long enough to allow the observation of an epr signal at room temperature. The longitudinal relaxation time for U^{5+} having eightfold cubic coordination is short due to the proximity of the lower Γ_7 and Γ_8 levels.

3. The crystal field parameters for U^{5+} in cubic oxides and fluorides are very similar.

4. Considerable covalency exists in the Γ_4 and Γ_5 orbitals of U^{5+} in uranium doped $LiNbO_3$.

Registry No. Uranium, 7440-61-1; $LiNbO_3$, 12031-63-9; $LiTaO_3$, 12031-66-2; $BiNbO_4$, 12272-28-5; Na_3UF_8, 22991-91-9.

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Kinetic Study of the Oxidation of *p*-Hydroquinone and *p*-Toluhydroquinone by Neptunium(VI) in Aqueous Perchlorate Media[1]

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The oxidation of *p*-hydroquinone and *p*-toluhydroquinone by Np(VI) in aqueous perchlorate media can be described by the empirical rate law $-d[\mathrm{Np(VI)}]/dt = k[\mathrm{Np(VI)}][H_2Q]$ where H_2Q is the appropriate hydroquinone. At 25° and $I = 1.00$ values determined for the rate parameters were $(4.52 \pm 0.24) \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ and $(6.26 \pm 0.33) \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$, respectively. No apparent effect of hydrogen ion was noted over the range $0.05 \leqslant [H^+] \leqslant 1.00\ M$. Values calculated for ΔH^* (kcal/mol), ΔS^* (eu) were $8.17 \pm 0.34, -9.8 \pm 1.1$ and $9.17 \pm 0.29, -5.81 \pm 0.97$ for the *p*-hydroquinone- and *p*-toluhydroquinone-Np(VI) reactions, respectively. The results are discussed in terms of Marcus' cross-reaction equation for electron-transfer reactions.

The oxidation of *p*-hydroquinone to the quinone is a reversible two-electron process.[4] Previous kinetic studies for the oxidation of this reactant with 1-,[5] 2-,[6] and 3-equiv[7] acceptors have been reported. The pertinent results of these investigations appear to be as follows: (a) the empirical form of the rate law is first order in each of the reactants; (b) there is no apparent relation between the kinetic parameters and the redox potentials of the oxidants as has been noted for the oxidation of formic acid.[8] However, Marcus[9a] has successfully demonstrated that an electron-transfer theory (based on first principles) is applicable for the oxidation of a series of hydroquinones by ferric ions. In the present investigation the more readily calculated Marcus cross relation is utilized to interpret the results of the oxidation of hydroquinone and toluhydroquinone by the 1-equiv oxidant Np(VI).

Experimental Section

The preparation and standardization of perchloric acid, lithium perchlorate, and neptunium(VI) perchlorate solutions have been previously described.[10] The hydroquinones and quinones (Eastman) were purified by double- and single-vacuum sublimations, respectively. The melting points determined for the products were as follows: *p*-hydroquinone, 171-172°; *p*-benzoquinone, 115-116°; *p*-toluhydroquinone, 125-126°; *p*-toluquinone, 66-67°. All solutions were prepared in triply distilled water that had been deoxygenated with argon and those containing the organic reagents were protected from exposure to light.

A Cary Model 14 recording spectrophotometer was used to determine molar extinction coefficients and reaction stoichiometries. A Durrum stopped-flow spectrophotometer, Model D-110, with a storage oscilloscope was used for the kinetic studies. From photographs of the oscilloscope screen 15-20 values of A,t were read for each experiment with triplicate replications. 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 for the functional form previously described.[11] The two-parameter expression reproduced the observed absorptivities to ±0.003 unit. The standard deviation computed for the rate parameters (based on external consistency) ranged from 1 to 4%.

Results and Discussion

For the reactions

$$2\mathrm{Np(VI)} + H_2Q = 2\mathrm{Np(V)} + Q + 2H^+ \tag{1}$$

$$2\mathrm{Np(VI)} + CH_3QH_2 = 2\mathrm{Np(V)} + CH_3Q + 2H^+ \tag{2}$$

the values of the potentials for the couples Np(V)-Np(VI) (−1.14 V),[12] H_2Q-Q (−0.699 V),[4] and CH_3QH_2-CH_3Q (−0.645 V)[4] provide necessary evidence that the reactions will go to completion. The products Np(V) and the quinones were identified spectrophotometrically.

