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Oxidation of Uranium(IV) by Vanadium(V) in Perchlorate Media

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The kinetics and mechanism of the oxidation of U(IV) by V(V) have been studied in perchlorate media. In the acid concentration range 0.1–2.0 M an [acid]-independent and an [acid]$^{-1}$-dependent reaction path dominate the reaction, and only minor differences were observed when $NaClO_4$ was replaced by $LiClO_4$ to maintain the ionic strength constant. However, at higher ionic strengths, significant differences in the observed rate constants were found when $LiClO_4$ was replaced by $NaClO_4$. The activation parameters of the rate constants were determined, and plausible reaction mechanisms are discussed.

Introduction

Vanadium(V) is a relatively powerful oxidizing agent with a formal oxidation potential of 1.00 V (1 M $HClO_4$)[1] for the V(V)–V(IV) couple, but the mechanisms of only a few of its reactions have been studied in detail. Newton and co-workers observed unusually complex acid dependences for the rate constants of the reaction of V(V) with Fe(II)[2] and V(III),[3] but the reactions with V(II)[4] and Sn(II)[5] were found to be relatively simple. The V(V)–Ti(III) reaction was reported[6] to result in the formation of a binuclear intermediate under certain experimental conditions, but a subsequent study of this reaction failed to reproduce this observation.[7]

Preliminary experiments[8] showed that the oxidation of U(IV) by V(V), although unexpectedly rapid, was amenable to study by stopped-flow techniques. These experiments also suggested that at constant high ionic strengths the rate of reaction increased as $NaClO_4$ was progressively replaced by $HClO_4$. Since nearly all reactions involving the oxidation of U(VI) ions exhibit an inverse acid concentration dependency,[8a] the above observation was rather unusual, and the reaction was studied in detail.

Experimental Section

Reagents. $UO_2(ClO_4)_2$, $NaClO_4$, $LiClO_4$, and $HClO_4$ were prepared and analyzed as described previously.[9] U(IV) solutions were prepared by electrochemical reduction of suitably diluted samples of the U(VI) stock solutions[10] and analyzed by titration with standard Ce(IV), using ferroin indicator. A V(IV) stock solution was prepared from a solution of $VOSO_4$ (Merck), which was treated with a slight excess of $Ba(ClO_4)_2$, filtered, and on subsequent analysis shown to contain 3.15×10^{-1} M V(IV), 1.80×10^{-3} M Ba(II), and 3.70×10^{-1} M H^+, while no detectable quantities of SO_4^{2-} ions were found. Samples of this solution were diluted as required and oxidized to V(V) at a platinum anode. The V(V) solutions were analyzed by titration with standardized Fe(II) solution in 6 N H_2SO_4 using ferroin indicator.

Rate Measurements. The reaction rates were measured using the stopped-flow apparatus and data acquisition system described elsewhere.[9] The reaction was followed by monitoring the V(V) concentrations at 270–330 nm and, as discussed below, analyzed according to the second-order rate law

$$-d[V(V)]/dt = 2k_1[V(V)][U(IV)] \tag{1}$$

All rate constants reported below represent the average and standard deviation of at least six independent determinations and all least-squares analyses (acid and temperature dependence) were carried out using a program described by Lietske,[11] the values being weighted according to the reciprocal of the standard deviation. Absorption spectra were measured using a Cary 118C spectrophotometer.

Results

(a) Low Ionic Strength. In the presence of excess V(V), the reaction of U(IV) with V(V) may be formally represented by the reaction sequence

$$U(IV) + V(V) \xrightarrow{k_2} U(V) + V(IV) \tag{2}$$

$$U(V) + V(V) \xrightarrow{k_3} U(VI) + V(IV) \tag{3}$$

or by the overall reaction

$$U(IV) + 2V(V) \rightarrow U(VI) + 2V(IV) \tag{4}$$

If $k_3 \gg k_2$, application of the steady-state approximation to the U(V) concentration readily leads to rate eq 1 with $k_2 = k_1$. Analysis of the present results in terms of eq 1 gave excellent straight lines to 85% reaction and values of k_1 which were constant over a considerable range of initial reagent concentrations (Table I).

