in equilibrium with its tautomer, XV. The latter is protonated at N-1 with the basic nitrogen not conjugated with $-COOCo^{III}$; it is therefore much less readily reduced.

Our evidence that remote attack in reduction by Cu^+ is confined, thus far, to a single heterocyclic species appears to reflect the circumstance that of the ligands studied, only the cinnolinecarboxylato system offers the combination of basicity, conjugation, and, most important, ready reducibility now thought to be necessary for electron passage through extended organic systems. Although cinnoline derivatives have long been known to be easily reduced,[26] no standard potentials appear to have been reported; however, as azobenzene-like bases, they may be assumed to have values of about +0.4 V,[11] *i.e.*, more strongly oxidizing than either pyridine systems (by 0.5–1.9 V[27]) or aldehydes and ketones (by at least 0.2 V.)

In summary, these attempts to compare the reducing action of Cu(I) and Cr(II) toward carboxylatocobalt(III) derivatives have met with the difficulty that most Co(III) complexes which are reduced at convenient rates by Cr^{2+} react immeasurably slowly with Cu^+, whereas many of those which react with measurable rates with Cu^+ are, under our conditions, reduced immeasurably rapidly by Cr^{2+}. Nevertheless, it has become clear that inner-sphere reduction paths are important for Cu^+ as well as for Cr^{2+}, and that the reactivity of both reducing centers may be strongly enhanced by chelation. Reduction by remote attack, although rare in the Cu(I) series, may be observed if the bridging ligand is judiciously chosen so that stronger basicity at the lead-in atom and greater ease of reducibility of the mediating path are made to compensate for the lower reducing potential of the metal center.

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(26) See, for example, P. W. Neber, G. Knoller, K. Herbst, and A. Trissler, *Justus Liebigs Ann. Chem.*, **471**, 113 (1929).

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Oxidation of Mercury(I) by Neptunium(VII)[1]

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Abstract: The empirical form of the rate law for the oxidation of Hg(I) by Np(VII) is $-d[\mathrm{Np(VII)}]/dt = k'\cdot[\mathrm{Np(VII)}][\mathrm{Hg(I)}]$, where $k' = k_1 + k_2[H^+]$. At 25° and $\mu = 1.0\ M$, $k_1 = 28.1 \pm 0.7\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_2 = 13.4 \pm 1.4\ M^{-2}\ \mathrm{sec}^{-1}$. The respective apparent activation energies are 12.2 ± 0.3 and 8.3 ± 0.8 kcal/mol. These results are consistent with Sykes' correlation of Hg(I) oxidation rate laws with the oxidation potential of the oxidant. Arguments are presented which indicate that, at least for the k_2 path, the rate of Np(VII) reduction is not sensitive to the nature of the reductant.

The rate laws determined for the oxidation of mercurous to mercuric ions in perchlorate media have, as noted by Sykes,[4] two forms which seem to correlate with the oxidation potential of the oxidant. The salient difference is the presence of a term in the rate law inverse in mercuric ion concentration when the relatively weak oxidants Tl(III)[5] and Mn(III)[6] are used. No such term appears when the oxidant is Co(III)[7] or Ag(II).[8] Among the considerations that prompted this investigation was the desire to test Sykes' correlation for a stronger oxidizing agent than Co(III) or Ag(III); Np(VII) is such a reagent, previous work having shown that it rapidly and quantitatively oxidizes Co(II) and Ag(I).[9] In addition it was desired to increase the limited amount of information available on the dynamic chemical behavior of the very strong oxidant Np(VII) in acid solution, detailed studies having been reported only for the oxidation of Tl(I)[10] and water[9] by this reagent. Thus, this paper presents the results obtained in a kinetic study of the reaction

$$Hg_2^{2+} + 2\mathrm{Np(VII)} = 2Hg^{2+} + 2\mathrm{Np(VI)} \qquad (1)$$

in acidic aqueous media.

