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Facile Electroreduction of Perrhenate in Weakly Acidic Citrate and Oxalate Media

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In weakly acidic solution, oxalate and citrate markedly increase the ease of reduction of ReO_4^- through reversible formation of 1:1 complexes. The citrate complex $(ReO_4{\cdot}H_2Cit)^{2-}$ is sufficiently stable that it yields a diffusion limited current, whereas the oxalate complex $(ReO_4{\cdot}H_2Ox)^-$ is formed only as a transient intermediate and it yields a kinetic limited current. Below pH 3 the mechanism of formation of the citrate complex corresponds to $ReO_4^- + H_3Cit \rightleftarrows (ReO_4{\cdot}H_2Cit)^{2-} + H^+$ while above pH 3 it corresponds to $ReO_4^- + H_2Cit^- \rightleftarrows (ReO_4{\cdot}H_2Cit)^{2-}$. The enhanced ease of reduction of the citrate and oxalate complexes is ascribed to expansion of the Re coordination sphere from 4 to, e.g., 6 through formation of chelated structures by a concerted process in which the incoming ligand transfers protons to coordinated oxo groups. The hydroxyl group of citric acid is necessary for formation of an easily reduced Re(VII) complex, and Dreiding models indicate that citrate is bidentate and occupies one face of the coordination octahedron, with the hydroxyl group H bonded to a coordinated oxo group.

Introduction

Electroreduction of ReO_4^- is highly irreversible, with the result that its polarographic reduction wave appears far cathodic of the reversible potential, an effect that is particularly acute in weakly acidic media. From pH 1 to pH 5 in most widely used supporting electrolytes, the ReO_4^- reduction wave occurs just before the onset of electrolyte decomposition, and it is often poorly defined. Thus, Geyer[1] observed half-wave potentials of −1.2 V vs. SCE in pH 4 acetate medium and −1.3 V vs. SCE in pH 2 sulfate medium, and Lingane[2] reported that in 0.1 M HCl ReO_4^- gives only a slight indication of a wave. In contrast to the marked difficulty of its electroreduction in most weakly acidic electrolytes, the electroreduction of ReO_4^- in weakly acidic citrate (2-hydroxy-1,2,3-propanetricarboxylate) or oxalate is facile, resulting in a polarographic wave at much more positive potentials. For example, although the half-wave potential of ReO_4^- in 1 M KCl at pH 2 is −0.72 V vs. SCE, addition of 0.1 M oxalate yields a wave at −0.12 V vs. SCE, and the effect of citrate is nearly as great. To influence the polarography of ReO_4^- to this degree, oxalate and citrate must interact very strongly with ReO_4^-, and it is clear that the interaction differs fundamentally from the catalytic hydrogen evolution reaction observed by Banerjea and Tripathi[3] in weakly alkaline oxalate medium. In weakly acidic solution, both citrate and oxalate facilitate the electroreduction of ReO_4^- through reversible complex formation, and systematic analysis of the polarographic limiting currents permits determination of both the composition and the kinetics of formation of these electroactive ReO_4^- complexes. In some respects the activation of ReO_4^- is similar to the activation of MoO_4^{2-} studied by Ogura et al.,[4,5] but there are important differences between the two reactions. We report here a detailed study of the formation kinetics, the composition, and the polarographic behavior of the electroactive complexes generated by reaction of ReO_4^- with citrate and with oxalate in weakly acidic solution.

Experimental Section

Except for $HReO_4$, which was Alfa Ventron 99.99% grade, and nitrogen for deoxygenation, which was Linde high-purity grade, all chemicals were reagent grade. Polarograms were secured in a thermostated cell with a conventional three-electrode polarograph using a dropping-mercury working electrode, a saturated calomel reference electrode, and a platinum-wire counterelectrode. The pH of the polarographic electrolyte, which was monitored in the polarographic cell with use of a combination electrode, was adjusted by dropwise addition of NaOH or HCl without significant dilution. Controlled-potential coulometry was performed at a stirred mercury pool cathode with use of a potentiostatic coulometer based on the design of van Swaaj.[6]

Results and Discussion

The reactions by which citric acid and oxalic acid activate perrhenate are similar in a general sense, but they differ in important respects. By far the most significant differences between these two mediators are the rate and the extent to which each reacts with perrhenate. Because these two factors govern the supply of electroactive material to the electrode surface, they control the nature of the polarographic limiting current. On the one hand, with moderate concentrations of citric acid, the equilibrium concentration of the electroactive ReO_4^-–citrate complex comprises a small but significant fraction of the total ReO_4^- concentration, but its rate of formation is slow enough that the equilibrium is essentially frozen. As a result, it is the diffusion of the electroactive ReO_4^-–citrate complex from bulk solution to the electrode surface that controls the polarographic limiting current, which is therefore a diffusion limited current. On the other hand, even with relatively high concentrations of oxalic acid, the equilibrium concentration of the electroactive ReO_4^-–oxalate complex comprises a negligible fraction of the total ReO_4^- concentration. However, the kinetics of its formation are sufficiently rapid that it is the rate of formation of the ReO_4^-–oxalate complex in the immediate vicinity of the electrode surface that controls the polarographic limiting current, which is denoted as a kinetic limited current.

