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Reactivity Pattern Governing Oxidation of Aquometal Ions by Neptunium(VII). Oxidation of Silver(I) and Cobalt(II) in Aqueous Perchloric Acid Media[1]

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The 1-equiv Np(VII) oxidations of Ag^+ and Co^{2+} have been studied by the stopped-flow technique as a function of acidity, ionic strength, and temperature. For the Ag(I)–Np(VII) reaction, the empirical form of the rate law is $-d[Np(VII)]/dt = b[Np(VII)][Ag(I)][H^+]$ where at 25°, $\mu = 1.00\ F$, $b = (3.54 \pm 0.05) \times 10^3\ F^{-2}\ sec^{-1}$, $\Delta H_b^* = 0.81 \pm 0.08$ kcal/mol, and $\Delta S_b^* = -41 \pm 3$ eu. For the Co(II)–Np(VII) reaction, the empirical form of the rate law is $-d[Np(VII)]/dt = \beta c[Np(VII)][Co(II)][H^+]/(1 + c[H^+])$ where at 25°, $\mu = 1.00\ F$, $\beta = (5.4 \pm 0.2) \times 10^4\ F^{-1}\ sec^{-1}$, $c = 1.83 \pm 0.09\ F^{-1}$, $\Delta H_\beta^* = 9.5 \pm 0.4$ kcal/mol, $\Delta H_c^\circ = -13.1 \pm 0.6$ kcal/mol, $\Delta S_\beta^* = -5.0 \pm 1.5$ eu, and $\Delta S_c^\circ = -42.9 \pm 2.8$ eu. These rate laws and rate parameters are compared to those previously measured for the Np(VII) oxidations of Tl^+, Hg_2^{2+}, and VO^{2+}, and it is suggested that the observed reactivity pattern could result if electron transfer proceeds primarily through a protonated binuclear intermediate. The driving force for this protonation, the relative rates of Ag(I) and Co(II) oxidation, and the failure of Hg_2^{2+} to satisfy the S^*–Z^* correlation met by the other reductants are also briefly discussed.

Introduction

During our previous studies[4] on the chemistry of Np(VII) we have investigated the dynamics of the oxidation in aqueous acidic media of the metal ions Tl^+,[4b] Hg_2^{2+},[4c] and VO^{2+}.[4e] While Tl^+ and Hg_2^{2+} function as 2-equiv reagents and VO^{2+} as a 1-equiv reagent, for all three ions the empirical form of the rate law is first order in Np(VII) and first order in reductant. However, for Tl^+ and Hg_2^{2+} the observed rate also increases markedly with increasing hydrogen ion concentration whereas for VO^{2+} the rate is essentially independent of $[H^+]$. In addition to this dissimilarity in dependencies on $[H^+]$, the difference in S^* values of the VO^{2+}- and Hg_2^{2+}-activated complexes for the hydrogen ion independent paths is much larger than would be predicted from the reported correlation[5] between S^* and Z^*, the formal charge of the activated complex.[4e] Therefore this investigation was undertaken in an effort to (a) further determine the hydrogen ion reactivity pattern for Np(VII) oxidation of metal ions not constrained to act as multiequivalent donors, (b) clarify the phenomenological S^*–Z^* relation[5] for Np(VII) as an oxidant, and (c) extend the limited information available on the kinetics of oxidation of Ag(I) and Co(II).

Experimental Section

Reagents. Unless otherwise specified, all common laboratory chemicals were of reagent grade. Perchloric acid was doubly vacuum distilled (G. F. Smith Chemical Co.) and water was triply distilled. Lithium perchlorate was prepared in the usual[6] fashion by neutralization of the carbonate followed by three recrystallizations; stock solutions of lithium perchlorate prepared in this fashion were standardized by a previously reported procedure.[7] Lithium perchlorate solutions were also prepared by stoichiometric neutralization of weighed amounts of Baker "Ultrex" lithium carbonate and subsequent quantitative dilution.[8] Three different stock silver(I) solutions were prepared; one resulted from direct neutralization of the carbonate (Alfa Inorganics) with perchloric acid, and the other two resulted from different batches of recrystallized silver(I) perchlorate (Alfa Inorganics). Cobalt(II) perchlorate was prepared from the carbonate and recrystallized three times; one stock solution of cobalt(II) perchlorate was prepared from this material and a second was prepared from material which suffered an additional recrystallization. Stock solutions of perchloric acid and silver(I) perchlorate were standardized by conventional titrimetric methods, and cobalt(II) perchlorate stock solutions were standardized spectrophotometrically at 510 nm (ϵ 4.77 $F^{-1}\ cm^{-1}$).[9] Kinetic experiments using the alternate stock solutions of $LiClO_4$, $AgClO_4$, and $Co(ClO_4)_2$ gave identical results to within experimental error and therefore stocks of a particular reagent were used interchangeably. The preparation and standardization of Np(VII) solutions have been previously described.[4a]

Equipment and Procedures. The computer-interfaced stopped-flow instrumentation, as well as the basic procedures and techniques, used in this study has been detailed previously.[4e]

The Np(VII)–Co(II) reaction was monitored at 440 nm where the molar extinction coefficient of Np(VII) (*ca.* 410 $F^{-1}\ cm^{-1}$) is much larger than that of any other species present in the reaction solution. The Np(VII)–Ag(I) reaction was monitored most often at 385 nm due to the smaller absorptivity of Ag(II) at this wavelength. Replicate Np(VII)–Ag(I) experiments at 440 and 385 nm showed that the rate parameters observed for this reaction are not dependent on which wavelength is used.

Slow oxidation of water by Np(VII)[4a] in the storage syringe results in continuously decreasing $[Np(VII)]_{sy}$ and concomitantly increasing $[Np(VI)]_{sy}$. (Initially $[Np(VII)]_{sy}$ was *ca.* $(1\text{–}2) \times 10^{-3}\ F$, and data collection was terminated once this dropped to *ca.* $1 \times 10^{-4}\ F$.) For both systems investigated in this work, the continuous variation of $[Np(VII)]_0$ and $[Np(VI)]_0$ (initial concentrations of Np(VII) and Np(VI) in reactant solution, equal to half respective concentrations in storage syringe) during a given series of experiments had no effect on the values of the rate parameters observed during the series. All reported rate parameters are accompanied by the range of $[Np(VII)]_0$ values encountered in determining that parameter.