Table I. Effect of Reactant Concentration on the Value of k_1[a]

10^4-[U(IV)], M	10^4-[V(V)], M	10^4-[V(IV)],[b] M	No. of detns	$10^{-4}k_1$,[c] M^{-1} s^{-1}
1.14	1.56		7	2.22 ± 0.16
1.14	3.11		7	2.11 ± 0.08
1.14	4.68		7	2.18 ± 0.06
1.14	9.36		7	1.95 ± 0.20
1.14	15.6		5	1.94 ± 0.10
0.570	9.36		5	1.94 ± 0.15
2.28	9.36		6	1.98 ± 0.10
4.56	9.36		8	2.00 ± 0.05
5.70	9.36		8	2.14 ± 0.07
1.14	4.68	12.6	8	2.18 ± 0.14
1.14	4.68	25.2	5	2.03 ± 0.06
1.14	4.68	63.0	6	2.12 ± 0.08
			79	Av 2.05 ± 0.15

[a] Reaction followed at 280 nm, $[H^+] = 2.00$ M, $I = 2.00$. [b] V(IV) added to V(V) solution. [c] Average and standard deviation.

In addition, the ratio of the observed amount of V(V) consumed to the theoretical quantity required by eq 4 was determined as 2.08 ± 0.09 for the 79 determinations summarized in Table I, thus confirming the stoichiometry of the reaction.

The reaction of U(V) with V(IV)

$$U(V) + V(IV) \xrightarrow{k_5} U(VI) + V(III) \tag{5}$$

which could then be followed by the reaction between V(III) and V(V) has a rate constant which has been variously estimated as 1.4×10^3 M^{-1} s^{-1} [12] and 5×10^4 M^{-1} s^{-1} [13] at 25 °C, $I = 2.0$, and $[H^+] = 1.0$ M and could therefore seriously interfere with reactions 2 and 3 if reaction 3 were relatively slow. The importance of reaction 5 in the present system can be estimated by examining the effect of the addition of excess V(IV) to the reagents on the rate constant as calculated by eq 1. As shown in Table I, the addition of a substantial excess of V(IV) (added to the V(V) reactant solution) had no measurable effect on the observed rate constant, hence justifying the conclusion that $k_3 \gg k_5$.

The rate constant of reaction 2 was also found to be independent of the wavelength of the analyzing light. With $[U(IV)]_0 = 0.570 \times 10^{-4}$ M, $[V(V)]_0 = 4.63 \times 10^{-4}$ M, and $[H^+] = 2.0$ M and at 16 °C, $10^{-4}k_1$ M^{-1} s^{-1} was determined as 2.08 ± 0.05 at 270 nm, 2.03 ± 0.08 at 310 nm, and 2.13 ± 0.05 at 330 nm. At all of the above wavelengths, the

Table II. Effect of Acid Concentration and Temperature on the Value of k_1 in $NaClO_4$ and $LiClO_4$ Media[a]

		$10^{-4}k_1$, M^{-1} s^{-1}	
Temp, °C	$[H^+]$, M	$LiClO_4$[b]	$NaClO_4$[b]
11.0	0.10	5.90 ± 0.20	6.17 ± 0.26
	0.20	3.91 ± 0.19	4.06 ± 0.14
	0.40	2.93 ± 0.14	2.61 ± 0.11
	0.60	2.36 ± 0.16	2.08 ± 0.17
	0.80	2.09 ± 0.06	1.77 ± 0.10
	1.00	1.91 ± 0.09	1.67 ± 0.07
	1.20	1.76 ± 0.09	1.51 ± 0.07
	1.40	1.65 ± 0.06	1.48 ± 0.09
	1.60	1.60 ± 0.07	1.45 ± 0.08
	1.80	1.53 ± 0.05	1.41 ± 0.07
16.10	0.10	9.80 ± 0.42	10.4 ± 0.5
	0.20	6.18 ± 0.58	6.41 ± 0.16
	0.40	4.68 ± 0.18	4.00 ± 0.09
	0.60	3.73 ± 0.27	3.03 ± 0.06
	0.80	3.12 ± 0.16	2.60 ± 0.11
	1.00	2.90 ± 0.14	2.32 ± 0.05
	1.20	2.68 ± 0.12	2.14 ± 0.02
	1.40	2.50 ± 0.12	2.09 ± 0.06
	1.60	2.34 ± 0.14	2.01 ± 0.05
	1.80	2.36 ± 0.11	2.03 ± 0.05
	2.00	2.05 ± 0.15	2.06 ± 0.10
20.0	0.10	14.3 ± 0.6	17.6 ± 0.1
	0.20	10.1 ± 0.6	10.0 ± 0.4
	0.40	6.44 ± 0.15	5.89 ± 0.12
	0.60	4.96 ± 0.14	4.46 ± 0.15
	0.80	4.17 ± 0.12	3.79 ± 0.15
	1.00	3.62 ± 0.11	3.26 ± 0.10
	1.20	3.42 ± 0.22	2.98 ± 0.11
	1.40	3.18 ± 0.10	2.77 ± 0.04
	1.60	3.04 ± 0.14	2.71 ± 0.04
	1.80		2.65 ± 0.13
24.0	0.20	13.0 ± 0.3	15.2 ± 0.6
	0.40	8.70 ± 0.26	9.13 ± 0.40
	0.60	6.57 ± 0.20	6.88 ± 0.19
	0.80	5.41 ± 0.15	5.62 ± 0.06
	1.00	4.89 ± 0.21	4.84 ± 0.07
	1.20	4.55 ± 0.09	4.50 ± 0.08
	1.40	4.20 ± 0.16	4.28 ± 0.10
	1.60	3.96 ± 0.05	4.07 ± 0.09
	1.80	3.74 ± 0.10	3.93 ± 0.11