Experimental Section

Reagents. Mercuric perchlorate stock solutions were prepared by dissolution of recrystallized $Hg(ClO_4)_2$ which had been prepared

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from mercuric oxide[11] and perchloric acid. The solution was standardized by titration with KCNS and the acidity determined by absorbing an aliquot of the solution on a cation-exchange column and titrating the eluent with standardized NaOH. A portion of this solution was shaken vigorously with metallic mercury to prepare the mercurous perchlorate stock solutions. The preparation and standardization of the Np(VII) solutions and all other reagents employed have been previously summarized.[10]

Procedures. A Cary Model 14MR recording spectrophotometer with a thermostated cell compartment was used for the majority of the spectrophotometric determinations. A limited number of kinetic studies were performed with a Cary Model 16 recording spectrophotometer also equipped with a thermostated cell compartment. In the kinetic studies an aliquot of the basic Np(VII) solution, equilibrated at a temperature sufficiently lower than the working temperature to compensate for the heat of neutralization, was rapidly injected into a spectrophotometer cell containing an acidic solution of reductant and other reagents, and the absorbance was recorded as a function of time at 4400 Å. All kinetic experiments were analyzed for periods up to at least 95% of completion. Initial estimates of the rate parameters were obtained from graphical treatment of the absorptivity *vs.* time data in the usual integrated form of the second-order rate law. Values reported for the rate parameters were obtained from a least-squares adjustment of the data (20–30 OD, *t* data points per experiment) for the functional form previously described.[12]

The absorptivity data for a given experiment were reproduced by the two-parameter adjustment to within ≤ 0.003 OD unit. Precision indices estimated for the rate parameter (based on external consistency) ranged from 0.1 to 0.8%.

The estimated value for the potential of the Np(VII)|Np(VI) couple[9] plus that measured for the Hg(II)|Hg(I) couple provide necessary evidence that reaction 1 will go to completion. To demonstrate that other possible reactions [such as the oxidation of water by Np(VII)] are not important, six independent measurements of the ratio $\Delta[\mathrm{Np(VII)}]/\Delta[\mathrm{Hg_2}^{2+}]$ were made, with initial concentrations of the reactants [and Hg(II)] similar to those employed in the kinetic studies. The average value determined for the ratio was 2.001 ± 0.038 at the 95% confidence level.

Results

A solution of mercurous perchlorate in perchloric acid, stored over metallic mercury, has concentrations of $\mathrm{Hg_2}^{2+}$, Hg(II), and Hg(0) fixed by the equilibria

$$\mathrm{Hg_{solid}} = \mathrm{Hg_{soln}} \tag{2}$$

$$\mathrm{Hg_2}^{2+} = \mathrm{Hg(II)} + \mathrm{Hg(0)} \tag{3}$$

Two solutions (both 0.12 *M* in mercurous perchlorate, 1.0 *M* in perchloric acid, total volume of 25 ml) were stored over metallic mercury; one was stored over *ca.* 1 ml of Hg(0) and the other over 10 μl of Hg(0). Aliquots of these solutions were used for a series of kinetic experiments over a 10-day period. At 25°, $\mu = 0.11$ *M*, $[\mathrm{H^+}] = 0.06$ *M*, with initial concentrations of Np(VII) = $(5.3\text{–}6.6) \times 10^{-4}$ *M*, Np(VI) = $(2.0\text{–}7.0) \times 10^{-5}$ *M*, Hg(I)[13] = 5.9×10^{-4} *M*, values calculated for the second-order rate parameter ranged from 50 to 30 M^{-1} sec^{-1}. In addition, the initial portion (up to 20%) of 6 out of the 12 rate plots exhibited deviation from a second-order rate law.

These difficulties were circumvented by the use of mixed Hg(II)–Hg(I) stock solutions.[14] Aliquots of a solution (0.119 *M* mercurous perchlorate, 0.239 *M* mercuric perchlorate and 1.0 M perchloric acid) were used in replicate kinetic experiments over a 14-day period. Under the same experimental constraints as specified above (plus an initial concentration of Hg(II) = $11.8 \times 10^{-4}M$) the average value calculated for the rate parameter k' was 22.9 ± 0.8 M^{-1} sec^{-1}. The uncertainty is at the 95% confidence level, and values of the individual determinations are 22.8, 22.2, 23.1, 24.2, 22.8, and 22.3 M^{-1} sec^{-1}. For a duplicate preparation of the Hg(II)–Hg(I) stock used over a 5-day period, a mean value of $k' = 23.1 \pm 0.6$ M^{-1} sec^{-1} was determined. Thus the mixed Hg(I)–Hg(II) stock solutions are stable over long periods of time and give consistent and constant rates of reaction, as opposed to Hg(I)–Hg(0) stocks which gave inconsistent and variable rates.

As pointed out earlier, the integrated form of the second-order rate law was found adequate to correlate the kinetic data. The information presented in Table I delineates the initial concentrations of products and reactants studied.

