doublets, which are usually separated by a few hundred reciprocal centimeters in Co(II) complexes. Thus if the g tensors for the various Kramer doublets differ, both the contact and dipolar shifts will deviate from Curie behavior. The contact shift is always proportional to some "average" g value for each level, while the dipolar shift is proportional to some function of the difference in $g_{||}$ and $g_{\perp}$, $(g_{||} + g_{\perp})(g_{||} - g_{\perp})$ in our case.[3,9] Thus if the *average g* values for the accessible Kramer doublets differ significantly less than their relative g-tensor anisotropies, the extent of deviation from Curie behavior is predicted to be much greater for the dipolar than the contact shifts. It could be stated that, in general, eq 2 predicts *different* temperature dependences for contact and dipolar shifts in such Co(II) systems.

Because of the lack of any experimental esr data, a detailed check of this postulate is not possible for our system at this time. However, a complete esr study[26] of the trigonally distorted six-coordinated bis Co(II) complexes of poly(pyrazolyl)borates has shown that $(g_{||} + g_{\perp})(g_{||} - g_{\perp})$ differs by a factor of $\sim$4 for the two lowest lying Kramer doublets, which are $\sim$90% populated at room temperature, while $(g_{||} + 2g_{\perp})$ differs by only <2 for the same levels. Therefore this system should show larger deviations from Curie behavior for its dipolar than contact shifts.

We therefore suggest that for the present Co(II) complexes, the magnetic anisotropies must differ more than the average g values for the accessible Kramer doublets. Furthermore, since the dipolar shifts increase faster than Curie behavior as the temperature is

(26) J. P. Jesson, *J. Chem. Phys.*, 45, 1049 (1966); 47, 582 (1967).

lowered, the lowest Kramers doublet must possess the greater magnetic anisotropy.

The observed correlation between the extents of deviation from Curie behavior and the dipolar contribution to the observed isotropic shift (in both relative signs and magnitudes), calculated by assuming similar σ spin density distributions in the Co(II) and magnetically isotropic Ni(II) chelates,[10] can be taken as evidence that, except for the 4,7 positions, similar spin delocalization mechanisms are operative in these Co(II) and Ni(II) chelates. Thus the previous contention[27] that this method of qualitatively separating contact and dipolar shifts in these Co(II) chelates is totally invalid is erroneous. Their[27] conclusions depended on comparing the isotropic shifts of sets of protons which obviously experienced different types of spin density, and thus put the method in its most unfavorable light.

Similar, though slightly more complicated, non-Curie behavior has been observed for other distorted octahedral complexes which are expected to exhibit sizable magnetic anisotropy,[28] suggesting that such anomalous behavior is more common than previously considered.[29]

(27) M. Wickolas and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 2196 (1968).

(28) G. N. La Mar, *ibid.*, 92, 1806 (1970).

(29) Note Added in Proof. B. R. McGarvey (private communication) has recently rederived the equations for the contact and dipolar shift (ref 3) for trigonally distorted Co(II) complexes, including the contributions from the second order Zeeman interaction. His equations predict essentially Curie behavior for the contact shifts, and a strong deviation from Curie behavior for the dipolar shifts, which serves to confirm our present qualitative experimental findings. Furthermore, McGarvey's specific predictions of non-Curie behavior for the dipolar shifts in the bis(pyrazolyl borate)cobalt(II) complexes have been experimentally observed (G. N. La Mar and J. P. Jesson, to be published).

Kinetic Study of the Oxidation of Thallium(I) by Neptunium(VII)[1]

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Abstract: The empirical form of the rate law for the reaction between Np(VII) and Tl(I) in acid perchlorate media is $-d[\text{Np(VII)}]/dt = k'[\text{Np(VII)}][\text{Tl(I)}]$, where $\ln k' = \ln k + n \ln [\text{H}^+]$. At 25° in 1 M perchloric acid $k = 4.46 \pm 0.04 \, M^{-1} \, \text{sec}^{-1}$ and $n = 0.901 \pm 0.008$. The apparent activation energy is 7.73 ± 0.42 kcal/mol. Results of ^{18}O tracer studies are presented.

When Tl(I) is oxidized by the reagents Co(III),[3] Ce(IV),[4] and Ag(II),[5] evidence has been presented for the existence of Tl(II) as an important kinetic intermediate oxidation state. It is of interest to ascertain if the production of this intermediate is

independent of the oxidant. This work presents such an attempt by the kinetic study of the reaction

$$2\text{Np(VII)} + \text{Tl(I)} = 2\text{Np(VI)} + \text{Tl(III)} \qquad (1)$$

In addition, the results to be presented extend the limited information available on the reaction characteristics of Np(VII) in acid media.[6]

Experimental Section

Reagents. The Np(VII) stock solutions in 1 M NaOH were prepared electrolytically as previously described.[6] Thallium(I)

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Argonne National Laboratory summer staff member.