[a] Conditions: $[V(V)]_0 = 4.78 \times 10^{-4}$ M, $[U(IV)]_0 = 1.13 \times 10^{-4}$ M, $I = 2.00$. [b] Average and standard deviation of six to eight determinations.

observed final absorbances agreed well with those calculated from the stoichiometry of the reaction (eq 4) and the measured extinction coefficients of the reactants and products. Unfortunately, because of the combination of fast reactions and low extinction coefficients, the reactions could not be followed at 640 nm, the absorption maximum of U(IV), or at 730 nm, the absorption maximum of V(IV).

The acid concentration dependence of k_1 was studied in the range 0.10–2.00 M H^+ at 11.0, 16.0, 20.0, and 24.0 °C, $LiClO_4$ being used to maintain the ionic strength (I) constant (Table II). Plots of log k_1 vs. log $[H^+]$ were straight lines with slopes in the range 0.4–0.5 suggesting the participation of an acid-independent and an inversely acid-dependent path in the reaction. For the analysis of these data, eq 1 was reformulated in terms of the principal metal ion species to give

$$-d[V(V)]/dt = 2k_6[U^{4+}][VO_2^+] \qquad (6)$$

where $k_6 = k_1\{1 + K^H/[H^+]\}$ and K^H is the hydrolysis constant of the U^{4+} ion.[14] The most important net activation processes can then be written as

$$U^{4+} + VO_2^+ \xrightarrow{k_7} [*]^{5+} \qquad (7)$$

$$U^{4+} + VO_2^+ + H_2O \xrightarrow{k_8} [*]^{4+} + H^+ \qquad (8)$$

This reaction sequence readily yields eq 9, which, as shown

$$k_6 = k_7 + k_8[H^+]^{-1} \qquad (9)$$

in Table III, reproduced the experimental rate constants very well. For these calculations, the values of K^H at the various temperatures were obtained by combining the value of $K^H = 0.023$ M[14] (25 °C, $I = 2.0$, $NaClO_4$) with a value of 11.7 kcal mol^{-1} for ΔH ($I = 0$) for the hydrolysis reaction.[15] The temperature coefficients ($\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$) of the rate constants k_7 and k_8 were obtained by nonlinear least-squares analysis of the data in terms of the Eyring equation[16] giving the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ summarized in Table III.

Similar experiments in which $NaClO_4$ was used to maintain the ionic strength yielded results essentially identical with those obtained in $LiClO_4$ media (Tables II and III). Although a slight upward curvature of plots of log k_1 vs. log $[H^+]$ was noted at the higher acid concentrations in the $NaClO_4$ solutions (cf. Figure 1b) which was absent in $LiClO_4$, this deviation was too small to affect the applicability of eq 9 to these data. As shown in Table III, the rate constants and rate parameters determined for the $NaClO_4$ solutions by this analysis are, within experimental error, similar to those found in $LiClO_4$ media. Only a very marginal improvement in the fit was obtained when the $NaClO_4$ data were analyzed in terms of

Table III. Summary of the Values of k_7 and k_8 Obtained at Various Temperatures in $LiClO_4$ and $NaClO_4$ Media