Table I. Effect of Metal Ion Concentrations on the Hg(I)–NP(VII) Reaction[a]

10^4[Hg(I)], *M*	10^4[Hg(II)], *M*	10^4[Np(VII)], *M*	k^1, M^{-1} sec^{-1}
5.90	11.8	5.40	36.9
6.16	12.4	0.626	38.0
6.29	12.6	6.29	37.4[b]
6.29	391.2	6.29	36.6
9.48	19.0	0.626	38.0
14.2	28.5	0.626	36.8
15.9	31.9	11.1	35.6[c]
15.9	31.9	13.3	31.1
19.0	38.1	0.626	34.4
23.7	47.6	0.626	35.9

[a] 25°, $\mu = 1.0$ maintained with $\mathrm{LiClO_4}$, $[\mathrm{H^+}] = 0.44$. Initial [Np(VI)] = 5–10% of initial [Np(VII)] listed in the table. Values of k' are averages of two to three determinations. [b] A second source of mercuric oxide used for the preparation of the Hg(II) and Hg(I) stock solutions. [c] Initial [Np(VI)] = 65.3×10^{-4} *M*.

From the data in Table I, the average value calculated for the rate parameter is $k' = 36.1 \pm 1.6$ (95% confidence level) M^{-1} sec^{-1}. Within the specified limits, these data demonstrate that the rate parameter is independent of either the source of mercuric oxide used to prepare the Hg(I) and Hg(II) solutions or the concentrations of reactants and products. It should also be noted that a dozen different preparations of the Np(VII) stock solutions were used in these experiments. Independent experiments also showed that no reaction between Np(VI) and Hg(I) could be detected under the conditions used in this work.

Data for the variation of the rate parameter as a function of hydrogen ion concentration and temperature are summarized in Table II. The change of the rate parameter as the hydrogen ion concentration is varied can be adequately correlated at each temperature by the expression

$$k' = a + b[\mathrm{H^+}] \tag{4}$$

A least-squares adjustment of the data[15] in terms of (4) produced values for *a* and *b* of 5.20 ± 0.09, 4.26 ± 0.22; 8.39 ± 0.27, 5.82 ± 0.56; 16.08 ± 0.16, 8.18 ± 0.39;

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[11] One sample of mercuric oxide (yellow) was from Alfa Inorganics and the second (red) was Mallinckrodt analytical reagent grade.

[12] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **89**, 1096 (1967).

[13] The symbol Hg(I) is defined to be $\mathrm{Hg_2}^{2+}$ + hydrolyzed forms.

[14] E. L. King, University of Colorado, personal communication, 1970.

[15] The individual values of the rate parameters, with weights estimated on the basis of the calculated standard deviations, were used in this adjustment. There were 11 data points for the set at 1.7°, 49 at 25°, and 12 at each of the other temperatures.

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

1.7°		9.0°		17.0°		25.0°		35.0°	
[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}	[H$^+$], M	k', M^{-1} sec^{-1}
0.856	8.87	0.855	13.1	0.855	22.9	0.952	41.7	0.942	77.9
0.596	7.77	0.595	11.9	0.595	21.0	0.741	37.4	0.788	75.1
0.471	7.33	0.470	11.8	0.470	20.0	0.440	36.1	0.588	70.5
0.296	6.37	0.295	10.2	0.295	18.5	0.298	29.8	0.388	68.6
0.196	6.12	0.195	9.61	0.195	17.4	0.123	27.9	0.188	62.0
0.096	5.58	0.095	8.48	0.095	16.8	0.023	26.2	0.078	57.4

[a] μ = 1.0 maintained with LiClO$_4$. Values of k' are averages of replicate determinations. Initial concentrations cover the same range as noted in Table I.

28.13 ± 0.73, 13.4 ± 1.4; and 57.16 ± 0.83, 22.98 ± 1.60 at 1.7, 9.0, 17.0, 25.0, and 35.0°, respectively.

One interpretation of these parameters is that they are a measure of parallel reaction paths.[16] Based upon this interpretation apparent energies of activation calculated for the hydrogen-ion-independent and -dependent paths respectively are 12.2 ± 0.3 and 8.3 ± 0.8 kcal/mol.

Table III summarizes the results obtained for the effect of varying the concentration of the supporting electrolytes lithium perchlorate or sodium perchlorate at a constant initial acidity. These results provide no compelling evidence for a significant reaction path that involves a perchlorate complex of either reactant.