For either a kinetic limited current resulting from a relatively fast preelectrochemical reaction or a diffusion limited current of the product of a very slow preelectrochemical reaction, the magnitude of the limiting current is sensitive to the concentration of any species involved in the preelectrochemical reaction. The dependence of the limiting current on the concentration of a given species therefore indicates the manner in which it participates in the preelectrochemical reaction, thus permitting establishment of the stoichiometry of the electroactive species.

Citrate–ReO_4^- Equilibrium. At 20 °C, the reaction of ReO_4^- with excess citrate is sufficiently rapid that the reaction is complete within 5 min or less after mixing, thus facilitating study of the equilibrium aspects of the reaction. Between pH 1.6 and pH 5.4, ReO_4^- in citrate medium exhibits a fairly well-defined, activation-controlled polarographic wave, the most striking feature of which is the unusually low value of the limiting current. Although the maximum limiting current is smaller by ca. 5-fold than the diffusion limited value to be

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(1) Geyer, R. *Z. Anorg. Allg. Chem.* **1950**, *263*, 47.
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(3) Banerjea, D.; Tripathi, K. *J. Inorg. Nucl. Chem.* **1961**, *21*, 307.
(4) Ogura, K.; Enaka, Y.; Yosino, T. *Electrochim. Acta* **1977**, *22*, 509.
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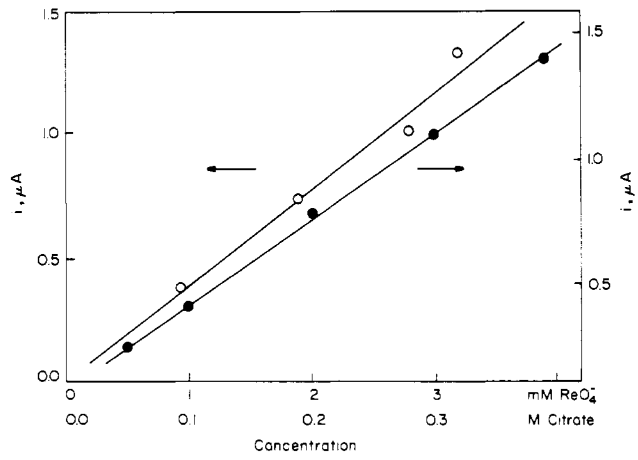

Figure 1. Dependence of Re(VII) limiting current on citrate and ReO_4^- concentrations in 1 M KCl at 20 °C. ●: ReO_4^-, 2.03 mM; citrate, variable; pH 3.30. ○: citrate, 0.30 M; ReO_4^-, variable; pH 3.12.

expected even if the reduction of ReO_4^- involved only one electron, it is clear that it is diffusion controlled. The critical feature of a diffusion-controlled limiting current is that it varies directly with the square root of the mercury column height,[7] a test to which the ReO_4^- limiting current conforms closely. For example, in 0.3 M citrate at pH 3 the limiting current increases from 1.09 μA at a column height of 40 cm to 1.60 μA at a column height of 80 cm. That is, doubling the mercury column height increases the limiting current by a factor of 1.48, which agrees well with the theoretical factor of 1.41. This result is significant because a diffusion-controlled limiting current is directly proportional to the bulk concentration of the electroactive species and thus provides a measure of the equilibrium concentration of the ReO_4^-–citrate complex. The unusually low value of the limiting current is important, because it demonstrates that the reaction of ReO_4^- with excess citrate consumes only a small fraction of the ReO_4^-. As a result, the equilibrium concentration of ReO_4^- is nearly equal to its analytical concentration.

This conclusion, which provides the basis for establishing the stoichiometry of the electroactive citrate–ReO_4^- complex, is confirmed by the effect of the citrate concentration on the limiting current. Figure 1 shows that for citrate concentrations up to 0.4 M, the limiting current increases in direct proportion to the citrate concentration, a result which can only occur if the equilibrium concentration of ReO_4^- remains essentially equal to its analytical concentration independent of the citrate concentration. More important, the direct dependence of the limiting current on the citrate concentration also shows that the electroactive complex contains one citrate moiety.