At 25° and 1.0 *M* $HClO_4$, for the initial concentrations $[\mathrm{Np(VI)}] = 1.16 \times 10^{-3}$ and $3.50 \times 10^{-3}\ M$ and [hydroquinone] $= 4.96 \times 10^{-4}$ and $9.92 \times 10^{-4}\ M$ the average value determined for the moles of Np(V) produced per mole of hydroquinone consumed was 1.998 ± 0.018 (95% confidence level, six independent determinations). At the same tem-

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[2] Participant in the Argonne National Laboratory 1972 Summer Student Training Program.

[3] Guest Scientist from the Chemistry Department, Rosary College, River Forest, Ill.

[4] D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic Press, New York, N. Y., 1961.

[5] (a) J. H. Baxendale and H. R. Hardy, *Trans. Faraday. Soc.*, 50, 808 (1954); (b) G. Davies and K. Kustin, *ibid.*, 65, 1630 (1969); (c) G. Davies and K. O. Watkins, *J. Phys. Chem.*, 74, 3388 (1970).

[6] E. T. Kaiser and S. W. Weidman, *J. Amer. Chem. Soc.*, 86, 4354 (1964).

[7] J. C. Sullivan and J. E. French, *J. Amer. Chem. Soc.*, 87, 5380 (1965).

[8] M. Thompson and J. C. Sullivan, *Inorg. Chem.*, 11, 1707 (1972), and references cited therein.

[9] (a) R. A. Marcus, *J. Chem. Phys.*, 26, 872 (1957); (b) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964).

[10] J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *J. Amer. Chem. Soc.*, 82, 5288 (1960).

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

[12] A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, 66, 1065 (1962).

perature and acidity the ratio with toluhydroquinone was 2.024 ± 0.018 (95% confidence level, five independent determinations) where respective initial Np(VI) and hydroquinone concentrations were 2.10 × 10^{-3}, 1.05 × 10^{-3} and 5.09 × 10^{-4}, 2.54 × 10^{-4} M.

The results of the kinetic studies are summarized in Tables I and II. From these data aspects that are common to both systems include the following: (a) the empirical composition of the activated complex consists of one molecule of Np(VI) and one molecule of the hydroquinone (plus an undetermined number of water molecules); (b) there is no indication that a hydrogen ion dependent path is of kinetic significance over the concentration range 1.00-0.05 M; there is no evidence for the kinetic significance of a semiquinone radical (no effect of products on rate parameter); there is no compelling evidence that dissolved oxygen (at the normal concentration level) has an effect on the rate of the reaction.

The values calculated for ΔH^*, ΔS^* are 8.17 ± 0.34 kcal/mol, −9.8 ± 1.1 eu for reaction 1 and 9.17 ± 0.29 kcal/mol, −5.81 ± 0.97 eu for reaction 2.[13]

The empirical form of the rate laws in the present study provide no evidence that the semiquinone intermediate is of kinetic significance. For all of the hydroquinone oxidation reactions that have been cited it is of interest to note that only with the 1-equiv acceptor, Fe(III), is such evidence presented. This may be a reflection of the importance of the redox potential of the oxidant. If such is the case, the recent observation of Newton[14] for the oxidant Pu(VI) (*i.e.*, a term inverse in Pu(V) in the empirical rate law) points out that small changes in the redox potentials may bring about marked changes in the kinetic path for the oxidation of hydroquinone.

Marcus has demonstrated that it is possible to calculate the value of ΔF^* for the oxidation of a series of hydroquinones by Fe(III). Since the cross relations[9b] provide an alternate viable approach to an understanding of electron-transfer reactions (and the relevant data are available) this approach is presented for the systems discussed.

The empirical form of the rate law for the oxidation of both hydroquinones by Np(VI) is consistent with the reaction

$$\mathrm{Np(VI)} + \mathrm{H_2Q} \rightarrow \mathrm{Np(V)} + \mathrm{H_2Q^+} \qquad (3)$$

as rate determining and subsequent rapid steps which yield the observed stoichiometry. The value of $\Delta F°$ for reaction 3 may be estimated from the known potentials for the reactants of (1) and (2) plus the equilibrium constants of reactions 4 and 5.[15] Then for (3), $\Delta F° = -RT \ln [(K_1K_4)^{1/2}K_5]$.

$$\mathrm{H_2Q} + \mathrm{Q} = 2\mathrm{HQ} \quad (\Delta F° = 2.3 \text{ kcal/mol}) \qquad (4)$$

$$\mathrm{HQ} + \mathrm{H^+} = \mathrm{H_2Q^+} \quad (\Delta F° = 1.4 \text{ kcal/mol}) \qquad (5)$$

The results obtained are presented in Table III along with values calculated for other systems where the relevant data are available. In addition, there are tabulated values for S^* of the activated complexes in the systems where the appropriate data could be obtained.