Data Analysis. The observed OD–t data from individual kinetic experiments were treated by standard nonlinear least-squares techniques, allowing k_{obsd}, OD_0, and OD_∞ to be adjustable parameters.[10] For reactions in which the concentration of reductant was present in pseudo-first-order excess ($[reductant]_{sy}$ at least 15 times greater than the *initial* $[Np(VII)]_{sy}$) the data were adjusted in terms of eq 1 where the subscripts on OD indicate the time of that optical

$$OD_t = (OD_0 - OD_\infty)e^{-k'_{obsd}t} + OD_\infty \qquad (1)$$

density reading and k'_{obsd} is the observed first-order rate parameter, as previously described.[4c] However, most of the Np(VII)–Co(II) reactions and one series of Np(VII)–Ag(I) reactions were conducted under second-order concentration conditions (excess reductant) and the usual formulation of the second-order rate expression is inapplicable to our experimental conditions because the continuous decay of Np(VII) in the storage syringe makes $[Np(VII)]_0$ an unknown parameter for each individual kinetic experiment. Therefore the second-order rate expression was recast as eq 2, wherein $[Np(VII)]_0$

$$OD_t = \frac{B_0E(OD_0 - OD_\infty) + S(OD_0 - OD_\infty)^2}{B_0Ee^{kt[B_0 - S(OD_0 - OD_\infty)/E]} - S(OD_0 - OD_\infty)} + OD_\infty \qquad (2)$$

appears in terms of the adjustable parameters OD_0 and OD_∞,[10] $k = k''_{obsd}$ = observed second-order rate parameter, B_0 = initial concentration of reductant (present in excess), S = stoichiometry factor = moles of reductant consumed per mole of Np(VII) consumed, $E = l(\epsilon_{Np(VII)} + S\epsilon_{Reductant} - \epsilon_{Np(VI)} - P\epsilon_{Product})$, l = path length in centimeters, ϵ_i = molar extinction coefficient of species i, and P = stoichiometry factor = moles of oxidized product produced per mole

Table I. Dependence of $\bar{k}'_{\text{obsd}}$ on $[\text{Ag(I)}]_0$[a]

$10^2[\text{Ag(I)}]_0$, F	$\bar{k}'_{\text{obsd}} \pm \sigma_m$, sec^{-1}	$10^{-3}k''$, F^{-1} sec^{-1}	$10^2[\text{Ag(I)}]_0$, F	$\bar{k}'_{\text{obsd}} \pm \sigma_m$, sec^{-1}	$10^{-3}k''$, F^{-1} sec^{-1}
0.201	. . .[b]	1.84 ± 0.30[b]	2.01	36.0 ± 1.0	1.80 ± 0.05
0.401	7.08 ± 0.06	1.77 ± 0.01	2.27	41.3 ± 0.5	1.82 ± 0.02
0.522	9.10 ± 0.40	1.74 ± 0.08[c]	3.22	55.8 ± 0.4	1.73 ± 0.01
0.569	10.7 ± 0.3	1.88 ± 0.05	5.00	85.0 ± 1.0	1.71 ± 0.02
1.005	17.7 ± 0.3	1.74 ± 0.03	8.65	153 ± 20	1.77 ± 0.20[c]
2.01	34.8 ± 1.0	1.73 ± 0.03	9.10	163 ± 6	1.79 ± 0.07[d]

[a] Conditions: 25°, $\mu = 1.00\ F$ (LiClO_4), $[\text{H}^+]_0 = 0.500 \pm 0.006\ F$, $[\text{Np(VII)}]_0 = (0.60\text{–}4.17) \times 10^{-4}\ F$. Values of k'' based on three to five independent determinations. [b] Reaction conducted under second-order concentration conditions; table entry is the direct second-order rate parameter $\bar{k}''_{\text{obsd}}$ calculated from eq 2. All other entries are calculated as $\bar{k}'_{\text{obsd}}/[\text{Ag(I)}]_0$. [c] Independent stock solution of silver perchlorate. [d] Alternate independent stock solution of silver perchlorate.

Table II. Dependence of k'' on $[\text{H}^+]$ and Temperature for the Np(VII)–Ag(I) Reaction[a,b]

2.0°		15.0°		25.0°	
$[\text{H}^+]$, F	$10^{-3}k''$, F^{-1} sec^{-1}	$[\text{H}^+]$, F	$10^{-3}k''$, F^{-1} sec^{-1}	$[\text{H}^+]$, F	$10^{-3}k''$, F^{-1} sec^{-1}
0.058	0.166 ± 0.001	0.058	0.196 ± 0.005	0.048	0.163 ± 0.005
0.133	0.39 ± 0.01	0.133	0.43 ± 0.01	0.121	0.41 ± 0.01
0.233	0.67 ± 0.01	0.233	0.77 ± 0.01	0.221	0.81 ± 0.01
0.383	1.09 ± 0.04	0.383	1.39 ± 0.05	0.371	1.35 ± 0.02
0.537	1.53 ± 0.03	0.537	1.93 ± 0.05	0.506	1.77 ± 0.01
0.885	2.58 ± 0.03	0.885	3.14 ± 0.10	0.873	2.99 ± 0.05

[a] Conditions: $\mu = 1.00\ F$ (LiClO_4), $[\text{Ag(I)}]_0 = 2.01 \times 10^{-2}\ F$. For 2.0, 15.0, and 25.0° respectively $10^4[\text{Np(VII)}]_0 = 2.8\text{–}5.95$, 0.52–3.44, and 0.92–4.54 F. [b] Reported values of k'' ($=\bar{k}'_{\text{obsd}}/[\text{Ag(I)}]_0$) are the means of at least three independent determinations, and the reported errors are $\pm\sigma_m$.