In a similar fashion, the influence of the ReO_4^- concentration on the limiting current can be analyzed to establish the number of rhenium atoms in the electroactive species. As Figure 1 shows, the limiting current for reduction of ReO_4^- in the presence of a large excess of citrate is directly proportional to the analytical concentration of ReO_4^-. Under these conditions, the direct dependence of the concentration of the electroactive species on the ReO_4^- concentration shows that the electroactive species is mononuclear in rhenium.

The last piece of information needed to define the equilibrium reaction between ReO_4^- and citrate is the pH dependence of the limiting current, which is reported in Figure 2. Because the pK_a of perrhenic acid is −1.25,[8] protonation of ReO_4^- is negligible under these conditions. The points represent the experimental values of limiting current in 0.4 M citrate from pH 1.6 to pH 5.4, and the solid line represents the theoretical current distribution calculated from the pK_a's of citric acid[9] on the assumption that the citrate species reacting with ReO_4^- is the monoanion, H_2Cit^-. The agreement of the theoretical and experimental values of the current is excellent, showing clearly that this assumption is correct. Hence the stoichiometry of the formation of the electroactive ReO_4^-–citrate complex is described by eq 1.

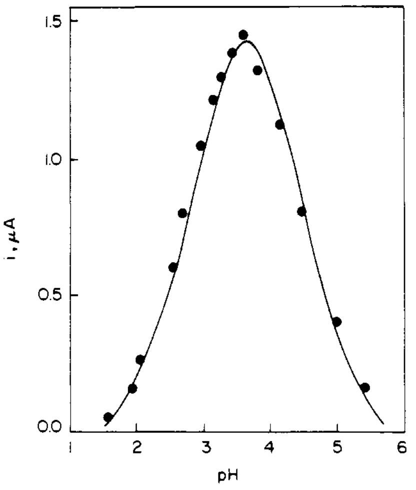

Figure 2. Dependence of the limiting current of 2.03 mM ReO_4^- on pH in 0.40 M citrate–1 M KCl at 20 °C.

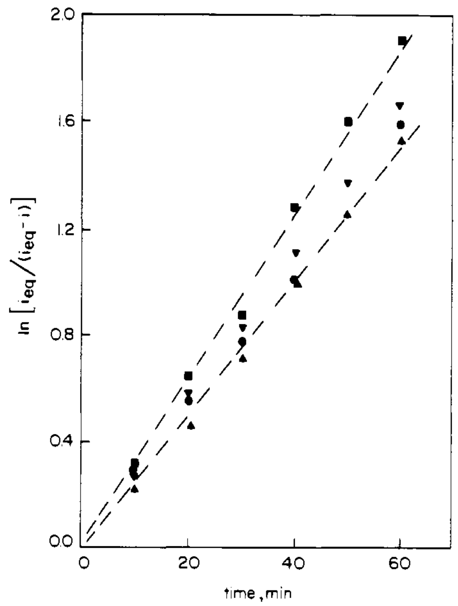

Figure 3. Plot of eq 2 at various citrate concentrations showing the effect of citrate concentrations on k_b', the pseudo-first-order rate constant for dissociation of $(H_2Cit{\cdot}ReO_4)^{2-}$ in 1 M KCl at pH 3.20 and 3 °C: ■, 0.40 M; ▼, 0.20 M; ▲, 0.10 M; ●, 0.050 M.

$$ReO_4^- + H_2Cit^- \rightleftarrows (ReO_4{\cdot}H_2Cit)^{2-} \qquad (1)$$

Citrate–ReO_4^- Kinetics. At 3 °C, the reaction of ReO_4^- with excess citrate is sufficiently slow that one can monitor the kinetics of the process beginning when the extent of reaction is less than 10%. The relationship of the instantaneous polarographic limiting current to the kinetic parameters of the reaction, which is derived in the Appendix, is given by eq 2,

$$\ln [i/(i_{eq} - i)] = k_b't \qquad (2)$$

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(7) Meites, L. "Polarographic Techniques", 2nd ed.; Wiley-Interscience: New York, 1965; pp 132–134.

(8) Bailey, N.; Carrington, A.; Lott, K. A.; Symons, M. C. *J. Chem. Soc.* **1960**, 290.

(9) Okac, A.; Kolarik, Z. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1.