			$10^{-4}k_7$, M^{-1} s^{-1}		$10^{-3}k_8$, M^{-1} s^{-1}		
Temp, °C	K^H	No. of detns	Obsd[a]	Calcd[b]	Obsd[a]	Calcd[b]	Rms dev,[c] %
			$LiClO_4$				
11.0	0.009	55	1.32 ± 0.05	1.35	5.40 ± 0.28	5.44	5.30
16.0	0.013	62	1.85 ± 0.09	1.72	9.89 ± 0.55	9.91	6.48
20.0	0.017	58	2.15 ± 0.15	2.09	16.5 ± 1.0	15.7	5.33
24.0	0.022	52	2.49 ± 0.07	2.51	24.7 ± 0.7	24.8	2.48
$\Delta H^{\ddagger}$, kcal mol^{-1}			7.44 ± 0.66		19.0 ± 0.1		
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}			−13.3 ± 2.3		25.6 ± 1.3		
Rms, %			3.80		2.20		
			$NaClO_4$				
11.0	0.009	54	1.11 ± 0.04	1.04	5.50 ± 0.20	5.40	3.55
16.0	0.013	68	1.36 ± 0.05	1.38	9.94 ± 0.40	10.20	4.62
20.0	0.017	56	1.62 ± 0.04	1.72	16.9 ± 0.3	16.8	2.31
24.0	0.022	52	2.31 ± 0.07	2.12	27.2 ± 0.4	27.2	5.30
ΔH, kcal mol^{-1}			8.53 ± 1.7		20.3 ± 0.4		
ΔS, cal deg^{-1} mol^{-1}			−10.0 ± 5.9		30.0 ± 1.1		
Rms, %			5.87		1.76		

[a] Values obtained by least-squares analysis of data by eq 9. [b] Values calculated by least-squares analysis of data by the Eyring equation.[16] [c] Root-mean-square percent deviation, defined as $100[(1/n)\Sigma(k_{obsd} - k_{calcd})^2/k_{obsd}^2]^{1/2}$.