of Np(VII) consumed. Least-squares adjustment of second-order OD–t data within eq 2 utilized values of $E/l = 396.8\ F^{-1}\ \text{cm}^{-1}$ for the Np(VII)–Co(II) reaction at 440 nm and $E/l = 352\ F^{-1}\ \text{cm}^{-1}$ for the Np(VII)–Ag(I) reaction at 385 nm; l is 2.00 cm for our apparatus, and data presented later show that $S = P = 1.00$ for both systems investigated in this work. For experiments conducted under both pseudo-first-order and second-order conditions, the initial concentration of Np(VII) in a given kinetic run was calculated from the optimized values of OD_0 and OD_∞ which always agreed with observed OD_0 and OD_∞ values to well within experimental error (see eq 3). Tests

$$[\text{Np(VII)}]_0 = (\text{OD}_0 - \text{OD}_\infty)/E \tag{3}$$

performed to show that the functional forms of eq 1 and 2 adequately describe the observed OD–t data satisfied the same criteria as previously reported,[4e] and results presented later show that for otherwise identical conditions values of $k'_{\text{obsd}}/[\text{reductant}]$ (from eq 1 when reductant is present in pseudo-first-order excess) are equal within experimental error to values of k''_{obsd} obtained from eq 2 under second-order conditions. As before, replicate measurements showed that the precision in the determination of k_{obsd} is limited by factors other than random errors.[4e] Therefore in this paper we again report rate parameters as the mean values of k_{obsd}, *i.e.*, $\bar{k}'_{\text{obsd}}$ or $\bar{k}''_{\text{obsd}}$, for a given set of replicate measurements (the number of values in a set are reported with the rate parameter) along with the standard deviation from this mean, σ_m.

Unless otherwise noted, all errors reported in this work are standard deviations.

Results

Stoichiometry. For the reactions

$$\text{Np(VII)} + \text{Ag(I)} \rightarrow \text{Np(VI)} + \text{Ag(II)} \tag{4}$$

and

$$\text{Np(VII)} + \text{Co(II)} \rightarrow \text{Np(VI)} + \text{Co(III)} \tag{5}$$

the stoichiometries were verified to be as indicated by spectrophotometric determinations of the amounts of Ag(II) and Co(III) produced from known amounts of Np(VII) reacted with excesses of Ag(I) and Co(II), respectively.

With initial concentrations of $10^3[\text{Np(VII)}]_0 = 1.21\ F$, $[\text{Ag(I)}]_0 = 0.273\ F$, and $[\text{H}^+]_0 = 1.08\ F$, the ratio of $\Delta[\text{Np(VII)}]/\Delta[\text{Ag(II)}] = 0.98 \pm 0.09$. The uncertainty in the molar extinction coefficient of Ag(II) (ϵ 140 ± 7 at 475 nm),[11] combined with the uncertainty involved in extrapolating the decaying Ag(II) absorbance back to the time of mixing, leads to the assigned precision index.

For two independent experiments, with initial concentrations of $10^3[\text{Np(VII)}]_0 = 2.97$ and 1.80 F, $10^2[\text{Co(II)}]_0 = 3.98$ and 1.13 F, and $[\text{H}^+]_0 = 2.02$ and 1.02 F, the observed ratios of $\Delta[\text{Np(VII)}]/\Delta[\text{Co(III)}]$ were 1.00 and 0.97, respectively. Co(III) was determined at 605 nm (ϵ 35.3 $F^{-1}\ \text{cm}^{-1}$)[12] and spectra of the spent reaction mixtures showed that Np(VI) and Co(III) were the only detectable products.[13]

Kinetics of Ag(I) Oxidation. Information presented in the Experimental Section suffices to show that when Ag(I) is present in great excess, the rate law governing disappearance of Np(VII) in reaction 4 is first order in Np(VII) and zero order in Np(VI). Table I presents the dependence of the observed first-order rate parameter, $\bar{k}'_{\text{obsd}}$, on $[\text{Ag(I)}]_0$ at constant $[\text{H}^+]$ and temperature. A weighted linear least-squares adjustment of this data set yields a statistically negligible intercept of $-0.036 \pm 0.067\ \text{sec}^{-1}$ and a slope of $(1.78 \pm 0.01) \times 10^3\ F^{-1}\ \text{sec}^{-1}$, showing that the rate is first order in $[\text{Ag(I)}]_0$. Also included in Table I is one value of $\bar{k}''_{\text{obsd}}$, the second-order rate parameter directly observed under second-order concentration conditions, which is seen to be equal within experimental error to the slope of the $\bar{k}'_{\text{obsd}}$–$[\text{Ag(I)}]_0$ plot. It is therefore convenient to refer to both $\bar{k}'_{\text{obsd}}/[\text{Ag(I)}]_0$ and $\bar{k}''_{\text{obsd}}$ as just k'', and Table II presents the hydrogen ion and temperature dependencies of k''. At each temperature the data are adequately correlated by the expression

$$k'' = a + b[\text{H}^+] \tag{6}$$

the resulting values of a being statistically insignificant. At 25.0, 15.0, and 2.0°, the respective values of $10^{-3}a$ ($F^{-1}\ \text{sec}^{-1}$) and $10^{-3}b$ ($F^{-2}\ \text{sec}^{-1}$) are as follows: -0.013 ± 0.013 and 3.54 ± 0.05; -0.008 ± 0.012 and 3.33 ± 0.06; -0.008 ± 0.018 and 2.87 ± 0.01. These results indicate that the empirical form of the rate law governing reaction 4 is

$$-\text{d}[\text{Np(VII)}]/\text{d}t = b[\text{Np(VII)}][\text{Ag(I)}][\text{H}^+] \tag{7}$$

Nonlinear least-squares minimization of 29 independently determined values of $k''/[\text{H}^+]$ (each weighted as $1/\sigma_m^2$) within the framework of the Eyring formalism leads to the activation parameters $\Delta H_b^* = 0.81 \pm 0.08$ kcal/mol and $\Delta S_b^* = -41 \pm 3$ eu. The dependence of k'' on ionic strength (maintained with lithium perchlorate at constant $[\text{H}^+]$ and temperature) is given in Table III.