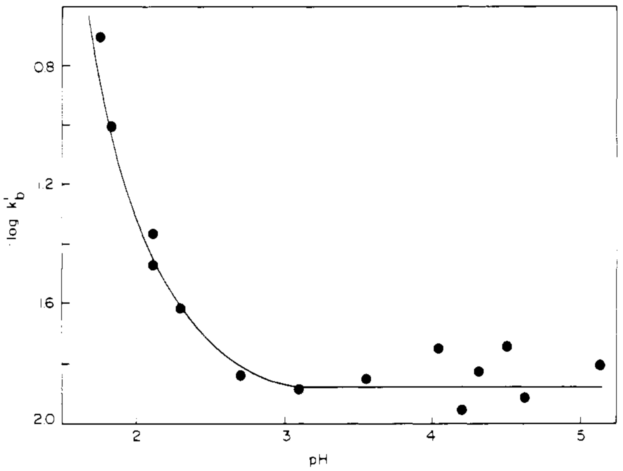

Figure 4. pH dependence of k_b', the pseudo-first-order rate constant for dissociation of $(H_2Cit{\cdot}ReO_4)^{2-}$ in 1 M KCl–0.20 M citrate at 3 °C.

where i is the limiting current at time t, i_{eq} is the equilibrium value of the limiting current, and k_b' is the value of the pseudo-first-order rate constant for dissociation of the $(ReO_4{\cdot}H_2Cit)^{2-}$ complex. The graphical evaluation of eq 2 at 3.0 °C in Figure 3 shows that it is consistent with the kinetics of the ReO_4^-–citrate reaction. Between 5% reaction and ca. 75% reaction, the plot for each citrate concentration is linear as required by eq 2. The slope increases ca. 20% as the citrate concentration is raised from 0.05 to 0.4 M, but in comparison with the 8-fold increase in the citrate concentration, this increase in the slope is small. If the dependence of the slope on the citrate concentration is considered in terms of reaction order, the order of the reverse reaction with respect to citrate is only 0.1. Although we are unable to ascribe the dependence on citrate concentration of the slopes of the plots in Figure 3 to a particular cause, we do not believe that it is significant in terms of the reaction mechanism.

The pH dependence of k_b' in Figure 4 shows that from pH 5.5 to ca. pH 3 the rate of dissociation of the $(ReO_4{\cdot}H_2Cit)^{2-}$ complex is independent of pH, whereas below pH 3 the dissociation rate increases rapidly with decreasing pH, approaching a first-order dependence on H^+ at pH 2. These results indicate a transition from a first-order dissociation of the $(ReO_4{\cdot}H_2Cit)^{2-}$ complex above pH 3 to a second-order acid-catalyzed dissociation below pH 3. The pK_a of H_3Cit is 3.0,[9] so that below pH 3 the predominant form of citrate is H_3Cit, but this fact alone does not explain the first-order proton dependence of the dissociation rate of the $(H_2Cit{\cdot}ReO_4)^{2-}$ complex below pH 3. The rate law shows that below pH 3 the proton is involved either before or in the rate-determining step, but not after. This means that the proton reacts with the $(H_2Cit{\cdot}ReO_4)^{2-}$ complex before it dissociates completely and not with free H_2Cit^-. Proton-transfer reactions are extremely rapid, so that if the role of the proton were to protonate H_2Cit^- after a slow dissociation step, the dissociation rate would be pH independent.

Because the solution is well buffered, citrate is present in large excess over ReO_4^-, and only a small fraction of the ReO_4^- is converted to the electroactive species, the only concentration which changes significantly during the reaction is that of the electroactive ReO_4^-–citrate complex. For this reason eq 2 yields kinetic information only about the reverse reaction, and the agreement of the experimental data with eq 2 signifies only that the formation of the ReO_4^-–citrate complex is reversible and that its dissociation is a pseudo-first-order process. As the Appendix shows, however, the kinetics of the formation of the ReO_4^-–citrate complex are accessible through assessment of the order of the forward reaction with respect to each component by means of eq 3, where A is an unknown constant,

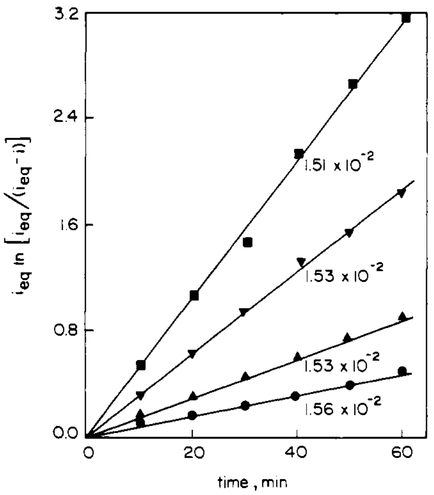

Figure 5. Plot of eq 3 at various citrate concentrations showing the effect on k_f', the pseudo-first-order rate constant for formation of $(H_2Cit{\cdot}ReO_4)^{2-}$ in 1 M KCl at pH 3.20 and 3 °C: ■, 0.40 M; ▼, 0.20 M; ▲, 0.10 M; ●, 0.050 M. The number next to each plot is the slope divided by the citrate concentration.