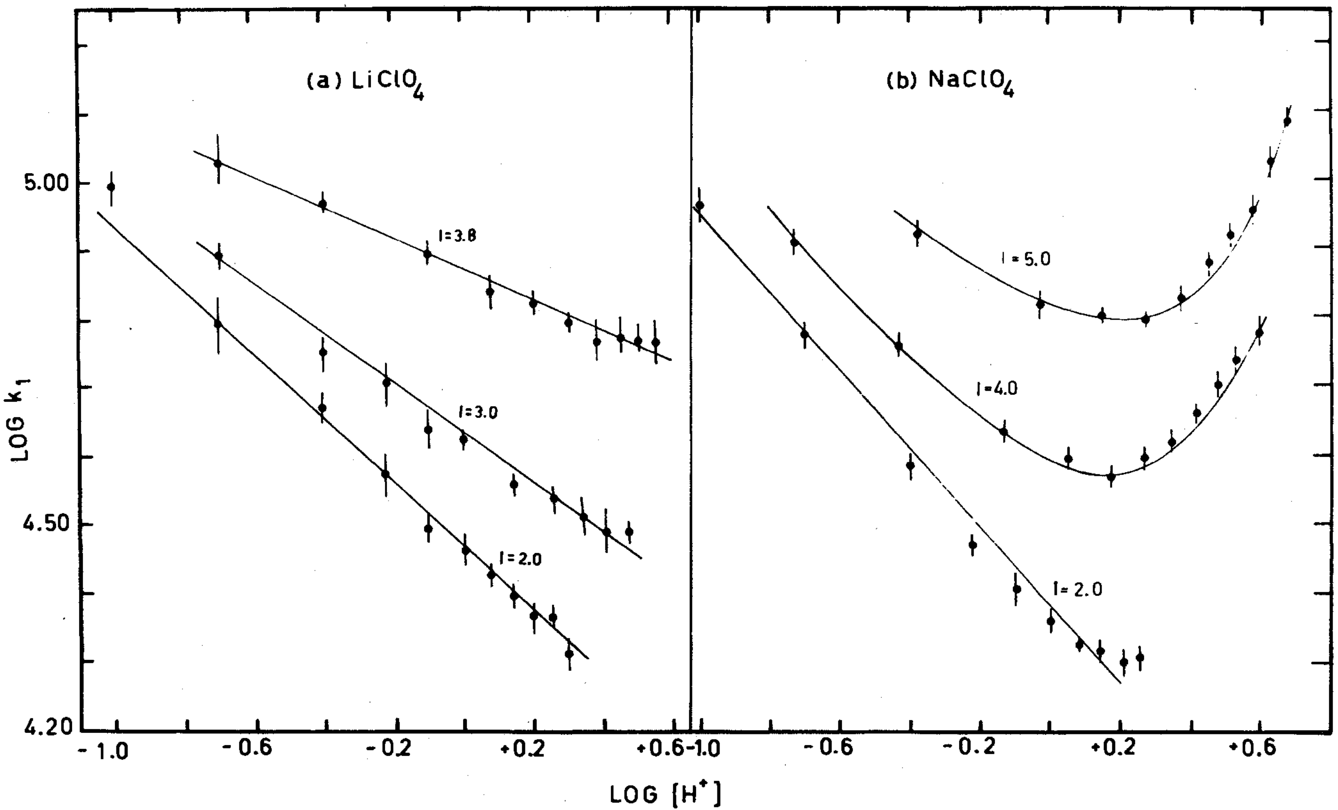


Figure 1. Plots of log k_1 vs. log [H$^+$] for LiClO$_4$ (a) and NaClO$_4$ (b) media at various ionic strengths at 16.0 °C, $[U(IV)]_0 = 1.13 \times 10^{-4}$ M, and $[V(V)]_0 = 4.78 \times 10^{-4}$ M, for all runs.

Table IV. Effect of Acid Concentration and Temperature on the Rate Constant of the U(IV)-V(V) Reaction in NaClO$_4$ Solution[a]

	$10^{-4}k_1$,[b] M^{-1} s^{-1}				
[Acid], M	11.0 °C	16.0 °C	20.0 °C	24.0 °C	28.0 °C
0.20	5.88 ± 0.15	8.13 ± 0.24	10.9 ± 0.46	15.0 ± 0.3	21.3 ± 0.8
0.40	4.01 ± 0.23	5.77 ± 0.15	7.12 ± 0.28	10.7 ± 0.3	14.5 ± 0.3
0.80	3.12 ± 0.12	4.33 ± 0.16	5.80 ± 0.21	8.04 ± 0.19	10.3 ± 0.4
1.20	2.86 ± 0.14	3.91 ± 0.13	4.98 ± 0.12	6.74 ± 0.29	8.85 ± 0.31
1.60	2.79 ± 0.18	3.72 ± 0.14	4.87 ± 0.25	6.65 ± 0.16	8.19 ± 0.28
2.00	2.87 ± 0.16	3.96 ± 0.16	4.93 ± 0.07	6.18 ± 0.16	8.10 ± 0.24
2.40	3.00 ± 0.19	4.17 ± 0.19	5.23 ± 0.16	6.41 ± 0.29	8.40 ± 0.09
2.80	3.29 ± 0.19	4.62 ± 0.29	5.62 ± 0.22	6.65 ± 0.14	8.65 ± 0.29
3.20	3.63 ± 0.12	5.02 ± 0.31	5.85 ± 0.13	7.26 ± 0.31	9.20 ± 0.28
3.60	4.06 ± 0.17	5.53 ± 0.20	6.56 ± 0.18	8.54 ± 0.12	9.71 ± 0.42
4.00	4.81 ± 0.17	6.04 ± 0.26	7.26 ± 0.38	9.00 ± 0.18	10.7 ± 0.24

[a] $[U(IV)]_0 = 1.13 \times 10^{-4}$ M; $[V(V)]_0 = 4.71 \times 10^{-4}$ M; reaction measured at 280 nm; ionic strength maintained at 4.00 using NaClO$_4$.
[b] Average and standard deviation of six to eight determinations.

eq 10 (vide infra) which includes an additional variable parameter in the form of a Harned correction.[17]

(b) High Ionic Strength. At higher ionic strengths ($I > 2$) significant differences in the acid dependency of the rate constant (k_1) were found when NaClO$_4$ replaced LiClO$_4$ as the inert electrolyte (Figure 1). These data suggest either the necessity for the inclusion of a large Harned parameter when eq 9 is applied to the data obtained for the NaClO$_4$ media or, alternatively, a significant contribution from a reaction path having a positive acid dependency. Accordingly, the results obtained for the effect of temperature and acid concentration on k_1 in NaClO$_4$ media at $I = 4$ (Table IV) were analyzed in terms of eq 10 and 11. For these analyses, the

$$k_6 = [k^0_{10} + k^{-1}_{10}] \exp \alpha[H^+] \qquad (10)$$

$$k_6 = k^0_{11} + k^{-1}_{11}[H^+]^{-1} + k^1_{11}[H^+] \qquad (11)$$

values of K^H at $I = 4.0$ and the various temperatures were obtained by extrapolation of the appropriate data reported by Kraus and Nelson.[15] As shown in Table V, both eq 10 and 11 fit the experimental data reasonably well although eq 10 does so slightly better than eq 11. It will be noted that the analysis of these data in terms of eq 10 required Harned parameters which are unusually large but which remain essentially independent of temperature.