Kinetics of Co(II) Oxidation. The oxidation of Co(II) by Np(VII) proceeds at too great a rate to allow extensive experimentation under reaction conditions where the reductant is present in pseudo-first-order excess. Therefore the range of reductant concentrations realized in this system is not as large as that attained in the Ag(I) system, and most experiments were carried out under second-order conditions. At

Table III. Ionic Strength Dependencies of the Np(VII) Oxidations of Ag(I) and Co(II)

Ag(I) + Np(VII)^{a,b}		Co(II) + Np(VII)^{a,c}	
μ, F	$10^{-4}k''$, F^{-1} sec^{-1}	μ, F	$10^{-4}k''$, F^{-1} sec^{-1}
0.30	2.84 ± 0.04	0.220	0.243 ± 0.004
0.60	3.63 ± 0.01	0.501	0.397 ± 0.001
1.00	4.35 ± 0.06^d	1.00	0.639 ± 0.005^e
1.50	5.65 ± 0.04	2.00	1.38 ± 0.05
2.00	6.27 ± 0.02	2.86	2.01 ± 0.01
3.00	8.00 ± 0.02		

[a] Conditions common to both reactions: 25°, μ maintained with $LiClO_4$. Reported values of k'' are means of three to five independent determinations; uncertainties are $\pm\sigma_m$. [b] Conditions: $[H^+] = 0.123\ F$, $[Ag(I)]_0 = 1.00 \times 10^{-2}\ F$, $[Np(VII)]_0 = (1.10-7.74) \times 10^{-4}\ F$. [c] Conditions: $[H^+] = 0.0725\ F$, $[Co(II)]_0 = 1.48 \times 10^{-3}\ F$, $[Np(VII)]_0 = (0.62$ to $1.92) \times 10^{-4}\ F$. [d] Calculated from $b = (3.54 \pm 0.05) \times 10^3\ F^{-2}$ sec^{-1} for 25° data of Table II. [e] Taken from Table V.

Table IV. Dependence of k'' on $[Co(II)]_0$ and $[Np(VII)]_0$^{a}

$10^4[Np(VII)]_0$, F	$10^3[Co(II)]_0$, F	$10^{-4}k''$, F^{-1} sec^{-1}	$10^4[Np(VII)]_0$, F	$10^3[Co(II)]_0$, F	$10^{-4}k''$, F^{-1} sec^{-1}
0.64–0.82	3.95	2.50 ± 0.09^b	1.07–2.11	0.995	2.69 ± 0.04
0.29–1.21	1.99	2.55 ± 0.07	1.20–2.04	0.498	2.63 ± 0.03
0.63–1.10	1.98	2.55 ± 0.04^c	0.89–1.22	0.247	2.61 ± 0.03^c
0.81–2.39	1.49	2.67 ± 0.06			

[a] Conditions: 25°, $\mu = 1.00\ F$ ($LiClO_4$), $[H^+] = 0.517\ F$. Values of k'' are means of four to five independent determinations; uncertainties are $\pm\sigma_m$. [b] Reaction conducted under pseudo-first-order concentration conditions; table entry is $\bar{k}'_{obsd}/[Co(II)]_0$. All other entries are directly observed values of $\bar{k}''_{obsd}$. [c] Independent stock solution of cobalt(II) perchlorate.

Table V. Dependence of k'' of $[H^+]$ and Temperature for the Np(VII)–Co(II) Reaction^{a,b}

3.8°		15.0°		25.0°	
$[H^+]$, F	$10^{-4}k''$, F^{-1} sec^{-1}	$[H^+]$, F	$10^{-4}k''$, F^{-1} sec^{-1}	$[H^+]$, F	$10^{-4}k''$, F^{-1} sec^{-1}
		0.050	0.517 ± 0.005		
0.0725	0.598 ± 0.005	0.0725	0.66 ± 0.01	0.0725	0.639 ± 0.005
0.133	0.84 ± 0.02	0.133	1.04 ± 0.01	0.133	1.05 ± 0.01
0.229	1.03 ± 0.01	0.229	1.43 ± 0.03	0.229	1.63 ± 0.03
0.325	1.15 ± 0.01	0.325	1.66 ± 0.03	0.325	2.00 ± 0.01
0.566	1.30 ± 0.03	0.566	2.00 ± 0.02	0.420	2.32 ± 0.01
0.933	1.38 ± 0.02	0.933	2.54 ± 0.01	0.517	2.60 ± 0.06
				0.933	3.56 ± 0.04

[a] Conditions: $\mu = 1.00\ F$ ($LiClO_4$), $[Co(II)]_0 = 1.48 \times 10^{-3}\ F$. For 3.8, 15.0, and 25.0° respectively $10^4[Np(VII)]_0 = 1.96-3.36$, $0.37-2.23$, and $0.35-2.39\ F$. [b] Reported values of k'' are the means of four to seven independent measurements, and the reported errors are $\pm\sigma_m$.

constant $[H^+]$ and temperature, the values of the observed second-order rate parameter, $\bar{k}''_{obsd}$, and one value of $\bar{k}'_{obsd}/[Co(II)]_0$ obtained under pseudo-first-order conditions are presented in Table IV where they are seen to be equivalent within experimental error; it is therefore again convenient to refer to both parameters as just k''. Combined with information presented in the Experimental Section, these data suffice to show that at constant $[H^+]$ the empirical form of the rate law governing reaction 5 is first order in Np(VII), zero order in Np(VI), and first order in Co(II). The variation of k'' with $[H^+]$ and temperature is given in Table V, and at each temperature the data are adequately correlated by the expression

$$k'' = \frac{b[H^+]}{1 + c[H^+]} \tag{8}$$

which for computational purposes is more conveniently written as

$$k'' = \frac{\beta c[H^+]}{1 + c[H^+]} \tag{8a}$$

where $b = \beta c$. Figure 1 shows a plot of k'' *vs.* $[H^+]$ for the 15° data, and it is readily seen that the deviation from linearity is so great that eq 6 could not satisfactorily fit the data. Thus the empirical form of the rate law governing reaction 5 may be expressed as

$$\frac{-d[Np(VII)]}{dt} = \frac{\beta c[Np(VII)][Co(II)][H^+]}{1 + c[H^+]} \tag{9}$$

