$[(NH_3)_5CoOP(O)(OH)OC_6H_4OH]^{2+}$ and k_A to the reaction of the corresponding monovalent cation, derived from the ionization of the phosphate O–H group. The pK_{AH} value obtained from the kinetic measurements at 70 °C, $\sum[ClO_4^-] = 1.0$ M, is smaller than pK_1 calculated from the 275-nm spectrophotometric titration at 25 °C, $\sum[ClO_4^-] = 0.05$ M, by about 1.0 unit. This difference appears reasonable, considering the enhancements in acid strength expected with increasing temperature and ionic strength.

The rate constants k_A and k_{AH} are comparable to those reported for the aquation of $[(NH_3)_5CoOPO_3H]^+$ (3.5×10^{-5} s^{-1}) and $[(NH_3)_5CoOPO_3H_2]^{2+}$ (4.5×10^{-4} s^{-1}) (70 °C, $I = 1.0$ M ($NaClO_4$)),[22] respectively. The ratio of rate constants for hydrolysis of 2+ and 1+ ions at 70 °C is somewhat larger in the phosphato system (13) than in the hydroxyphenyl phosphato system (2.7). This small difference may reflect the electron-donating capability of the C_6H_4OH substituent, resulting in the partial neutralization of positive charge added to the coordinated phosphate group through protonation. Finally, it may be noted that the absence of phosphate ester hydrolysis accompanying the aquation of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion is consistent with the observations of Schmidt and Taube on Co(III)-complexed dimethyl and trimethyl phosphate.[21]

Our preliminary results demonstrate that induced electron transfer occurs in the reaction of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion with Ce(IV) and that the trend in % Co(II) with increasing [Ce(IV)] is as expected from the competition between external and internal oxidants for a semiquinone phosphate intermediate. Unfortunately, the low Co(II) yields prevent us from quantitatively estimating the ratio of rate constants for electron transfer from this intermediate to Co(III) and Ce(IV). Weaker oxidants such as $Mo(CN)_8^{3-}$ will be employed in future studies of induced electron transfer in hydroquinone ester complexes in the hope that higher Co(II) yields will be attained.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Technical assistance was provided by Mary L. Ettel.

Registry No. I, 74206-92-1; II, 80963-06-0; III, 940-75-0; $[Co(NH_3)_5(O_3POC_6H_4OH)]^+$, 80964-53-0; $Ba[HOC_6H_4OPO_3]$, 80963-07-1; $POCl_3$, 10025-87-3; $[Co(NH_3)_5CO_3](NO_3)$, 15244-74-3.

(22) The rate constants cited were derived from *k* (60 °C) and $\Delta H^{\ddagger}$ values reported in: Lincoln, S. F.; Jayne, J.; Hunt, J. P. *Inorg. Chem.* **1969**, *8*, 2267.

Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

Comparative Studies of the Reduction of Bis(2,9-dimethyl-1,10-phenanthrolinediyl-4,7-bis(benzenesulfonato))copper(II) and Bis(2,9-dimethyl-1,10-phenanthroline)copper(II) Ions by Hydroquinone

Robert A. Holwerda

Received June 9, 1981

Considerable uncertainty currently exists concerning the intrinsic electron-transfer reactivity of cuprous/cupric systems. Widely divergent estimates of the Cu(I,II) self-exchange rate constant (k_{11}) in copper–phenanthroline complexes have been obtained by applying the relative Marcus theory to cross-reaction data.[1-4] Justification of this indirect approach is required, as cross reactions must satisfy the weak-overlap, outer-sphere criterion of the Marcus theory.

A comparison of rate parameters for the hydroquinone (H_2Q) reduction of bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ($Cu(dmp)_2^{2+}$) and bis(2,9-dimethyl-1,10-phenanthrolinediyl-4,7-bis(benzenesulfonato))copper(II) ($Cu(dpmp)_2^{2-}$) ions is presented in this note. Relative Marcus theory is applied, as in our previous work,[4] to estimate the k_{11} values of the $Cu(dmp)_2^{2+/+}$ and $Cu(dpmp)_2^{2-/3-}$ couples. For this application, hydroquinone is a good choice of reductant. Thus, the Marcus relationship successfully correlates rate constants with thermodynamic driving force in the oxidation of substituted hydroquinones by $Cu(dmp)_2^{2+}$ and other one-electron oxidants.[4] Furthermore, apparent self-exchange rate parameters for the $Mo(CN)_8^{3-/4-}$ and $Fe(CN)_6^{3-/4-}$ couples, derived from cross reactions with hydroquinone, are consistent with the experimental rate constant of the $Fe(CN)_6^{4-}$ – $Mo(CN)_8^{3-}$ reaction under the same conditions.[5]