Table III. Effect of Ionic Strength Variation[a]

k', M^{-1} sec^{-1}	μ (LiClO$_4$)	k', M^{-1} sec^{-1}	μ (NaClO$_4$)
24.4	0.30	25.1	0.63
26.4	0.43	26.9	1.59
27.3	0.56	27.8	3.52
30.0	0.82	27.9	4.49
32.8	1.08	29.7	5.45
34.0	1.34	32.1	6.41
34.2	1.87		
38.7	3.70		

[a] 25°, [H$^+$] = 0.090 M. Initial concentrations (M) are: $10^4 \cdot$ [Np(VII)] = 3.85, 10^4[Hg(I)] = 6.36, 10^4[Hg(II)] = 12.8. Values of k' are averages of two to three determinations.

Discussion

The use of mixed Hg(I)–Hg(II) stock solutions must be rationalized without violating the relevant thermodynamic relationships, eq 2 and 3. An explanation, other than invoking a ubiqutous impurity scavenged by the added mercuric ions, is provided by the suggestion[17] that colloidal suspensions of metallic mercury are readily formed during the preparation of Hg(I) stock solutions. Colloidal Hg(0) could catalyze or interfere with the Np(VII)–Hg(I) reaction by a variety of mechanisms. Excess Hg(II) in the stock solutions eliminates this problem by converting colloidal Hg(0) to Hg(I) *via* reaction 3.

The term in the rate law first order in hydrogen ion may reflect a preequilibrium involving the oxidant. This is consistent with the observation of such a term in the oxidation of water[9] and Tl(I)[10] by NP(VII). The value of E_A = 7.7 ± 0.4 kcal/mol determined for this term in the latter system is the same, within the experimental uncertainties, as the value of E_A = 8.3 ± 0.8 kcal/mol obtained for the hydrogen-ion-dependent path in the present study. The values for the rate constants differ by a factor of *ca.* 3. These facts suggest that the energetics of oxidations by Np(VII) *via* the hydrogen-ion-dependent path are not strongly influenced by the nature of the reductant.

There is a term in the empirical form of the rate law for the oxidation of Hg(I) by Co(II)[7] that defines an activated complex which consists of one molecule of mercury(I) dimer and one molecule of cobalt(III). A value for k = 0.14 M^{-1} sec^{-1} at 25° may be calculated for this path.[18] The value for the path in which the activated complex consists of one molecule of the mercury(I) dimer and one molecule of neptunium(VII) is k = 28 M^{-1} sec^{-1}. This increase in rate arises from the difference in ΔH^* for the two reactions [22.1 kcal/mol for Co(III) and 11.6 kcal/mol for Np(VII)] since the ΔS^* term operates in the opposite direction [9.6 eu for Co(III) and −13.0 for Np(VII)].[19] This then implies that detailed structures of the activated complexes contribute significantly to the observed rate differences.

The above comparison indicates there is no compelling reason to indicate that the increase in rate is attributable solely to the difference in potential of the oxidants. However, as Sykes[4] has pointed out, for the limited number of Hg(I) oxidations that have been studied there seems to be a correlation of empirical rate law with oxidation potential. Our results agree with this correlation. Thus, the empirical rate laws contain no term inverse in Hg(II) when Co(III), Ag(II), or Np(VII) ($E°$ values of −1.84, −1.98, and more negative than −2.0 V, respectively) are used as oxidants. Such a term has been observed in oxidations with Mn(III) and Tl(III) ($E°$ values of −1.15 and −1.25 V, respectively).

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(16) More than one parameter is required for an adequate correlation of the variation of k' with change in hydrogen ion concentration. The two-parameter adjustment of the data is consistent with the principle, "Entia non sunt multiplicanda praeter necessitatem" (William of Ockham). The interpretation that these parameters describe parallel reaction paths is not necessarily unique.

(17) J. Halpern, University of Chicago, personal communication, 1970.

(18) Calculated from the parameters of the Arrhenius plot presented in ref 6. It should be noted that this involves an extrapolation, since the highest temperature at which rate parameters were determined was 20°. This slight extrapolation and the differences in ionic media should not seriously affect the comparisons.

(19) T. W. Newton, Los Alamos Scientific Laboratories, personal communication, 1971. A recalculation of the Hg(I)–Co(III) data resulted in ΔS^* = 0 ± 5 eu and ΔH^* = 19.2 ± 1.5 kcal/mol for the path independent of [H$^+$]. These revised values do not affect the above argument.