The smooth curve of Figure 1 was calculated from β and c values which were obtained by a nonlinear least-squares adjustment of k'' data (weighted as $1/\sigma_m^2$) within eq 8a. Optimized values of $10^{-4}\beta$ (F^{-1} sec^{-1}) and c(F^{-1}) calculated by this procedure at 25.0, 15.0, and 3.8°, respectively, are as follows: 5.38 ± 0.17 and 1.83 ± 0.09; 3.27 ± 0.07 and 3.59 ± 0.16; 1.558 ± 0.005 and 8.60 ± 0.07. Nonlinear least-squares minimization of 27 independently determined k'' values (each weighted as $1/\sigma_m^2$) within eq 8a, with β expressed in terms of the Eyring formalism

$$\beta = (k_B T/h)e^{\Delta S_\beta^*/R}e^{-\Delta H_\beta^*/RT} \tag{8b}$$

and c expressed in the usual form for an equilibrium parameter

$$c = e^{\Delta S_c^\circ/R}e^{-\Delta H_c^\circ/RT} \tag{8c}$$

leads to the following parameter values: $\Delta H_\beta^* = 9.5 \pm 0.4$ kcal/mol, $\Delta S_\beta^* = -5.0 \pm 1.5$ eu, $\Delta H_c^\circ = -13.1 \pm 0.8$ kcal/mol, $\Delta S_c^\circ = -42.9 \pm 2.8$ eu. From these parameters it can be calculated that $\Delta H_b^* = 3.6 \pm 0.9$ kcal/mol and $\Delta S_b^* = -47.9 \pm 3.2$ eu. The dependence of k'' on ionic strength (maintained

Table VI. Hydrogen Ion Dependence of k'' in the Rate Law $-d[Np(VII)]/dt = k''[Np(VII)][reductant]$ Governing Np(VII) Oxidation of Aquometal Ions

Reductant	pK_a of reductant^a	Empirical form of k''	Ref
Tl^+ ^{b}	13.5	$b[H^+]/(1 + c[H^+])$	4b
Hg_2^{2+}	5.0	$a + b[H^+]$	4c
VO^{2+}	4.8	a	4e
Ag^+	11.7	$b[H^+]$	c
Co^{2+}	9.6	$b[H^+]/(1 + c[H^+])$	c

[a] pK_a values (25°, $\mu \rightarrow 0.0\ F$) taken from L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964). [b] Recalculation of the k''–$[H^+]$ data summarized in ref 4b shows that at each temperature investigated these data are adequately correlated by eq 8a. At 24.9, 19.2, 14.5, and 9.2° respectively values of β (F^{-1} sec^{-1}) and c (F^{-1}) are as follows: 26.1 ± 3.4 and 0.204 ± 0.030; 25.1 ± 7.7 and 0.162 ± 0.055; 16.0 ± 4.3 and 0.207 ± 0.064; 12.1 ± 1.7 and 0.218 ± 0.036. [c] This work.