Experimental Section

Materials amd methods described by Clemmer et al.[4] were employed in kinetic studies of the hydroquinone reduction of $Cu(dpmp)_2^{2-}$. The disodium salt of 2,9-dimethyl-1,10-phenanthrolinediyl-4,7-bis(benzenesulfonic acid) (Sigma) was used as received. The oxidant and reductant were prepared in the same sodium acetate buffer (ionic strength = 0.2 M), and, in most runs, the $dpmp^{2-}$ ligand was contained initially in the copper(II) solution.

Hydrogen ion concentrations were derived from pH readings (Brinkmann pH-104 meter) by using relationship 1, based on an

$$-\log [H^+] = pH - 0.12 \qquad (1)$$

activity coefficient of 0.757 for 0.2 M NaOAc.[6] In pH-dependence studies, the total ligand concentration ($[dpmp]_{tot}$) was adjusted to give a $[dpmp^{2-}]/[Cu^{II}]_{tot}$ ratio of 18, taking protonation of $dpmp^{2-}$ to $Hdpmp^-$ into account (pK_a($Hdpmp^-$) = 5.80).[7] Although formation constants in the Cu^{II}–$dpmp^{2-}$ system are not known, drawing the analogy to the structurally similar Cu^{II}–dmp system indicates that an 18-fold excess of $dpmp^{2-}$ should be adequate to convert 98+% of the available copper(II) into the $Cu(dpmp)_2^{2-}$ ion.[4,8] This assumption was justified by showing that observed rate constants ($[H_2Q] = 1$ mM, pH 6.02) are independent of ligand concentration in the range 20- to 100-fold excess of dpmp over Cu, in agreement with findings on Cu^{II}–dmp solutions.[4]

Formation of $Cu(dpmp)_2^{3-}$ was followed at 483 nm (ϵ_{483} 1.225×10^4 M^{-1} cm^{-1})[7] on a Durrum D-110 stopped-flow apparatus, with the total copper concentration held constant at 10 μM and with at least a 10-fold excess of reductant. Fast and slow increases in 483-nm absorbance were noted in all runs, suggesting the presence of Cu^{II}–$dpmp^{2-}$ complexes other than $Cu(dpmp)_2^{2-}$. The contribution of the slow phase to ΔA_{483} is considerably smaller when the $dpmp^{2-}$ ligand is present initially in the reductant solution, rather than the copper(II) solution. It seems reasonable to conclude, therefore, that the slow phase corresponds primarily to the reduction of Cu^{II}–$dpmp^{2-}$ complexes which are formed slowly on the time scale required for the formation and subsequent reduction of $Cu(dpmp)_2^{2-}$.

Fortunately, the difference in rate between the fast and slow components of ΔA_{483} was sufficiently large to allow the evaluation of observed first-order rate constants for the predominant fast phase (k_{obsd} (fast)) from standard ln ($A_\infty - A_t$) vs. time or Guggenheim[9] plots. In most runs a reliable A_∞ (fast) was established on the os-

---

(1) Yoneda, G. S.; Blackmer, G. L.; Holwerda, R. A. *Inorg. Chem.* **1977**, *16*, 3376.

(2) Yandell, J. K.; Augustin, M. A. *Inorg. Chem.* **1979**, *18*, 577.

(3) Lappin, A. G.; Youngblood, M. P.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 407.

(4) Clemmer, J. D.; Hogaboom, G. K.; Holwerda, R. A. *Inorg. Chem.* **1979**, *18*, 2567.

(5) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1978**, *17*, 1688.

(6) "CRC Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1980; p D-169.

(7) Blair, D.; Diehl, H. *Talanta* **1961**, *7*, 163.

(8) Al-Shatti, N.; Lappin, A. G.; Sykes, A. G. *Inorg. Chem.* **1981**, *20*, 1466.

(9) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538.

(10) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.