Table I. Rate Parameters for the Reaction Np(VI) + *p*-Hydroquinone[a]

$10^3[\mathrm{Np(VI)}]_0, M$	$10^4[\mathrm{H_2Q}]_0, M$	$10^{-4}k$,[b] M^{-1} sec^{-1}
1.00–2.69	4.87–34.9	4.52 ± 0.24[c]
1.36	10.5	4.74 ± 0.32[d]
1.36	10.5	4.76 ± 0.16[e]
1.08	10.6	4.94 ± 0.49[f]
1.40	13.4	4.23 ± 0.26[g]
1.11	10.3–21.2	2.92 ± 0.14[h]
0.99	10.0	7.59 ± 0.67[i]

[a] 25°, 1.00 M $\mathrm{HClO_4}$, 3500 Å. [b] Average value of 3–8 independent determinations. Uncertainties calculated for 95% confidence level. [c] Average of 20 individual determinations. $0.29 \leqslant [\mathrm{Np(VI)}]_0/[\mathrm{H_2Q}]_0 \leqslant 4.6$. [d] $[\mathrm{Np(V)}]_0 = 3.46 \times 10^{-3}$ M. [e] [*p*-benzoquinone]$_0$ = 48.8 × 10^{-4} M. [f] Solutions not deoxygenated. [g] 0.048 M $\mathrm{HClO_4}$; $I = 1.00$ M maintained with $\mathrm{LiClO_4}$. [h] 15.0°. [i] 35.0°.

Table II. Rate Parameters for the Reaction Np(VI) + *p*-Toluhydroquinone[a]

$10^3[\mathrm{Np(VI)}]_0, M$	$10^3[\mathrm{CH_3H_2Q}]_0, M$	$10^{-4}k$,[b] M^{-1} sec^{-1}
0.207–2.44	0.254–1.38	6.26 ± 0.33[c]
1.06	1.02	6.34 ± 0.45[d]
1.08	1.08	6.16 ± 0.42[e]
1.02	1.01	6.12 ± 0.32[f]
1.07	1.02	6.44 ± 0.38[g]
1.12	1.01–2.01	3.80 ± 0.10[h]
0.99_5	1.00	10.94 ± 0.79[i]

[a] 25°, 1.00 M $\mathrm{HClO_4}$, 3400 Å. [b] Average of 3–6 independent determinations. Uncertainties calculated for the 95% confidence level. [c] Average of 38 independent determinations. $0.30 \leqslant [\mathrm{Np(VI)}]_0/[\mathrm{CH_3H_2Q}]_0 \leqslant 4.1$. [d] $[\mathrm{Np(V)}]_0 = 4.20 \times 10^{-3}$ M. [e] Solutions not deoxygenated. [f] 3200 Å. [g] $[\mathrm{H^+}] = 0.044$ M; $I =$ 1.0 maintained with $\mathrm{LiClO_4}$. [h] 15.0°. [i] 35.0°.

Table III

Oxidizing agent	$\Delta F°$,[a] kcal/mol	$\Delta F^*_{\mathrm{exptl}}$, kcal/mol	$\Delta F^*_{\mathrm{calcd}}$,[e] kcal/mol	S^*,[f] cal/deg mol
$\mathrm{M}^{n+} + \mathrm{H_2Q} = \mathrm{M}^{(n-1)+} + \mathrm{H_2Q^+}$				
Co(III)	−23.8	+12.9[b]	+5.4	−7.7
Mn(III)	−16.2	+12.4[c]	+10.9	
Np(VI)	−6.7	+11.1	+11.3	+17.5
Fe(III)	+1.59	+14.1[d]	+13.9	−4.3
$\mathrm{M}^{n+} + \mathrm{CH_3H_2Q} = \mathrm{M}^{(n-1)+} + \mathrm{CH_3H_2Q^+}$				
Np(VI)	−8.0	+10.9	+10.7	
Fe(III)	+0.32	+13.2[d]	+13.2	