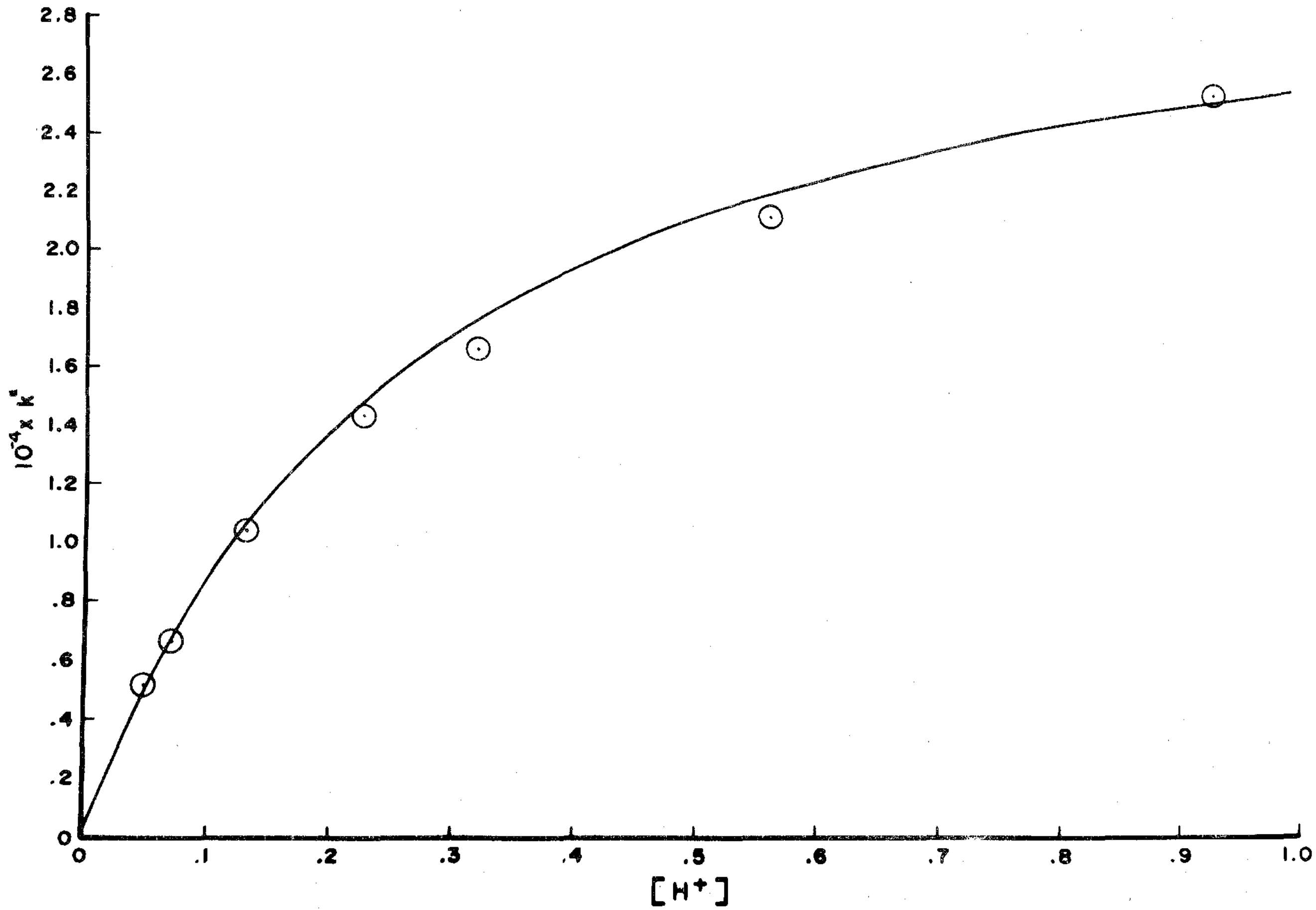

Figure 1. Plot of $10^{-4}k''$ (F^{-1} sec^{-1}) *vs.* [H$^+$] (*F*) for the Np(VII)-Co(II) reaction at 15.0°. Individual points are taken from the data of Table V, and the smooth curve is calculated from optimized β and c values within eq 8a.

with lithium perchlorate at constant [H$^+$] and temperature) is given in Table III.

Discussion

Table VI presents the dependence of k'' on [H$^+$] for the five Np(VII) oxidations of aquometal ions studied to date. The observed rate laws can all be viewed as limiting forms of the general rate law

$$k'' = a + b[\mathrm{H}^+]/(1 + c[\mathrm{H}^+]) \tag{10}$$

where, in any particular case, one or two of the parameters *a*, *b*, and *c* may be too small to detect experimentally.

Rate terms of the form $b[\mathrm{H}^+]/(1 + c[\mathrm{H}^+])$ may reasonably be taken to reflect operation of a mechanism in which protonation affects the net reaction rate.[14] This protonation cannot simply be an equilibrium involving the Np(VII) oxidant, for in this case the *c* parameter would be identical for every reductant investigated and this situation does not obtain

$$\mathrm{H}^+ + \mathrm{Np(VII)} \overset{K_{\mathrm{Np}}}{\rightleftharpoons} \mathrm{I} \tag{11a}$$

$$\mathrm{I} + \text{reductant} \xrightarrow{k} \text{products} \tag{11b}$$

$$k'' = kK_{\mathrm{Np}}[\mathrm{H}^+]/(1 + K_{\mathrm{Np}}[\mathrm{H}^+]) \tag{11c}$$

$$c \equiv K_{\mathrm{Np}} \tag{11d}$$

Likewise, we cannot simply have protonation of the various reductants since the observed hydrogen ion dependencies are not noted when other oxidants react with the reductants of Table VI. It is possible that this protonation involves a binuclear complex. Several stable binuclear complexes of "yl" ions have been characterized[5a,15] and analogous species have been proposed as intermediates in electron-transfer reactions.[5a] Especially pertinent to this discussion are the Fe(II)–Pu(VI),[16] U(VI)–Pu(VI),[17] and V(III)–U(VI)[18] reactions for which observed complex hydrogen ion dependencies of k'' are interpreted as reflecting the presence of metastable binuclear intermediates which interact with protons.[5a] It should be noted, however, that in the cited reactions the [H$^+$] dependencies arise from *deprotonation* of the binuclear intermediate, whereas the proposed Np(VII) reaction pattern involves *protonation* of binuclear intermediates.

The following is a simple example of one of the many possible mechanisms consistent with the rate term $b[\mathrm{H}^+]/(1 + c[\mathrm{H}^+])$ and the supposition of a binuclear intermediate

$$\text{reductant} + \mathrm{Np(VII)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \tag{12a}$$

$$\mathrm{I} + \mathrm{H}^+ \overset{K_2}{\rightleftharpoons} \mathrm{IH}^+ \tag{12b}$$

$$\mathrm{IH}^+ \xrightarrow{k_3} \text{products} \tag{12c}$$

$$k'' = \frac{(k_1k_3K_2/k_{-1})[\mathrm{H}^+]}{1 + (k_3K_2/k_{-1})[\mathrm{H}^+]} \tag{12d}$$

In this scheme $c \equiv k_3K_2/k_{-1}$ which is dependent upon the nature of the reductant and may vary from one system to the next. A complete rationalization of the tendency of Np(VII) to react *via* a proton-assisted pathway is hindered by our lack of knowledge of the chemical form of Np(VII) in acid solution. However, there are three points relevant to this proposed reaction scheme: (1) evidence has recently been obtained which indicates that in basic solution Np(VII) maintains the linear O=Np=O structure of Np(VI)[19] and it is not unreasonable to assume that this also obtains in acid; (2) since the hydrogen ion dependencies of Table VI are not observed for other

Table VII. Summary of Kinetic Data for the Np(VII) Oxidation of Various Aquometal Ions in Terms of the Rate Law $-d[\mathrm{Np(VII)}]/dt = [\mathrm{Np(VII)}][\mathrm{reductant}]\{a + b[\mathrm{H}^+]/(1 + c[\mathrm{H}^+]\}$, Where $b = \beta c$[a]