0020-1669/82/1321-2107$01.25/0

Table I. Marcus Calculations for the Reactions of $Cu(dpmp)_2^{2-}$ and $Cu(dmp)_2^{2+}$ with HQ^{-} [a]

oxidant	k_{12}, M^{-1} s^{-1}	$\Delta G°_{12}$ [b]	w_{12}	w_{11}	ΔG^*_{11} [c]	$\Delta G^*_{11}{}^{cor}$ [d]	k_{11}, [e] M^{-1} s^{-1}	$k_{11}{}^{cor}$, [f] M^{-1} s^{-1}
$Cu(dpmp)_2^{2-}$	1.4×10^8	−3.00	0.354	0.319	6.28	5.97	2.5×10^6	4.2×10^6
$Cu(dmp)_2^{2+}$	2.5×10^7 [g]	−2.89	−0.354	0.106	8.21	8.55	9.6×10^4	5.4×10^4

[a] 25.0 °C, $I = 0.2$ M (acetate). All work terms and free energies expressed in kcal/mol. Work terms calculated with the assumption $R(Cu(dpmp)_2^{2-}) = R(Cu(dmp)_2^{2+}) = 7$ Å[12] and $R(HQ^-) = 1.4$ Å (Marcus, R. A. *J. Chem. Phys.* 1957, *26*, 872). Work terms (w_{21} and w_{22}) for reactions involving HSQ assumed to be zero. $\Delta G^*_{22} = 4.5$ kcal/mol (Pelizzetti, E.; Mentasti, E.; Baiocchi, C. *J. Phys. Chem.* 1976, *80*, 2979). [b] $\Delta G°_{12} = -RT \ln K_{12}$, where $K_{12} = (K_0 K_{sq})^{1/2}/K_{a1}(H_2Q)$.[4] Further details of this calculation are given in ref 4. K_0 was calculated from $E°(Cu(dpmp)_2^{2-/3-}) = 0.620$ V and $E°(Cu(dmp)_2^{2+/+}) = 0.615$ V.[3] [c] $\Delta G^*_{11} = 2\Delta G^*_{12} - \Delta G^*_{22} - \Delta G°_{12}$. [d] Calculated from the complete equation of relative Marcus theory, including the *f* term and electrostatic work terms.[12] [e] Derived from ΔG^*_{11}. [f] Electrostatics–corrected apparent Cu(I,II) self-exchange rate constant, derived from $\Delta G^*_{11}{}^{cor}$. [g] Reference 4.

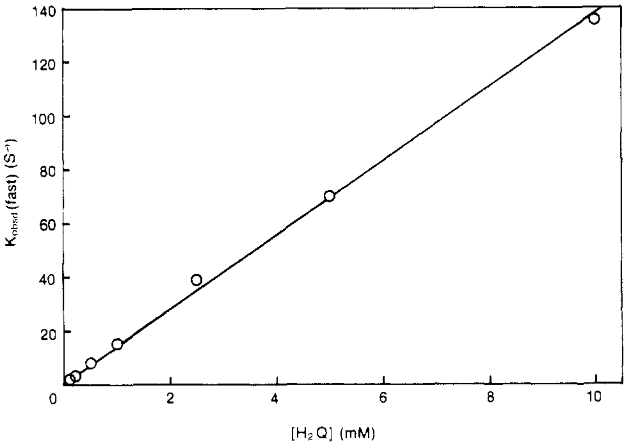

Figure 1. Plot of k_{obsd} (fast) vs. $[H_2Q]$ (25.0 °C, pH 6.03, $I = 0.2$ M (acetate), $[dpmp]_{tot} = 0.30$ mM).

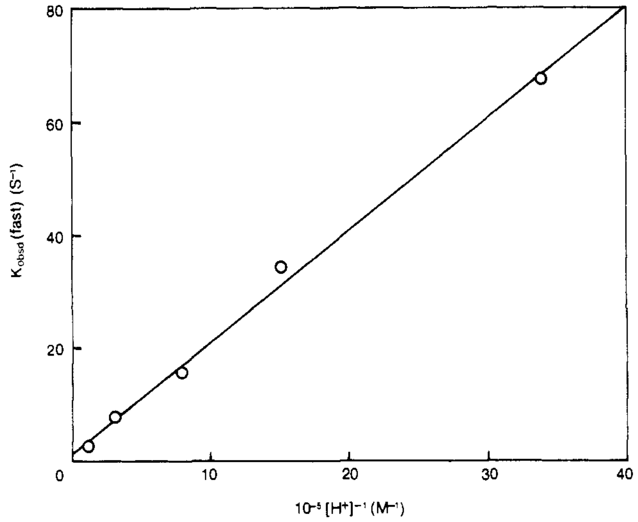

Figure 2. Plot of k_{obsd} (fast) vs. $[H^+]^{-1}$ (25.0 °C, $I = 0.2$ M (acetate), $[H_2Q] = 1.0$ mM. $[dpmp]_{tot}$ adjusted to give a $[dpmp^{2-}]/[Cu]_{tot}$ ratio of 18).