$$i_{eq} \ln [i_{eq}/(i_{eq} - i)] = k_f't/A \tag{3}$$

k_f' is the pseudo-first-order rate constant for formation of the $(ReO_4{\cdot}H_2Cit)^{2-}$ complex, and the other symbols have their prior meanings. Figure 5 shows the application of eq 3 to the determination of the order of the forward reaction with respect to citrate using the kinetic data obtained at four citrate concentrations ranging from 0.05 to 0.4 M. As is clear from the constancy of the ratio of the slope to the citrate concentration reported next to each plot, the slope of each plot is directly proportional to the citrate concentration. That is, the formation of the ReO_4^-–citrate complex is first order in citrate. Collectively, the kinetic information suggests that the mechanism of the ReO_4^-–citrate reaction follows eq 4a above pH

$$ReO_4^- + H_2cit^- \rightleftarrows (H_2cit{\cdot}ReO_4^-)^{2-} \tag{4a}$$

$$ReO_4^- + H_3cit \rightleftarrows (H_2cit{\cdot}ReO_4^-)^{2-} + H^+ \tag{4b}$$

3 and eq 4b below pH 3. Comparison of eq 4a and 4b with the equilibrium reaction in eq 1 shows that in terms of net stoichiometry eq 4a and 4b are equivalent to eq 1. Consideration of the structure of the $(ReO_4{\cdot}H_2Cit)^{2-}$ complex will be deferred until after the discussion of the kinetics of the ReO_4^-–oxalate reaction as it appears that the two complex species are similar in many respects.

Although the polarographic data do not indicate the oxidation state of Re generated by electroreduction of the $(H_2Cit{\cdot}ReO_4)2^-$ complex, controlled-potential coulometry at a stirred mercury pool indicates a 2.0 ± 0.1 electron change. The resulting blue Re(V) species (λ_{max} = 630 nm), which can also be prepared by reduction with Sn(II), is easily reduced further to yield a yellow product, which is probably Re(IV).

Oxalate–ReO_4^- Kinetics. In the presence of oxalate, the ReO_4^- limiting current is governed entirely by the kinetics of formation of the electroactive ReO_4^-–oxalate complex in the vicinity of the electrode surface. This process is represented in eq 5 where Y stands for ReO_4^-, which is not electroactive,

$$Y \underset{k_b}{\overset{k_f}{\rightleftarrows}} O \tag{5}$$

O denotes the ReO_4^-–oxalate complex, which is electroactive, and k_f and k_b represent, respectively, the forward and reverse rate constants of the prior chemical step. Koutecky[10,11] has

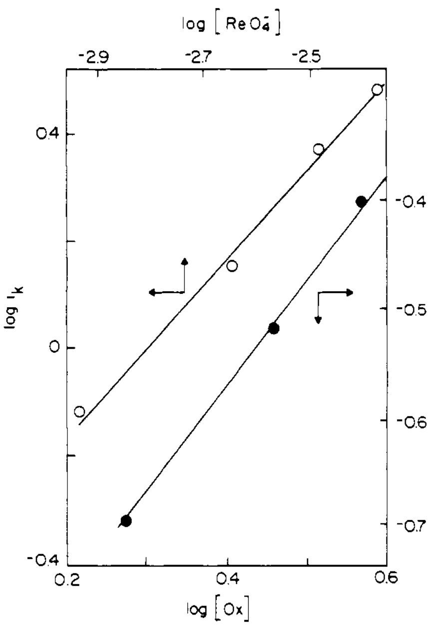

Figure 6. Dependence of the Re(VII) limiting current on oxalate and ReO_4^- concentrations in 0.1 M NaCl at 25 °C. ○: oxalate, 0.30 M; ReO_4^-, variable; pH 1.40 (the order with respect to ReO_4^- is 1.01). ●: ReO_4^-, 2.32 mM; oxalate, variable; pH 0.80 (the order with respect to oxalate is 0.97).