The possible formation of certain V(V) complexes, e.g., dimers, under the various experimental conditions used in the present study was examined by carefully measuring the extinction coefficient (E) of the V(V) ion at 280 nm. At 25 °C and [H$^+$] = 2.0 M, the value of E was determined to be 751 ± 9 M^{-1} and, in agreement with previous observations,[5,18] to be independent of V(V) concentration in the range 9.63×10^{-5} to 6.44×10^{-3} M. Similarly, the extinction coefficient was found to be independent of acid concentration in the range 0.20–4.00 M ($I = 4.0$) in both NaClO$_4$ ($E = 748 \pm 11$ M^{-1}) and LiClO$_4$ ($E = 746 \pm 8$ M^{-1}) media.

Discussion

As shown above, the results obtained at low ionic strength in either LiClO$_4$ or NaClO$_4$ media are readily interpreted in

Table V. Summary of Rate Constants and Activation Parameters Obtained from Analysis of the Data in Table IV

(a) Analysis According to Eq 10

Temp, °C	K^H	$10^{-4}k^0_{10}$, $M^{-1}\ s^{-1}$	$10^{-3}k^{-1}_{10}$, $M^{-1}\ s^{-1}$	α	% Rms
11.0	0.0073	1.22 ± 0.13	9.21 ± 0.41	0.28 ± 0.03	3.7
16.0	0.0105	1.72 ± 0.16	13.4 ± 0.06	0.27 ± 0.02	2.9
20.0	0.0139	2.27 ± 0.15	17.6 ± 0.25	0.23 ± 0.02	3.1
24.0	0.0182	2.72 ± 0.53	27.3 ± 2.0	0.24 ± 0.04	5.7
28.0	0.0240	3.13 ± 0.29	42.1 ± 1.38	0.23 ± 0.02	2.8
$\Delta H^{\ddagger}$, kcal mol^{-1}		8.81 ± 0.82	13.6 ± 1.5		
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}		−8.6 ± 2.3	7.4 ± 5.1		
% Rms		4.3	8.10		

(b) Analysis According to Eq 11

Temp, °C	K^H	$10^{-4}k^0_{11}$ $M^{-1}\ s^{-1}$	$10^{-3}k^{-1}_{11}$ $M^{-1}\ s^{-1}$	$10^{-3}k^1_{11}$, $M^{-1}\ s^{-1}$	% Rms
11.0	0.0073	1.14 ± 0.26	9.77 ± 0.78	7.26 ± 0.87	6.0
16.0	0.0105	1.62 ± 0.29	14.3 ± 1.1	9.16 ± 1.14	4.7
20.0	0.0139	2.19 ± 0.26	18.4 ± 0.5	9.85 ± 1.06	4.6
24.0	0.0182	2.79 ± 0.77	28.1 ± 2.9	12.7 ± 2.4	7.0
28.0	0.0240	3.11 ± 0.53	44.6 ± 2.6	15.1 ± 1.76	3.9
$\Delta H^{\ddagger}$, kcal mol^{-1}		9.18 ± 1.01	15.1 ± 2.1	6.61 ± 0.71	
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}		−7.46 ± 3.5	12.6 ± 7.0	−17.6 ± 2.4	
% Rms		5.9	9.7	3.9	

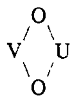
Table VI. Summary of the Characteristics of Reactions Involving the Oxidation of Uranium(IV) Ions

Oxidant[a]	Formal oxidn potential of oxidant,[b] V	k_{obsd} (1 M H^+, $I = 2.0$, 25 °C)	Acid dependence term, n[c]	Ref
Np^{4+}	0.16	5×10^{-5}	−2.5	19
Tl^{3+}	0.3[d]	3.9×10^{-1}	−1.39	20
NpO_2^+	0.74	8×10^{-6}	−2.0	21
Fe^{3+}	0.7	1.3×10	−1.8	22
PuO_2^{2+} [f]	0.91	3.1	−1.2	23
VO_2^+	1.02	4.9×10^4	−0.4	This work
NpO_2^{2+}	1.14	2.2×10^1	−0.97	24
$HCrO_4^-$	1.2[e]	6.3×10^4	−1.0	25
Ce^{4+}	1.7	8.7×10^3	−1.2	26

[a] The predominant form of the ion in solution is shown to emphasize structural similarities where applicable. They are not necessarily the forms of the ion which take part in the reaction. [b] Values obtained from ref 1. [c] The term n is defined by the expression rate = $k_{obsd}[U(IV)][oxidant][H]^n$. [d] Value refers to the Tl(III)/Tl(II) couple. [e] Value refers to the Cr(VI)/Cr(III) couple. [f] This reaction may involve a binuclear intermediate.