[a] Values for Np(V)–Np(VI) couple from ref 12. Co(II)–Co(III) and Mn(II)–Mn(III) values from W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, New York, N. Y., 1952. Equilibrium constants for Fe(III) + hydroquinones from ref 5a. Values for hydroquinone–quinone couples from ref 4. [b] Reference 5c. [c] Reference 5b. [d] Calculated using k_{redox} of ref 5a and $K_{\mathrm{hydrolysis}} = 1.64 \times 10^{-3}$: R. M. Milburn, *J. Amer. Chem. Soc.*, 79, 537 (1957). [e] $\Delta F^*_{\mathrm{calcd}} = {}^1/_2(\Delta F_1{}^* + \Delta F_2{}^* + \Delta F_{1,2}{}°) + (\Delta F_{1,2}{}°)^2/8(\Delta F_1{}^* + \Delta F_2{}^*)$. Values of $\Delta F_2{}^* = 14.0$ kcal/mol estimated from ref 15. Values for $\Delta F_1{}^*$: Np(V)–Np(VI) = 14.85 kcal/mol, D. Cohen, J. C. Sullivan, and J. C. Hindman, *J. Amer. Chem. Soc.*, 76, 352 (1954); Co(II)–Co(III) = 15.9 kcal/mol, H. S. Habib and J. P. Hunt, *ibid.*, 88, 1668 (1966) (data at $\mu = 3.0$ extrapolated to 25° give $k_{\mathrm{exchange}} = 13.2$ M^{-1} sec^{-1}); Mn(II)–Mn(III) = 22.2 kcal/mol, H. Diebler and N. Sutin, *J. Phys. Chem.*, 68, 174 (1964); $\mathrm{Fe^{2+}}$–$\mathrm{Fe(OH)^{2+}}$ = 12.2 kcal/mol, J. Silverman and R. W. Dodson, *ibid.*, 56, 846 (1952). [f] Value of $S°_{\mathrm{H_2Q,aq}} = 47.3$ cal/deg mol, G. Pilcher and L. E. Sutton, *J. Chem. Soc.*, 2695 (1956); $S°_{\mathrm{H_2Q(s)}} =$ 33 cal/deg mol, $\Delta H_{\mathrm{soln}} = 4.69$ kcal/mol (solubility 0.494 mol/l.). Values of $S°_{\mathrm{aq}}$: for Fe(III), −75.5 cal/deg mol; for Co(III), −73 cal/deg mol, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-4** (1969); $S°_{\mathrm{Np(VI),aq}} = -20$ cal/deg mol, J. R. Brandt and J. W. Cobble, *Inorg. Chem.*, 9, 912 (1970).

The difference between observed and calculated values of ΔF^* is greatest when the oxidant is hexaaquocobalt(III). A rationale of the apparent failure of the Marcus cross relation when one of the reactants is Co(III) has been presented

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[13] The functional form utilized is $k = 2.08365 \times 10^{10}T \times e^{-\Delta H^*/1.98717T}e^{\Delta S^*/1.98717}$ with 42 data points for the *p*-hydroquinone–Np(VI) system and 52 for the *p*-toluhydroquinone–Np(VI) system. Weights were assigned based on the standard deviations of the computed rate parameters.

[14] T. W. Newton, Los Alamos Scientific Laboratory, personal communication, 1972.

[15] J. M. Hale and R. Parsons, *Trans. Faraday Soc.*, 59, 1429 (1963).

(with voluminous documentation) by Rillema and Endicott[16] so the present result is not unexpected. When Mn(III) is the oxidant, the agreement is rather poor—but this is the only system considered in which the metal ion exchange reaction has not been directly measured. For the other entries it is evident that there is a reasonable correlation between the theoretical and experimental values.

The result that the absolute values calculated for ΔF^* in the oxidation of benzo- and toluhydroquinones by Np(VI) and Fe(III) are in such good agreement with experimental results may be, in part, fortuitous. This is evident for the systems in which Fe(III) is the oxidant. For these cases there is an ambiguity in the mechanism that arises from the term in the rate law inverse in hydrogen ion concentration. Marcus[9] assumed that this term was a reflection of the preequilibrium $QH_2 = QH^- + H^+$. The differences $\Delta F^*_{calcd} - \Delta F^*_{exptl}$ he reported were 1.1 and 1.6 kcal/mol for the benzo- and toluhydroquinones, respectively. In spite of some reservations, however, it appears that the Marcus cross relation concept may be applicable to the class of reversible organic redox reactions.

Registry No. Neptunium, 7439-99-8; H_2Q, 123-31-9; CH_3H_2Q, 95-71-6.

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[16] D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, 11, 2361 (1972).