cilloscope before the contribution of the slow phase, followed on an X-Y recorder, was significant. For example, with $[H_2Q] = 1$ mM, pH 6.02, $[dpmp]_{tot}/[Cu^{II}]_{tot} = 40$, ΔA_{483} (fast) (88% of total ΔA_{483}) was complete within 0.2 s, while ΔA_{483} (slow) required 6.3 s. First-order plots based on ΔA_{483} (fast) were found to be linear for at least three half-lives. Reported rate constants are the average of three or more determinations, with precision being better than ±5%.

Results and Discussion

The fast component of ΔA_{483} exhibits a first-order dependence on hydroquinone over a 100-fold concentration range (0.10–10 mM) (Figure 1). Hydrogen ion dependence results (pH 5.19–6.65), shown as a plot of k_{obsd} (fast) vs. $[H^+]^{-1}$ (Figure 2), demonstrate that the complete rate law is of the same form as that reported[4] for the H_2Q-$Cu(dmp)_2^{2+}$ reaction, eq 2, where $k_2 = (1.98 \pm 0.08) \times 10^{-2}$ s^{-1} (25.0 °C, $I = 0.2$ M). A precise value of k_1 cannot be reported ($(1.2 \pm 1.5) \times 10^3$ M^{-1} s^{-1}) in view of the very small contribution of the H$^+$-independent pathway to k_{obsd} (fast) under our conditions.

$$d[Cu(dpmp)_2^{3-}]/dt = (k_1 + (k_2/[H^+]))[H_2Q][Cu(dpmp)_2^{2-}] \quad (2)$$

While considerably more work will be required to understand the unexpected slow component in the reaction of H_2Q with Cu^{II}–$dpmp^{2-}$ solutions, the interpretation of the fast phase is straightforward. The predominant k_2 term in the rate law is readily assigned to the reduction of $Cu(dpmp)_2^{2-}$ by the hydroquinone monoanion, HQ^-. On this basis, the rate constant of the HQ^-–$Cu(dpmp)_2^{2-}$ reaction ($=k_2/K_{a1}(H_2Q)$) is calculated to be 1.4×10^8 M^{-1} s^{-1} (25.0 °C, $I = 0.2$ M; $pK_{a1}(H_2Q) = 9.85$[11]). This value is ca. 6 times larger than that for the analogous reduction of $Cu(dmp)_2^{2+}$ under the same conditions (2.5×10^7 M^{-1} s^{-1})[4] in spite of the unfavorable Coulombic interaction between the redox partners. The reactivity advantage of $Cu(dpmp)_2^{2-}$ is not linked to thermodynamic driving force, as the reduction potentials of $Cu(dmp)_2^{2+}$ (0.615 V) and $Cu(dpmp)_2^{2-}$ (0.620 V) are nearly identical.[3]

So that the intrinsic electron-transfer reactivities of the $Cu(dmp)_2^{2+/+}$ and $Cu(dpmp)_2^{2-/3-}$ couples could be compared, electrostatics-corrected apparent self-exchange rate constants ($k_{11}{}^{cor}$) were calculated from cross-reaction rate constants (k_{12}) by the method of Wherland and Gray[12] (Table I). In performing these calculations, it was assumed that the rate-limiting electron-transfer process is eq 3, where HSQ represents

$$HQ^- + Cu^{II} \underset{}{\overset{K_{12}}{\rightleftharpoons}} HSQ + Cu^I \quad (3)$$

singly protonated benzosemiquinone. Equations given by Wherland and Gray were used to calculate activation free energies (ΔG^*) and estimate electrostatic work terms for the cross reactions and Cu(I,II) self-exchange reactions (w_{12} and w_{11}, respectively). The separation of charge in the $Cu(dpmp)_2^{2-/3-}$ complexes complicates the choice of an effective radius for work term calculations. Fortunately, the magnitude of the electrostatic correction in the HQ^-–$Cu(dpmp)_2^{2-}$ system is not very sensitive to this choice of radius, as the reactants both are anions.

