2 must be greater than that of the reaction

$$Am(IV) + Am(IV) \rightleftarrows Am(V) + Am(III) \qquad (6)$$

Since the second-order rate parameter for the latter reaction[3] is 5×10^6 M^{-1} s^{-1}, it is apparent that the former reaction must proceed at near the diffusion-controlled limit.

Previous studies of the oxidation of V(IV) by cations in aqueous perchlorate media in which the empirical form of the rate law has a major or sole term independent of hydrogen ion have been reported for Mn(III)[13] and Np(VII)[5] as oxidants. The respective reduction potentials (volts) for the Np(VII)/(VI), Mn(III)/(II), and Am(V)/(IV) couples are 2.0, 1.5, and 1.3. There is a parallel between the decrease in these potentials and the values of ΔG^* for the oxidation reactions (kcal/mol) of 13.3, 14.5, and 16.5, respectively. The respective enthalpies of activation also show parallel behavior with values (kcal/mol) of 6.7 ± 0.9, 11.1 ± 0.7, and 12.7 ± 0.3. The values of the entropies of activation, however, do not provide any obvious correlations with the other rate parameters or the potential values.

Registry No. AmO_2^+, 22878-02-0; VO^{2+}, 20644-97-7.

References and Notes

(1) Investigation conducted under the auspices of the Office of Basic Energy Sciences of the Department of Energy.
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(11) It should be emphasized that stock solutions of Am(V) were prepared fresh daily from the solid carbonate salt. The results we obtained in preliminary experiments with a stock solution of $VO(ClO_4)_2$ in 1 M $HClO_4$ (that had been stored in the dark in a Pyrex bottle for over 1 year) were erratic and led to the preparation of the two stock solutions of $VO(ClO_4)_2$ that were used in this investigation.
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Kinetics and Mechanism of Aquation of the *trans*-Bis(nitrilotriacetato-*N,O,O'*)chromate(III) Ion

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The *trans*-bis(nitrilotriacetato-*N,O,O'*)chromate(III) ion, *trans*-$Cr(NTA)_2^{3-}$, aquates in phthalate buffers to equilibrium mixtures of diaqua(nitrilotriacetato-*N,O,O',O''*)chromium(III), $Cr(NTA)(H_2O)_2$, and the (nitrilotriacetato-*N,O,O',O''*)(phthalato-*O,O'*)chromate(III) ion, $Cr(NTA)(phthalate)^{2-}$, in the pH range 1.50–6.00. The equilibrium constant for the formation of the $Cr(NTA)(phthalate)^{2-}$ ion from $Cr(NTA)(H_2O)_2$ and the phthalate ion was determined as $K_f = (1.6 \pm 0.2) \times 10^3$ M^{-1} at 25.0 °C and an ionic strength of 1.00 M. The kinetics of the single observed reaction step of this process was studied under pseudo-first-order conditions from pH 0.50 to pH 5.00 in phthalate buffers at four temperatures from 15.0 to 30.0 °C at an ionic strength of 1.00 M. The pseudo-first-order rate constant k_{obsd} was determined to be of the form given by $k_{obsd} = \{k_1 + k_4K_1[H^+] + k_5K_1K_2[H^+]^2 + k_HK_1K_2[H^+]^3\}/\{1 + K_1[H^+] + K_1K_2[H^+]^2\}$. The individual kinetics parameters of this expression were determined by a computer curve-fitting process at each temperature. Rate constants at 25.0 °C (s^{-1}), activation enthalpies (kcal mol^{-1}), and activation entropies (cal mol^{-1} K^{-1}) are as follows: k_1, 1.28×10^{-4}, 14.3 ± 0.6, −28.4 ± 2.2; k_4, 6.26×10^{-3}, 14.7 ± 0.1, −19.4 ± 0.3; k_5, 3.06×10^{-3}, 14.8 ± 0.7, −20.3 ± 2.3; k_H, 1.66×10^{-2} M^{-1} s^{-1}, 16.5 ± 0.8, −11.4 ± 2.6. Enthalpy changes associated with K_1 and K_2 were 1.6 ± 0.2 and −1.6 ± 0.4 kcal mol^{-1}. Entropy changes associated with K_1 and K_2 were 20.0 ± 0.7 and 3.3 ± 1.2 cal mol^{-1} K^{-1}. K_1 and K_2 have been interpreted as equilibrium constants for the protonation of the free carboxylate groups of *trans*-$Cr(NTA)_2^{3-}$, while k_1, k_4 and k_5 represent rate constants for the dissociation reactions of *trans*-$Cr(NTA)_2^{3-}$ and its two protonated forms, *trans*-$Cr(NTA)(HNTA)^{2-}$ and *trans*-$Cr(HNTA)_2^-$. The rate constant k_H was assigned to a hydrogen-ion-catalyzed steady-state dissociation process of *trans*-$Cr(HNTA)_2^-$. The observed rate law and kinetic parameters have been interpreted in terms of a mechanism where dissociation of a complete nitrilotriacetato-*N,O,O'* ligand is limited by dissociation at its nitrogen chromophore. An activation mechanism which includes a critical proton-transfer step has been proposed to explain the influence of protonated carboxylate groups on the rate of dissociation at the nitrogen chromophore.

Introduction

During the first observed step in the aquation of *cis*-$Cr(IDA)_2^-$ to $Cr(IDA)(H_2O)_3^+$ and *trans*-$Cr(MIDA)_2^-$ to $Cr(MIDA)(H_2O)_3^+$, the nitrogen chromophore of an IDA or MIDA ligand is replaced by an aqua ligand via hydrogen-ion-dependent pathways.[1,2] Simple amines and substituted amines generally undergo aquation through hydrogen-ion-independent pathways. Therefore it was proposed that dissociation and protonation of a carboxylate group of the ligand undergoing replacement preceded dissociation of the nitrogen