Contribution from the Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720

Crystal Structure of *l*-Tris(1,10-phenathroline)iron(II) Bis(antimony(III) *d*-tartrate) Octahydrate[1]

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The compound *l*-tris(1,10-phenanthroline)iron(II) bis(antimony(III) *d*-tartrate) octahydrate, $Fe(C_{12}N_2H_8)_3(C_4O_6H_2Sb)_2 \cdot 8H_2O$, crystallizes in the trigonal space group $P3_221$. Three formula units occupy a unit cell of dimensions $a = 18.58$ (2) and $c = 12.04$ (2) Å. Intensities were measured by the stationary-crystal, stationary-counter technique using a scintillation counter and Mo Kα X-rays. The structure was refined by full-matrix least-squares to a conventional R factor of 0.048 for 1600 reflections whose intensities were observed to be greater than their estimated standard deviations. The structure consists of a ferrous tris(1,10-phenanthroline) cation and a bis(antimonous *d*-tartrate) anion. The iron atom lies on a twofold axis and is octahedrally coordinated to the nitrogen atoms of the three phenanthroline groups at an average distance of 1.97 (1) Å. The antimony tartrate complex is a dimer in which each of the two antimony atoms is coordinated to four oxygen atoms of the tartrate; Sb–O distances average 1.94 (1) and 2.13 (2) Å, respectively, for alcohol and carboxyl oxygen atoms. The absolute configurations of the complex ions were determined by the anomalous dispersion effect. The cation Λ-$(-)_{589}[Fe(phen)_3]^{2+}$, phen = phenanthroline, has a pseudo-threefold axis and resembles a three-bladed left-handed propeller, the blades being the planar phenanthroline ligands. The configuration of the *d*-tartrate in the $[Sb(+)tart]_2{}^{2-}$ ion is in agreement with previous determinations.

Introduction

Ferrous ion and 1,10-phenanthroline make octahedral complexes which exist in enantiomers that can be resolved by precipitation of the *l* isomer with antimony *d*-tartrate as shown by Dwyer and Gyarfas.[2] Professor R. E. Powell of this University provided us with crystals of this precipitate and suggested that we determine the structure and absolute configuration by X-ray diffraction to permit a check of methods of configuration determination by theoretical analysis of the optical properties. This paper reports such a study.[3] We show that the $(-)[Fe(phen)_3]^{2+}$ which precipitates with *d*-tartrate is in the conformation of a left-handed propeller, in agreement with the assignment of McCaffery, Mason, and Norman[4] on the basis of analysis of circular dichroism, thus providing a confirmation of the validity of that method.

Another result of this study is that the antimony tartrate, which has been formulated classically in tartar emetic and similar salts as "antimonyl tartrate," $SbO(C_4H_4O_6)^-$, or sometimes[5] as $H_2OSb(C_4H_2O_6)^-$, exists in this crystal as a cyclic dimer of composition $((C_4H_2O_6)Sb)_2{}^{2-}$. In this complex Sb(III) has displaced hydrogen from the alcohol groups as well as the carboxyl groups and is complexed only by tartrate. The same complex anion has been found by Kiosse, Golovastikov, and Belov[6] in *dl*-$(NH_4)_2Sb_2(C_4H_2O_6)_2 \cdot 4H_2O$, by Kiosse, Golovastikov, Ablov, and Belov[7] in *d*-$(NH_4)_2Sb_2(C_4H_2O_6)_2 \cdot 3H_2O$, and by Kamenar, Grdenic, and Prout[8] in *dl*-$K_2Sb_2(C_4H_2O_6)_2 \cdot 3H_2O$. Earlier reports[9] of a different structure for this anion in the *d,l* K salt have been revised,[8] and the dimer structure is the only one known in crystals.

Experimental Section

The sample of *l*-ferrous tris(1,10-phenanthroline) bis(antimonous *d*-tartrate) octahydrate consisted of crystals in the form of small deep red needles. A fragment ~0.1 mm in diameter and ~0.3 mm in length was glued to a Pyrex fiber, and subsequent Weissenberg photography showed the needle axis to be *c* of a trigonal unit cell. Cell dimensions and intensities were measured with a manual General

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

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[6] G. A. Kiosse, N. I. Golovastikov, and N. V. Belov, *Dokl. Akad. Nauk SSSR*, 155, 545 (1964).

[7] G. A. Kiosse, N. I. Golovastikov, A. V. Ablov, and N. V. Belov, *Dokl. Akad. Nauk SSSR*, 177, 329 (1967).

[8] B. Kamenar, D. Grdenic, and C. K. Prout, *Acta Crystallogr., Sect. B*, 26, 181 (1970).

[9] D. Grdenic and B. Kamenar, *Acta Crystallogr.*, 16, A40 (1963); 19, 197 (1965).