Reductant	$S°$ [b]	Ref	Kinetic data[c]
Ag^+	+17	*d*	$b = 3540 \pm 50$ ($\Delta H^* = 0.81 \pm 0.08$; $\Delta S^* = -41 \pm 3$) $S_b^* - S°_{\mathrm{Np(VII)}} = -30$[h]
Tl^+ [e]	+30	4b	$\beta = 26.1 \pm 3.4$ ($\Delta H^* = 7.6 \pm 3.1$; $\Delta S^* = -26 \pm 11$) $c = 0.204 \pm 0.030$ ($\Delta H° = -0.6 \pm 3.5$; $\Delta S° = -5 \pm 12$) $b = 5.3 \pm 1.0$ ($\Delta H^* = 7.0 \pm 5.0$; $\Delta S^* = -32 \pm 16$)[f] $S_b^* - S°_{\mathrm{Np(VII)}} = -8$[h]
Co^{2+}	−27	*d*	$\beta = 53{,}800 \pm 1700$ ($\Delta H^* = 9.5 \pm 0.4$; $\Delta S^* = -5.0 \pm 1.5$) $c = 1.83 \pm 0.01$ ($\Delta H° = -13.1 \pm 0.8$; $\Delta S° = -42.9 \pm 2.8$) $b = 98{,}500 \pm 5800$ ($\Delta H^* = -3.6 \pm 0.9$; $\Delta S^* = -48 \pm 3$)[f] $S_b^* - S°_{\mathrm{Np(VII)}} = -80$[h]
$\mathrm{Hg_2}^{2+}$	+20	4c	$b = 13.4 \pm 1.4$ ($\Delta H^* = 7.8 \pm 0.6$; $\Delta S^* = -27 \pm 2$) $S_b^* - S°_{\mathrm{Np(VII)}} = -12$[h]
$\mathrm{Hg_2}^{2+}$	+20	4c	$a = 28.1 \pm 0.7$ ($\Delta H^* = 11.6 \pm 0.2$; $\Delta S^* = -13 \pm 1$) $S_a^* - S°_{\mathrm{Np(VII)}} = +7$[h]
VO^{2+} [g]	−32	4e	$a = 1440 \pm 20$ ($\Delta H^* = 6.8 \pm 0.4$; $\Delta S^* = -21 \pm 1$) $S_a^* - S°_{\mathrm{Np(VII)}} = -53$[h]

[a] Data taken from references noted and recalculated in terms of eq 10 where necessary. [b] $S°$ values (eu) taken from M. Kh. Karapet'yants and M. L. Karapet'yants, "Thermodynamic Constants of Inorganic and Organic Compounds," Humphrey Science Publishers, Ann Arbor, Mich., 1970. [c] Rate parameters, at 25° and $\mu = 1.00\ F$ ($\mathrm{LiClO_4}$), are given in appropriate units of F^{-n} and sec^{-1}. Equilibrium parameters are in units of F^{-1}. Enthalpies are in kcal/mol and entropies are in units of eu. [d] This work. [e] See footnote *b* of Table VI. [f] Values calculated from appropriate β and c parameters; errors propagated in the usual fashion. [g] Activation parameters refer to $[\mathrm{H}^+] = 1.00\ F$. [h] Calculated according to ref 5a: $S^* = \Delta S^* + \Sigma S°(\text{reactants}) - \Sigma S°(\text{other products of net activation process})$. $S°_{\mathrm{H}^+}$ was taken to be −5.5 eu.

oxidants, protonation most likely occurs on Np(VII); (3) binuclear "yl" complexes are formed by the "yl" oxygen functioning as a ligand to a Lewis acid.[5a,15,20] From these observations a working model for the structure of the protonated intermediate, IH^+, may be proposed to be

H–O=Np=O–reductant

Reaction *via* this intermediate is then hypothesized to be favored because protonation of the oxygen trans to O—reductant weakens the trans O═Np bond making attainment of the transition state more favorable (similar reasoning has been proposed by Haim to account for the acid-catalyzed reduction of Co(III) complexes containing a basic ligand trans to the electron-transfer bridge).[21]

The *a* terms noted in Table VI may arise from direct decomposition of the unprotonated binuclear intermediate

$$\mathrm{I} \xrightarrow{k_\mathrm{I}} \text{products} \tag{13a}$$

$$a \equiv k_\mathrm{I} K_1/(k_{-1} + k_\mathrm{I}) \tag{13b}$$

when $(k_{-1} + k_\mathrm{I}) \gg k_1 k_3 K_2[\mathrm{H}^+]$ or from direct reaction of Np(VII) and the reductant

$$\text{reductant} + \mathrm{Np(VII)} \xrightarrow{k_2} \text{products} \tag{14a}$$

$$a \equiv k_2 \tag{14b}$$

but examination of Table VI in light of the preceding discussion requires that a third possibility also be considered. Table VI shows that those reductants which exhibit detectable *a* terms ($\mathrm{Hg_2}^{2+}$ and VO^{2+}) are just those species which have the greatest tendency to donate a proton (small $\mathrm{p}K_\mathrm{a}$). It is tempting to speculate that for these reductants the proton required by Np(VII) in the activated complex originates on the reductant rather than in bulk solution, leading to the observed acid-independent path

$$\text{reductant–H} + \mathrm{Np(VII)} \overset{Q'}{\rightleftharpoons} \text{H–O=Np=O–reductant} \quad (Q' << 1) \tag{15a}$$

$$\text{H–O=Np=O–reductant} \xrightarrow{k'} \text{products} \tag{15b}$$

$$a \equiv k'Q' \tag{15c}$$

Activated complexes which contain the same number of protons as the reactants, but yet have them arranged differently, have been postulated for both electron-transfer[7] and ligand-aquation[22] reactions and can be conveniently described as "tautomeric." In this view it is the driving force for Np(VII) to be protonated during electron transfer that dominates the hydrogen ion reactivity pattern of Np(VII) oxidations of aquometal ions, although it is of course possible that a combination of reactions 13–15 may be responsible for the *a* term in any particular system.