terms of an acid-independent and inversely acid-dependent reaction path, the latter presumably reflecting the participation of the species UOH^{3+} in the reaction, and its inclusion in the reaction scheme readily yields eq 9. However, comparison of the characteristics of the present reaction with those involving the oxidation of U(IV) by other oxidants (Table VI) shows that the V(V) reaction both is very much faster and exhibits a less pronounced acid dependence than any of the other reactions examined to date.[8a] The unusual features of the V(V) reaction are particularly emphasized when it is compared with those of Pu(VI) and Np(VI), both of which are oxygenated cations formally similar to V(V) and have only slightly different oxidation potentials.

One possible explanation which may be considered for this aspect of the V(V)–U(IV) reaction is that it may involve the transfer of an oxygen atom from the V(V) to the U(IV). The occurrence of such a transfer has been established for the Cr(VI)–U(VI) reaction,[24,26] and it would be surprising if the U(V) metal–oxygen bonds were as stable as those of the actinide(VI) ions. Furthermore, the O–V–O$^+$ ion is believed[27] to be nonlinear in the solid state in contrast to the actinide ions whose linearity is well established.[28] It might be noted that if the nonlinear structure of the VO_2^+ ion is maintained in solution, it would be conducive to the formation of an activated complex similar to I for the acid-independent path



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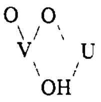
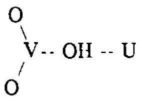


IIa



IIb

and either IIa or IIb for the inversely acid-dependent path.

The results obtained in the $NaClO_4$ solutions at high ionic strength are difficult to interpret. In most electron-transfer reactions,[29] the differences in the rate constants when $LiClO_4$ is replaced by $NaClO_4$ are quite small and can be interpreted with confidence in terms of relatively minor changes in the appropriate activity coefficients. However, much larger effects have been noted in the determination of the $E°$ values of the Np(VI)/Np(V) couples[30] and, perhaps more significantly, in the oxidation of U(IV) by Np(VI)[23] where a 24% increase in rate constant was observed when $LiClO_4$ was replaced by $NaClO_4$ as the inert electrolyte. It has also been reported[31] that the rate constant of the U(IV)–Np(V) reaction, although decreasing with increasing acid concentration at low (<2.0 M) acid concentrations, increases with increasing acid concentration if the latter exceeds 2.0 M. These studies were however not extended to $LiClO_4$ media and the observed effect was attributed to the presence of a side reaction between U(IV) and Np(IV).

In summary, the V(V)–U(IV) reaction displays two unusual features, showing first a much higher rate constant and less pronounced acid dependence than any other U(IV) reaction and being second an example of the kinetic nonequivalence of high concentrations of Li^+ and Na^+ ions as the supporting electrolyte.

Registry No. U^{4+}, 16089-60-4; VO_2^+, 18252-79-4.

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Synthesis and Characterization of $(NF_4)_2SnF_6$ and NF_4SnF_5

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The novel NF_4^+ salt $(NF_4)_2SnF_6$ was prepared by metathesis between Cs_2SnF_6 and NF_4SbF_6 in HF solution. It is a white solid, stable to above 200 °C. Based on its x-ray powder data, it crystallizes in the tetragonal system and is isotypic with $(NF_4)_2GeF_6$. Its composition was established by elemental analysis, and the presence of tetrahedral NF_4^+ and octahedral SnF_6^{2-} ions in the solid state and in BrF_5 solution was demonstrated by vibrational and ^{19}F NMR spectroscopy, respectively. The salt NF_4SnF_5 was obtained in quantitative yield from the displacement reaction between equimolar amounts of NF_4BF_4 and SnF_4 in HF solution. When a large excess of NF_4BF_4 was used, the main product was again NF_4SnF_5 and only a small amount of $(NF_4)_2SnF_6$ was formed. The NF_4SnF_5 salt was characterized by elemental analysis, vibrational and ^{19}F NMR spectroscopy, and x-ray powder data. The vibrational spectra of the solid and the ^{19}F NMR spectra of BrF_5 solutions show that SnF_5^- possesses a polymeric structure of cis-fluorine-bridged SnF_6 octahedra, analogous to that observed for GeF_5^- in NF_4GeF_5. The potential of $(NF_4)_2SnF_6$ for a "self-clinkering" NF_3–F_2 gas generator is briefly discussed.