shown that, provided both the forward and reverse reactions of the chemical step are first order or pseudo first order, one can establish the rate law for the chemical step. If, as is true for the ReO_4^-–oxalate system, i_k, the kinetic limited current, is no more than ca. 20% of i_d, the diffusion limited current, determination of the rate law is particularly easy. Then the dependence of the kinetic limited current on the kinetic parameters of the prior chemical step follows eq 6, where t is

$$i_k = \frac{(3\pi t)^{1/2}}{7}\,\frac{k_f}{k_b^{1/2}} = \frac{\pi^{1/2}}{2}\chi \qquad (6)$$

the lifetime of the mercury drop, k_f and k_b denote the pseudo-first-order rate constants of the forward and reverse chemical steps, and χ is the Koutecky variable. The slope of a log–log plot of i_k vs. the concentration of a species participating in the chemical step is the order of χ with respect to that species. Because χ is a function of both k_f and k_b, one cannot rigorously partition the order of χ with respect to k_f and k_b. Although, in principle, more than one set of reaction orders can be consistent with a given set of data, in practice one can usually reduce the number of reasonable rate laws to one.

Because of experimental constraints, study of the kinetics of the ReO_4^-–oxalate reaction is restricted to a narrow range of conditions. The oxalate concentration must be at least 0.1 M for the kinetic current to be readily measurable and no larger than 0.5 M for χ to remain a linear function of i_k. Also, above pH 2, the current becomes quite small, thus limiting the accessible pH range to ca. 0–2. Within these limits, ReO_4^- in the presence of oxalate exhibits a well-defined polarographic reduction wave with a half-wave potential of ca. –0.1 V and a limiting current which is kinetic in nature. The major diagnostic feature of such a kinetic limited current is that it is independent of the mercury column height,[12] a criterion to which the limiting current of ReO_4^- in oxalate conforms closely. For instance, in 0.1 M NaCl–0.2 M oxalic acid at

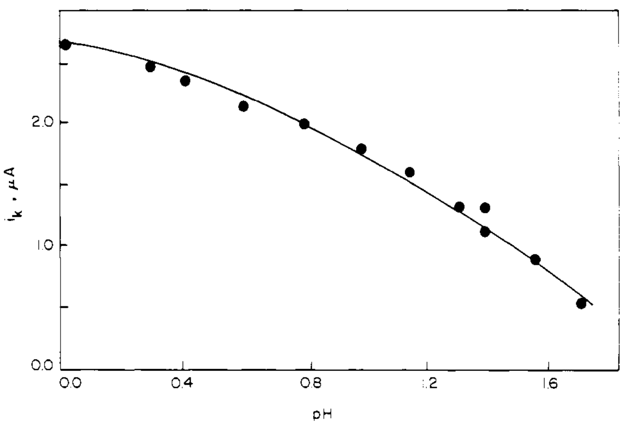

Figure 7. pH dependence of the limiting current of 2.32 mM ReO_4^- in 0.20 M oxalate–0.1 M NaCl at 25 °C. The points are experimental data and the line represents the pH dependence on the assumption that the oxalate species forming the electroactive species is H_2Ox.

pH 1, the limiting current for 2.32 mM ReO_4^- is 1.68 μA when the mercury column height is 40 cm and 1.75 μA when the mercury column height is 80 cm.

To establish the rate law for the prior chemical step, it is necessary to determine the order of χ with respect to the concentrations of oxalic acid, ReO_4^-, and protons. The data in Figure 6 show that χ is first order with respect to both ReO_4^- and oxalic acid, the slopes of the respective plots being 1.01 and 0.85. Figure 7 shows the pH dependence of the limiting current of 2.32 mM ReO_4^- in 0.2 M oxalic acid, the points representing experimental limiting currents and the solid line being the theoretical current distribution calculated from the pK_a's of oxalic acid,[13] on the assumption that the oxalate species reacting with ReO_4^- is the diprotonated acid, H_2Ox. The excellent agreement of the data points with the theoretical curve indicates that the oxalate species which reacts with ReO_4^- is H_2Ox and that neither the forward reaction nor the reverse reaction involves free protons.

Nature of Electroactive Re(VII) Complexes. The rate laws for the formation of the electroactive Re(VII) complexes of citrate and of oxalate demonstrate that the electroactive species are formed in 1:1 reactions of ReO_4^- with H_2Cit^- and H_2Ox, thus defining their compositions with respect to ReO_4^-, the ligand, and the protons. However, the rate laws do not define unambiguously the structure of the electroactive species. For example, they do not indicate whether the 1:1 complexes undergo subsequent intramolecular proton transfers leading to elimination of H_2O. Suggestions as to the probable structures of these complexes must rest mainly on indirect evidence, because the low stabilities of both complexes preclude conventional structural studies. The oxalate complex exists only as a transient intermediate, and although the citrate complex does not suffer this limitation, its stability is so low that our attempts to characterize it by UV spectrophotometry as Ogura et al.[4,5] had done for MoO_4^{2-} complexes were unsuccessful.