(3) K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 343 (1956).

(4) J. W. Gryder and M. C. Dorfman, *J. Amer. Chem. Soc.*, 83, 1254 (1961).

(5) R. W. Dundon and J. W. Gryder, *Inorg. Chem.*, 5, 986 (1966).

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

perchlorate solutions were prepared from the carbonate plus perchloric acid followed by two to three recrystallizations. The Tl(III) solution was prepared electrolytically at a Pt gauze electrode using a counterflow shielded electrode that has been previously described.[7] The preparation and standardization of the perchloric acid and lithium perchlorate solutions have been previously described.[8]

Total Np concentration was determined by reduction in acid solution with sodium nitrite and spectrophotometric measurement of the absorptivity at 9800 Å where Np(V) has a molar absorptivity 400 M^{-1} cm^{-1} in 1 M perchloric acid. The Np(VII) concentration was determined spectrophotometrically from the Cr(VI) produced by the reaction

$$3Np(VII) + Cr(III) = 3Np(VI) + Cr(VI) \qquad (2)$$

At 3500 Å in 2 M HClO$_4$ the pertinent molar absorptivities in M^{-1} cm^{-1} are 1345 ± 21 for Cr(VI) and 102.7 ± 4.5 for Np(VI). Tl(I) solutions were standardized by conventional gravimetric procedures and Tl(III) solutions by a titrimetric method.[9]

Procedures. A Cary Model 14MR recording spectrophotometer with a thermostated cell compartment was used for all spectrophotometric determinations. In the kinetic studies an aliquot of the Np(VII), maintained at a temperature sufficiently lower than the working temperature to compensate for the heat of neutralization, was rapidly injected into a spectrophotometer cell and absorbance recorded as a function of time at the appropriate wavelength. The spent reaction mixtures were analyzed for total Np and titrated with standard NaOH to determine the hydrogen ion concentration.

In the oxygen isotopic studies the reaction between Np(VII) and water in perchloric acid solution was carried out in a two-tube mixing vessel which could be evacuated to less than 10^{-5} mm. One tube contained the Np(VII) in 1 M NaOH and the other the HClO$_4$ and H$_2$O enriched in ^{18}O (Volk Radiochemical Co.). The reactant solutions were outgassed five times in an effort to remove atmospheric oxygen and then mixed at *ca.* 0°. After the reaction was completed, the oxygen produced was collected over liquid nitrogen by means of a Toepler pump. The 34/32 mass ratio was measured with a Nuclide RMS-16 mass spectrometer. The standard oxygen sample was prepared as above except that normal water was used instead of the enriched water. Solvent water was distilled from the spent reaction mixture and converted to CO$_2$ by the Anbar technique.[10] The CO$_2$ was purified by gas chromatography and the 46/(44 + 45) ratio measured.

To test for the possible oxidation of water by Np(VII) in the presence of Tl(I), a procedure similar to that described above was used. A larger reaction vessel was used to contain the 15 ml of 0.014 M Np(VII)—an increase of a factor of 3 over the amount used in the reactions previously described. In addition an attempt was made to collect noncondensable gases both before and after the reaction was completed.

Calculations. The results of the mass spectrometric measurements are reported as enrichments, defined as mass ratio of species/ mass ratio of the appropriate standard species. With this spectrometer the 34/32 mass ratio was 0.003933 for the standard oxygen, and the 46/(44 + 45) mass ratio was 0.004273 for the standard CO$_2$.

The reactions were carried out with a large excess of Tl(I) to minimize complications due to the oxidation of water by Np(VII). Under these conditions the kinetic data could be adequately described by the usual integrated form of the first-order rate law

$$\ln (A - A_\infty) = I + kt \qquad (3)$$

Each kinetic experiment was monitored for at least three halflives. Between 20 and 30 sets of A, t data were adjusted by a least-squares computation in terms of (3). A constant error was assumed for each absorbance measurement and the input weighted by A^2. All computations were carried out on an IBM 360.

The absorptivity data for a given experiment were reproduced by eq 3 to within 0.002–0.003 OD unit. Precision indices estimated for the rate parameter (based on external consistency) ranged from 0.1 to 0.8%. The spread in the reproducibility of the rate parameters is illustrated by the following data.