Introduction

Perfluoroammonium salts are of significant interest owing to their potential for solid propellant NF_3–F_2 gas generators for chemical HF–DF lasers.[1] Salts are known of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6^- \cdot nSbF_5$, BiF_6^-, $BiF_6^- \cdot nBiF_5$, BF_4^-, GeF_5^-, and GeF_6^{2-}.[1,2] All of these salts are derived from Lewis acids which are volatile and either completely or at least partially monomeric at temperatures below the thermal decomposition temperature of their NF_4^+ salts. Since these volatile Lewis acids are undesirable for NF_3–F_2 gas generators, they must be removed by complexing (clinker formation) with a strong Lewis base, such as KF. Since the addition of a clinker-forming component degrades the performance of an NF_3–F_2 gas generator, the synthesis of NF_4^+ salts, derived from nonvolatile Lewis acids, became very desirable. However, this objective presented a synthetic challenge, since nonvolatile Lewis acids are highly polymeric and already possess favorable high coordination numbers. Consequently, these polymeric compounds are quite unreactive and do not behave like strong Lewis acids, thus rendering a direct synthesis[3] from NF_3, F_2, and the Lewis acid impossible. In this paper we report the synthesis of NF_4^+ salts derived from SnF_4, a doubly trans-fluorine-bridged polymer[4,5] subliming at 704 °C, using metathetical[6,7] and displacement[1,2] reactions.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those recently described.[1,2] The NF_4BF_4[1] and NF_4SbF_6[2] starting materials were prepared as previously reported. The SnF_4 (Ozark Mahoning) and $SnCl_4$ (Baker) were used as received. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[8] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. The CsF was fused in a platinum crucible and powdered in the drybox.

Synthesis of Cs_2SnF_6. Dry CsF (10.45 mmol) and $SnCl_4$ (5.22 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (10 mL of liquid) was added, and the mixture was agitated at 20 °C for several hours until HCl evolution had ceased and a clear solution was obtained. The volatile materials were pumped off at 50 °C. The white solid residue (2.604 g; weight calculated for 5.22 mmol of Cs_2SnF_6 2.600 g) was shown by infrared and Raman spectroscopy[9,10] and its x-ray diffraction powder pattern[11] to be of excellent purity.

If SnF_4 is readily available, the following synthesis of Cs_2SnF_6 was found to be somewhat more convenient. A mixture of CsF and SnF_4 (2:1 mole ratio) was fused in a covered platinum crucible until a clear melt was obtained. Alternately, CsF and SnF_4 (2:1 mole ratio) were agitated in anhydrous HF until a clear solution was obtained (SnF_4 is only very sparingly soluble in HF). In both cases the resulting products were shown by spectroscopic techniques to be undistinguishable from that obtained by the above method.

Synthesis of $(NF_4)_2SnF_6$. The small-scale metathetical reactions were carried out in the apparatus depicted in Figure 1. It consisted of three Teflon FEP U-traps interconnected by Monel unions (Swagelok) and closed off at both ends by a Monel valve. The union between trap II and trap III contained a Teflon filter (porous Teflon sheet, $^1/_{16}$-in. thickness from Russel Assoc. Inc.) and was held in place by a press fit. The passivated apparatus was taken to the drybox and Cs_2SnF_6 and NF_4SbF_6 (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous HF, in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the Cs_2SnF_6 solution to run into trap II containing the NF_4SbF_6 solution. Upon contact of the two solutions, copious amounts of a white precipitate ($CsSbF_6$) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to −80 °C. After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of $CsSbF_6$, whereas the solid collected in trap III was mainly the desired $(NF_4)_2SnF_6$.

The following example gives a typical product distribution obtainable with the above procedure and apparatus: starting materials NF_4SbF_6 (9.72 mmol), Cs_2SnF_6 (4.86 mmol); weight of solid on filter 4.24 g; weight of solid in trap III 1.36 g (weight calculated for 4.86 mmol of $(NF_4)_2SnF_6$ 2.01 g). Anal. Calcd for solid from trap III, a mixture of 82.8% $(NF_4)_2SnF_6$, 12.9% NF_4SbF_6, and 4.3% $CsSbF_6$: NF_3, 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43. Found: NF_3, 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3.

Synthesis of NF_4SnF_5. A mixture of NF_4BF_4 and SnF_4 (9.82 mmol each) was placed into a passivated Teflon–FEP ampule containing a Teflon-coated magnetic stirring bar. Anhydrous HF (10 mL of