Comparative studies of the polarographic reduction of ReO_4^- in the presence of a number of ligands which are structural subunits of citric acid reveal that only one yields a detectable reduction wave. Among the ligands that are inactive are glycolic acid, lactic acid, malonic acid, succinic acid, glutaric acid, and propane-1,2,3-tricarboxylic acid. The inactivity of the latter ligand as well as that of acetylcitric acid shows clearly that the hydroxyl group of citric acid plays a direct role in the formation of the electroactive ReO_4^-–citrate complex. Addition of a hydroxyl group to succinic acid also activates ReO_4^-, but to a much smaller extent. Whereas succinic

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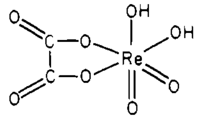
(10) Koutecky, J. *Collect. Czech. Chem. Commun.* **1953**, *18*, 597.
(11) Weber, J.; Koutecky, J. *Collect. Czech. Chem. Commun.* **1955**, *20*, 980.
(12) Delahay, P. *J. Am. Chem. Soc.* **1952**, *74*, 3506.
(13) Schwarzenbach, G.; Fisher, A. *Helv. Chim. Acta* **1960**, *43*, 1365.

acid is inactive, malic acid yields a small but definite ReO_4^- reduction wave that is kinetic limited and whose limiting-current pH dependence indicates that the malate species involved is the monoanion.

Perhaps the most important clue to the general nature of the oxalate and citrate complexes of Re(VII) is the remarkable increase in the ease of reduction which these ligands confer on ReO_4^-. This result suggests that the reaction of these ligands with ReO_4^- greatly reduces the extent to which the geometry of the Re coordination sphere must change during the electrode reaction. It is well established both experimentally[14] and on theoretical grounds[15] that, for a given central ion, the larger the change in the geometry of the coordination sphere which must occur in a redox process, the more irreversible is that redox process. Clearly, the reduction of ReO_4^-, which is tetrahedral,[16,17] to Re(V), which almost certainly has a coordination number of 6 or higher, involves major changes in the geometry of the rhenium coordination sphere. The striking increase in the ease of reduction of the Re(VII) complexes of citrate or oxalate strongly suggests that a critical feature of these reactions is expansion of the coordination sphere of Re(VII). Although precise specification of the coordination geometry of these Re(VII) complexes is not possible, the structures of both citrate and oxalate are consistent with the formation of 6-coordinate species.

Formation of a 6-coordinate oxalate complex with the stoichiometry $(H_2Ox{\cdot}ReO_4)^-$ can be envisioned as a concerted process in which oxalic acid binds to Re(VII) as a bidentate ligand and simultaneously transfers its protons to two of the coordinated oxo groups. Bailey et al.[8] have pointed out that expansion of the coordination sphere of perrhenic acid by insertion of two water molecules would increase the basicity of the oxo groups substantially, and a similar increase in basicity may be anticipated when the Re(VII) coordination sphere is expanded by insertion of oxalate. The greater basicity of the oxo groups in turn facilitates the chelation of the oxalate group by providing low-energy binding sites for the oxalic acid protons. The chemistry of the well-characterized Mo(VI) octahedral complexes provides an interesting analogue which supports such a structure for the $(H_2Ox{\cdot}ReO_4)^-$ species. Substituted Mo(VI) oxoions are characterized by *cis*-dioxo (MoO_2^{2+})[18] cores suggesting that the species $(H_2Ox{\cdot}ReO_4)^-$ may have a similar structure as illustrated by I.