The calculations shown in Table I indicate that the activation free energy of the $Cu(dpmp)_2^{2-/3-}$ exchange reaction is 2.6 kcal/mol smaller than $\Delta G^*_{11}{}^{cor}$ ($Cu(dmp)_2^{2+/+}$), implying that the rate of the former reaction is larger by nearly 2 orders of magnitude. Our $k_{11}{}^{cor}$ ($Cu(dmp)_2^{2+/+}$) value agrees quite well with those derived by Yandell and Augustin[2] from cross reactions with $Co(phen)_3^{2+}$ (4.4×10^4 M^{-1} s^{-1}) and ferrocytochrome *c* (1.7×10^4 M^{-1} s^{-1}). The $Cu(dmp)_2^{2+/+}$

---

(11) Baxendale, J. H.; Hardy, H. R. *Trans. Faraday Soc.* **1953**, *49*, 1140.

(12) Wherland, S.; Gray, H. B. In "Biological Aspects of Inorganic Chemistry"; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977; p 289.

self-exchange rate constant calculated by Margerum and coworkers from the $Cu(dmp)_2^+$–$IrCl_6^{2-}$ reaction (9.0×10^8 M^{-1} s^{-1})[3] is considerably larger, however, even after making electrostatic corrections (1.4×10^7 M^{-1} s^{-1}). Surprisingly good agreement exists between our $k_{11}^{cor}(Cu(dpmp)_2^{2-/3-})$ value and the self-exchange rate constant derived from the $Cu(dpmp)_2^{3-}$–$IrCl_6^{2-}$ reaction (3.7×10^7 M^{-1} s^{-1};[3] 1.1×10^7 M^{-1} s^{-1} obtained by correcting for noncancelling electrostatic work terms). Chloride bridging, reported recently in the oxidation of copper(II)–peptide complexes by $IrCl_6^{2-}$,[13] or other nonelectrostatic stabilization of the precursor complex in the $Cu(dmp)_2^+$–$IrCl_6^{2-}$ reaction may be partially responsible for the discrepancy between our $k_{11}(Cu(dmp)_2^{2+/+})$ value and that reported by Margerum et al.[3]

Quantitative understanding of the redox reactivity difference between the $Cu(dmp)_2^{2+/+}$ and $Cu(dpmp)_2^{2-/3-}$ couples is made difficult by the approximate nature of the Marcus calculations, the nonspherical structures of the reactants, and the likelihood that changes in both the coordination geometry and number of copper accompany the conversion of Cu(II) to Cu(I). The 4,7-benzenesulfonate substituents should reduce the outer-sphere rearrangement contribution to $\Delta G^*{}_{11}{}^{cor}$ in $Cu(dpmp)_2^{2-/3-}$ relative to $Cu(dmp)_2^{2+/+}$. With the assumption that the $C_6H_5SO_3^-$ substituents contribute 4.5 Å to the radius (r) of $Cu(dpmp)_2^{3-/2-}$ (11.5 Å),[12] approximate outer-sphere rearrangement activation free energies of 2.0 kcal/mol for this couple and 3.2 kcal/mol for $Cu(dmp)_2^{2+/+}$ are obtained from eq 4,[14] where n is the number of electrons transferred (1). It

$$\Delta G^*{}_0 = 22.7n^2/r \qquad (4)$$

should be noted that this expression pertains rigorously only to self-exchange reactions of spherically symmetric ions in water at 25 °C. We estimate, therefore, that the outer-sphere rearrangement requirement accounts for ca. 1.2 kcal/mol of the 2.6 kcal/mol difference between $\Delta G^*{}_{11}{}^{cor}$ values for the two Cu(I,II) couples.