Table VII summarizes the rate and activation parameters observed to date for Np(VII) oxidation of metal ions. For the pair of 1-equiv reductants considered in this work, Co^{2+} reacts faster than Ag^+. This difference may be understood on the basis that Co^{2+} is the stronger reductant ($E°(\mathrm{Co}^{2+}) = 1.95$ V; $E°(\mathrm{Ag}^+) = 2.00$ V)[23] and is at odds with the previously presented[24] generalization that "the reductions by Ag(I)... proceed at least as rapidly as the reductions by Co(II)." The composite nature of *a* and *b* terms makes direct interpretation of activation parameters difficult, but in general it is seen that the large differences in the net reaction rates of the various systems result from differences in ΔH^* terms. Since the value of $S°_{\mathrm{Np(VII)}}$ is unknown, activation entropies are tabulated relative to this value (*i.e.*, as $S^* - S°_{\mathrm{Np(VII)}}$) and it is seen that the previously noted correlation between S^* and Z^*, the formal charge on the activated complex,[5] is obeyed for all combinations except those involving $\mathrm{Hg_2}^{2+}$. In the context of Np(VII) oxidations and the S^*–Z^* correlation,[5] $\mathrm{Hg_2}^{2+}$ behaves as though its effective net charge were 1+ rather than 2+.

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Registry No. Ag(I), 14701-21-4; Co(II), 22541-53-3; Np(VII), 20826-07-7.

References and Notes

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(2) (a) University of Chicago and University of Cincinnati. (b) Argonne National Laboratory. (c) Participant in the Argonne National Laboratory Summer Faculty Research Participation Program.

(3) Presently located at University of Cincinnati.

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Triboluminescence of Uranyl Nitrate

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The triboluminescence (TL) of uranyl nitrate hexahydrate is a phosphorescence centered on the uranyl ion. The vibronic structure in both the TL and the photoluminescence spectra have the same relative intensities and energy spacings as is expected when the lifetime of the TL is long compared to mechanical relaxation processes in the crystal. The title compound is the first nonaromatic molecule whose TL originates from a molecular excited state and not from a gas discharge. The physical origins of the TL within a crystal and the implausibility of an intramolecular TL excitation mechanism are discussed.

Triboluminescence (TL) is the emission of light caused by the application of mechanical stress of crystals. The phenomenon was known in the 16th century[1] and was named by Wiedemann in 1895.[2] The prefix originates from the Greek "tribein," to rub. Historically, the best known triboluminescent crystal was sugar.[1]

The original explanation of TL was based on triboelectrification or piezoelectrification, *i.e.*, the buildup of a static charge as a result of the mechanical action applied to the solid, followed by electrical arcing to produce a gas discharge. Nonspectroscopic proof of the gas-discharge origin of TL was provided by the observation that *cis*-octene produced blue-white TL flashes in air but orange-red flashes in an atmosphere of neon.[3] The gas-discharge origin of the TL of NaF was proven spectroscopically.[4] The motion of mercury over solids has been shown to produce both luminescence and a large electric potential difference.[5,6] Two additional excitation mechanisms, intermolecular interactions and intramolecular deformations, have been recently proposed (*vide infra*).

Our interest in TL stems from our discovery that the emission can occur from sources other than ambient gas discharge. In particular, we have spectroscopically found examples of fluorescence (coumarin),[7] phosphorescence (hexaphenylcarbodiphosphorane[8] and phthalic anhydride[9]), and both simultaneously (acenaphthene[9]) from the respective molecules in the crystal. The latter two compounds are unusual because the tribophosphorescence occurs at room temperature while the photophosphorescence occurs only at much lower temperatures. Together with the semiquantitatively identified tribophosphorescence of tetrakis(dibenzoylmethido)europium(III) salts,[10] the above list encompasses all of the previously known triboluminescent compounds whose emission origins are excited states of molecules in crystals.

TL originating from excited states of molecules in the crystal is important for two reasons. First, for practical applications, it will be desirable to be able to "tune" the wavelength and intensity of the emission by modifying the molecular constituents of the crystal. Second, new excitation mechanisms may be operating which will probe the mechanical and optical properties of the triboluminescent crystals. We have found[7] that the short-lived ($\sim 10^{-9}$ sec) fluorescence of coumarin contains new dynamic features, absent in the photoluminescence spectrum, which are characteristic of the crystal under stress.

A feature common to all of the above triboluminescent molecules whose TL has been identified as a molecular fluorescence or phosphorescence is the presence of one or more phenyl groups. In this paper the TL of uranyl nitrate hexahydrate, the first example of tribophosphorescence originating from a nonaromatic molecule in a crystal, is reported. The photoluminescence spectra and TL excitation mechanism are also discussed.

Experimental Section

All spectra were recorded using a Jarrell-Ash 0.25-m grating monochromator with an EMI 9558 photomultiplier in a Products for Research variable-temperature refrigerator housing and were not corrected for the response characteristics of the instrument. The photoluminescence spectra were excited by a 100-W high-pressure mercury lamp focused through a Bausch and Lomb grating monochromator. The spectra were unaffected by the wavelength of the exciting light. The samples for both the photoluminescence and the TL spectra were contained in Pyrex vials.

The TL spectra were obtained by grinding 4-g samples contained in 0.75-in. diameter Pyrex vials with a stainless steel rod. TL was also excited by grinding the sample with nonconducting implements such as quartz, wood, and Teflon as well as with metals other than stainless steel. Intense TL could also be excited by the thermal shock of dipping the sample into liquid nitrogen. All of the above mechanical methods produced TL of qualitatively the same intensity and all methods produced the same TL spectrum as visually observed through a spectroscope.

The TL is emitted in the form of green flashes whose intensity is directly related to the mechanical energy exerted on the crystals. As the crystals were ground to an increasingly fine powder, the intensity diminished. In order to obtain the TL spectrum, the intensity at a given wavelength was normalized using the experimental arrangement shown in the block diagram in Figure 1. A TL flash was monitored at a given wavelength with the monochromator described above. The total intensity of the flash was simultaneously monitored using a 1P28 photomultiplier. The two signals were recorded and the ratio of "wavelength" intensity to total intensity was computed and plotted. The primary source of error in the spectrum is the slightly different geometric positions of the two photomultipliers relative to the TL flash. The signal to noise ratio is 53.