At 9.1°, I = 1.0, [H$^+$] = 0.91M, [Np(VII)]$_0$ = 3.0 × 10^{-4} M, [Tl(I)]$_0$ = 8.0 × 10^{-3} M; values obtained for the first-order rate constant k × 10^{-3} sec^{-1} were 16.27 ± 0.04, 16.46 ± 0.05, and 16.47 ± 0.04. At the same temperature and initial Np(VII) concentration with [Tl(I)]$_0$ = 8.3 × 10^{-3} M and I = 1.925, [H$^+$] = 0.195M, values obtained for the first-order rate constant in the same units were 5.03 ± 0.02 and 4.37 ± 0.02.

Results and Discussion

Stoichiometry. The estimated potential of the Np-(VII)–Np(VI) couple, > −2.0 V,[6] is sufficient evidence to indicate that reaction 1 will go to completion. However, since it is also known that Np(VII) will oxidize water, the following extrakinetic evidence is cited to support the premise that H$_2$O oxidation is not of importance under the experimental conditions of this study.

The gas produced when Np(VII) oxidized an aqueous solution of perchloric acid (normal abundance of oxygen isotopes in the solvent) contained only oxygen as determined by a mass spectrometric scan. When the experiment was repeated with enriched water, the enrichment in the oxygen evolved was 2.395 and 2.387 in duplicate runs. These values compared to the enrichment determined in the solvent of 2.351 and 2.354, respectively, demonstrate that all the oxygen produced comes from the solvent water of the spent reaction mixture. When the Np(VII) was reduced in a solution containing a 20-fold excess of Tl(I), the mass spectrometric evidence indicated that reaction 1 was the predominant if not sole reaction path.[11]

The analysis for the Tl(III) produced in reaction 1 was based on a semimicro modification of the EDTA titrimetric procedure developed by Yamamura.[9] Neither the precision nor accuracy of the results was at the desired confidence level, but the procedure resulted in a direct determination of the Tl(III) produced.[12] For example, from a solution with initial concentrations of [Np(VII)] = 17.4 × 10^{-4} M, [Np(VI)] = 1.65 × 10^{-4} M, [H$^+$] = 1.0 M, and [Tl(I)] = 4.51 × 10^{-2} M, the ratio of initial Np(VII)/Tl(III) produced was 2.03 ± 0.06. The uncertainty reflects the precision of replicate titrations as well as that obtained in the determination of the initial Np(VII).

Kinetic Studies. The variation of the apparent firstorder rate parameter k' as a function of initial Tl(I) concentration is presented in Table I. Based on this

Table I. Tl(I) Dependency of k' [a]

10^3[Tl(I)], M	10$^3 k'$, sec^{-1}	k, M^{-1} sec^{-1}
1.38	0.708	0.513 ± 0.015
3.52	1.80	0.511 ± 0.016
4.80	2.44	0.508 ± 0.007
8.28	4.23	0.511 ± 0.007
13.6	6.95	0.511 ± 0.007

[a] At 9.1°, I = 1.0 maintained with LiClO$_4$. Initial concentrations: [H$^+$] = 0.20 M, [Np(VII)] = 3.0 × 10^{-4} M, [Np(VI)] = 1.5 × 10^{-5} M. Uncertainties are standard deviations from replicate experiments.

(7) A. J. Zielen and D. Cohen, *J. Phys. Chem.*, **74**, 394 (1970).
(8) R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, **6**, 1795 (1967).
(9) S. S. Yamamura, *Anal. Chem.*, **40**, 1898 (1968).
(10) M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isotopes*, **5**, 233 (1959).

(11) The values obtained in the mass spectrometric measurements of the isotopic ratios are of doubtful significance because of the small quantity of noncondensable gases collected in these experiments.

(12) The procedure as developed in ref 8 is of suitable accuracy for usual analytical determinations. However, it was necessary to apply large "blank" corrections in the semimicro technique that was used. Such corrections were due to the presence of Np(VI) which was chelated by the EDTA and also oxidized the indicator.

Table II. [H⁺] and Temperature Dependencies of k^a

—9.1°—		—14.5°—		—19.3°—		—24.9°—	
[H⁺], M	k, $M^{-1}\,sec^{-1}$	[H⁺], M	k, $M^{-1}\,sec^{-1}$	[H⁺], M	k, $M^{-1}\,sec^{-1}$	[H⁺], M	k, $M^{-1}\,sec^{-1}$
0.919	2.01 ± 0.05	0.917	2.57 ± 0.07	0.931	3.32 ± 0.02	0.938	4.19 ± 0.06
0.655	1.50 ± 0.02	0.663	1.89 ± 0.02	0.691	2.45 ± 0.04	0.692	3.25 ± 0.05
0.437	1.03 ± 0.01	0.437	1.32 ± 0.01	0.449	1.69 ± 0.02	0.450	2.17 ± 0.04
0.200	0.510 ± 0.006	0.200	0.674 ± 0.008	0.207	0.845 ± 0.006	0.208	1.08 ± 0.03
0.128	0.330 ± 0.020						