Other factors which should be considered in comparing the redox reactivities of the $Cu(dpmp)_2^{2-/3-}$ and $Cu(dmp)_2^{2+/+}$ couples include changes in coordination geometry, ligand field stabilization energy, and coordination number required to bring the reactants into the activated complex. The coordination geometries of $Cu(dmp)_2^{2+}$ and $Cu(dmp)_2^+$ are flattened tetrahedral and tetrahedral, respectively,[15] and strong evidence has been presented that the former ion is five-coordinate ($[Cu(dmp)_2(H_2O)]^{2+}$) in aqueous solution.[8,16] The closeness of $Cu(dmp)_2^{2+}$ and $Cu(dpmp)_2^{2-}$ $E°$ values[3] indicates that *net* changes in coordination number and geometry associated with reduction of these complexes must be comparable. Analogous changes associated with the activation process need not be identical, however, particularly with respect to the extent of Cu^{II}–H_2O bond breaking in the activated complex. Al-Shatti et al.[8] propose that the reduction of $Cu(dpmp)_2^{2-}$ by $Fe(CN)_6^{4-}$ occurs via an activated intermediate, generated through the displacement of water from $[Cu(dpmp)_2(H_2O)]^{2-}$ to form a reactive tetrahedral species. While our kinetic data do not require complete displacement of H_2O from the first coordination sphere of Cu(II) in the activated complexes for reduction of $Cu(dpmp)_2^{2-}$ and $Cu(dmp)_2^{2+}$ by HQ^-, Cu^{II}–H_2O bond breaking is, no doubt, an important (and variable) aspect of the electron-transfer mechanism. Indeed, differences between the extent of Cu^{II}–H_2O bond breaking (and Cu^I–H_2O bond making) in the activated complexes of self-exchange and cross reactions probably are largely responsible for the notable lack of consistency among k_{11} values calculated for copper(I,II)–phenanthroline couples from the Marcus relationship. Thus, a k_{11} value derived from the reduction rate of a copper(II)–phenanthroline complex will be lower than the actual value if the extent of Cu^{II}–H_2O bond breaking in the rate-limiting step exceeds that required in the self-exchange reaction. Consistent k_{11} values from reduction and oxidation cross reactions may in fact be obtained for Cu(I,II) couples under conditions where solvation of Cu is precluded, i.e., in the blue copper protein stellacyanin.[17]

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant D-735) is gratefully acknowledged.

Registry No. $Cu(dpmp)_2^{2-}$, 72244-80-5; $Cu(dmp)_2^{2+}$, 14875-91-3; H_2Q, 123-31-9.

---

(13) Owens, G. D.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1446.

(14) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press: New York, 1966; p 129.

(15) Hall, J. R.; Marchant, N. K.; Plowman, R. A. *Aust. J. Chem.* **1963**, *16*, 34.

(16) Davies, G.; Higgins, R.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 700.

(17) Holwerda, R. A.; Knaff, D. B.; Gray, H. B.; Clemmer, J. D.; Crowley, R.; Smith, J. M.; Mauk, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 1142.

Contribution from the Department of Chemistry,
Osmania University, Hyderabad 500 007, India

Dioxygen Complexes of Ruthenium(III) in Aqueous Solution

M. M. Taqui Khan* and G. Ramachandraiah

Received July 8, 1981

The dioxygen complexes of transition-metal ions have been extensively studied during the last decade.[1–4] The most important areas of research in metal dioxygen chemistry have been the cobalt(II) dioxygen complexes,[3] the picket fence and picket fence type of iron(II) porphyrin oxygen complexes,[2] and the manganese(II) porphyrin complexes.[4] The platinum group metal ions, rhodium(I), iridium(I), ruthenium(0), platinum(0), and palladium(0), are sufficiently soft and give[1,5,6] metal dioxygen complexes mostly with soft donors such as tertiary phosphines, arsines, etc. The only example of a hard donor such as EDTA as a ligand in metal–dioxygen complexes is the complex[7] $Ti(EDTA)O_2^{2-}$. To our knowledge, except for the cobalt(II) dioxygen complexes,[3] equilibrium and other studies have not been conducted on any other metal dioxygen system in aqueous solution. Besides, there are no examples of a platinum group metal–dioxygen complex with hard donor ligands such as EDTA and HEDTA. In the present investigation ruthenium(III) dioxygen complexes are reported for the hard donor ligands EDTA and HEDTA in aqueous solution.

The potentiometric titrations of 1:1 Ru^{III}–EDTA and Ru^{III}–HEDTA systems were conducted with continuous bubbling of oxygen through the experimental solutions. The Ru^{III}–EDTA and Ru^{III}–HEDTA systems gave inflections at $a = 2.5$ and 4.5, respectively, indicative[3] of the formation of binuclear μ-hydroxo-μ-peroxo complexes in solution. The pH of the solution was measured in each case after sufficient time

---

(1) Taqui Khan, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes": Academic Press: New York, 1974; Vol. 1.

(2) "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980.

(3) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1 and references therein.

(4) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(5) Vaska, L. *Acc. Chem. Res.* **1976**, *1*, 175.

(6) Choy, V. J.; O'Connor, C. J. *Coord. Chem. Rev.* **1972**, *9*, 145.

(7) Kristine, F. J.; Shepherd, R. E. *J. Chem. Soc., Chem. Commun.* **1980**, 132.

0020-1669/82/1321-2109$01.25/0