ᵃ μ = 1.00 maintained with LiClO₄. Initial concentrations (M): 10⁴[Np(VII)] = 2.9–4.9, 10³[Tl(I)] = 1.38–8.38, [Np(VI)] = 5–20% [Np(VII)]. Each entry is the average of from two to six independent observations. Uncertainties are standard deviations from the mean. Measurements at 4400 Å.

data the empirical form of the rate law is

$$-d[Np(VII)]/dt = k[Np(VII)][Tl(I)] \qquad (4)$$

At 19.3° and an ionic strength of 1.0 with initial concentrations (M) of [H⁺] = 0.45, [Np(VII)] = 5 × 10⁻⁴, [Np(VI)] = 2 × 10⁻⁵, [Tl(I)] = 8.3 × 10⁻³, values for the second-order rate parameter k (M^{-1} sec⁻¹) were 1.71 and 1.66. Values calculated under the same experimental restraints for a second preparation of Tl(I) were 1.62 and 1.60. With the only variation an initial concentration of [Np(VI)] = 2.62 × 10⁻³ M, the rate parameters were 1.74 and 1.75. Under conditions as originally described except for the addition of 3.46 × 10⁻³ M Tl(III) initially, the rate parameter values were 1.72 and 1.75.

The variation of the empirical rate constant as a function of hydrogen ion concentration and temperature is summarized in Table II.

Under the same conditions described in Table II for 9.1° and [H⁺] = 0.200 M, additional experiments were performed at ionic strengths of 0.28, 1.93, and 2.86. The respective values calculated for k were 0.367 ± 0.020, 0.568 ± 0.040, and 0.501 ± 0.034.

The empirical dependence of the rate parameter with variation in hydrogen ion concentration, expressed in the usual manner, is

$$\ln k = \ln k_0 + n \ln [H^+] \qquad (5)$$

At 9.1, 14.5, 19.3, and 24.9°, respectively, values computed for ($\ln k_0$, n) were (0.7733 ± 0.0082, 0.896 ± 0.008), (0.9976 ± 0.0068, 0.869 ± 0.008), (1.250 ± 0.013, 0.907 ± 0.017), and (1.496 ± 0.008, 0.901 ± 0.008). The apparent energy of activation calculated from these rate parameters is 7.73 ± 0.42 kcal/mol.

The empirical formula of the activated complex for the predominant reaction path is defined as one molecule of Np(VII), one molecule of Tl(I), with one molecule more than the usual number of hydrogen ions associated with these species. A detailed structure of the activated complex is not presented because of a paucity of relevant information.[13]

The number of reasonable mechanisms that can be postulated for this reaction is severely limited by the form of the rate law. The first-order hydrogen ion dependence possibly reflects a preequilibrium involving the oxidant. The fact that a term [Np(VII)]·[H⁺] has previously been demonstrated in the oxidation of water by Np(VII) provides at least minimal support for such an interpretation.

In this system there is no evidence that Tl(II) is a kinetically important intermediate. Available data are not sufficient to distinguish between a reaction scheme of successive one-equivalent steps or a sequence such as

$$Np(VII) + Tl(I) \longrightarrow Np(V) + Tl(III)$$

$$Np(VII) + Np(V) \longrightarrow 2Np(VI) \qquad (rapid)$$
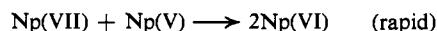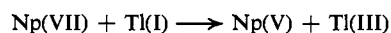
This precludes detailed comparison between the results presented here and those obtained in other kinetic studies of the oxidation of Tl(I).[14] The difference in the empirical forms of the rate laws may be due, at least in part, to the fact that Np(VII) is a more powerful oxidant than is Ce(IV), Co(III), or Ag(II).

(13) In addition to the usual uncertainty as to the number of molecules of water in the activated complex, there exists a limited amount of indirect evidence as to the structure of the oxidant.

(14) Studies of the oxidation of Tl(I) by Ce(IV) and Ag(II) were carried out in nitric acid media, and the mechanisms of the reactions may involve both NO₃ and Tl(II) as kinetically significant intermediates.⁵ The predominant path for the oxidation of Tl(I) by Co(III) is first order in each of the metal ions but independent of hydrogen ion, and qualitative evidence suggests that Tl(II) is an intermediate.