I

Formation of a 6-coordinate citrate complex with the stoichiometry $(H_2Cit{\cdot}ReO_4)^{2-}$ is envisioned to occur by a similar concerted process. Because the three carboxylate groups and the hydroxyl group of citrate can all interact with ReO_4^-, the nature of the $(H_2Cit{\cdot}ReO_4)^{2-}$ complex is not immediately apparent, but Drieding molecular models indicate that a chelated structure, in which the hydroxyl group of citric acid is hydrogen bonded to an oxo group, is stable. In constructing this model, we have approximated the octahedral rhenium–oxygen distance as the tetrahedral value of 1.84 Å[19] and the oxygen–oxygen distance of the hydrogen bonded oxo and hydroxyl groups as 2.70 Å.[20] The model shows that citric acid occupies one face of the rhenium coordination octahedron with the terminal carboxylate groups filling the coordination sites at two corners of the face and the hydroxyl group hydrogen bonded to an oxo group at the third corner. This interaction of the citric acid hydroxyl group with the Re(VII) oxo group is particularly interesting in view of the inactivity of acetylcitric acid and of propanetricarboxylic acid. It suggests strongly that this interaction is essential for the electroactivity of the Re(VII)–citrate complex. Evidence in favor of Re(VII) species with expanded coordination spheres is indirect, but it is sufficient to provide support. To explain the kinetics of oxygen exchange between ReO_4^- and water, Murmann[21] proposed an Re(VII) intermediate of increased coordination. Structures similar to this have been proposed to explain the kinetics of the reactions of MoO_4^{2-} with 8-hydroxyquinoline[22] and with catechol,[23] and in the mechanism for condensation of Mo(VI),[24] a key intermediate is a protonated octahedral species. Collectively these results lend considerable support to the proposal that formation of the citrate and oxalate complexes involves expansion of the Re(VII) coordination sphere.

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Appendix

For a reversible equilibrium between ReO_4^- and a ligand L yielding product P, R, the net rate of formation of P, is given by eq A-1 where k_f and k_b denote, respectively, the forward

$$R = k_f(\mathrm{ReO_4^-})^a(\mathrm{L})^b(\mathrm{H^+})^c - k_b(\mathrm{P})(\mathrm{H^+})^d \tag{A-1}$$

and reverse rate constants. If the ligand is present in large excess over ReO_4^- and the pH is well buffered, both the proton concentration and the ligand concentration remain fixed at their initial values. Further, if the fraction of ReO_4^- consumed in the reaction is small, the ReO_4^- concentration may also be approximated as remaining at its initial value. Under these conditions, eq A-1 reduces to eq A-2, where the constant

$$R = k_f' - k_b'(\mathrm{P}) \tag{A-2}$$

concentrations have been incorporated into the effective rate constants k_f' and k_b'. The values of k_f' and k_b' are related to K', the effective equilibrium constant in the usual manner, and this quantity is in turn equal to $(\mathrm{P_{eq}})$ as shown in eq A-3.

$$k_f'/k_b' = K' = (\mathrm{P_{eq}}) \tag{A-3}$$

Substitution of eq A-3 into eq A-2 and integration yield the rate law in eq A-4, where t is the time elapsed since the start

$$\ln\,[(\mathrm{P})/[(\mathrm{P_{eq}}) - (\mathrm{P})]] = k_b't \tag{A-4}$$

of the reaction, and (P) is the instantaneous concentration of P. Because the polarographic limiting current is directly proportional to the bulk concentration of P, one can replace the concentrations in eq A-4 by the corresponding currents as shown in eq A-5. An equation that permits study of certain

$$\ln\,[i/(i_{eq} - i)] = k_b't \tag{A-5}$$

aspects of the forward reaction can be derived from eq A-5

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as follows. Multiplication by K' and simplification of the right-hand side yield eq A-6. Although the quantity K' is not

$$K' \ln [i/(i_{eq} - i)] = k_f' t \qquad (A\text{-}6)$$

directly measurable because it equals (P_{eq}), it is directly proportional to i_{eq}, the limiting current at equilibrium, and thus can be replaced by Ai_{eq} where A is an (unknown) proportionality constant. Making this substitution in eq A-6 and rearranging yield eq A-7, which, by permitting determination

$$i_{eq} \ln [i/(i_{eq} - i)] = k_f' t/A \qquad (A\text{-}7)$$

of the quantity k_f'/A for different reactant concentrations, allows establishment of the order of the forward reaction with respect to each reactant.

Registry No. ReO_4^-, 14333-24-5; citric acid, 77-92-9; oxalic acid, 144-62-7.

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Relationships between Valence Orbital Binding Energies and Crystal Structures in Compounds of Copper, Silver, Gold, Zinc, Cadmium, and Mercury

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Theoretical calculations and X-ray spectral data are used to determine the relative binding energies of the Cu, Ag, Au, Zn, Cd, and Hg d orbitals and the ligand p orbitals in the metal chlorides and sulfides. Compared to the S 3p nonbonding orbitals, the metal d orbitals are of lower binding energy for Cu, of slightly higher binding energy for Au, Ag, and Hg, and of considerably higher binding energy for Zn and Cd. Transformation from gaseous monomer to gaseous polymer to condensed phase is shown to raise the metal (M) d orbital energy with respect to the ligand (L) p, resulting in a larger L p–M d energy separation and smaller L p–M d covalent mixing for Cu compounds and a smaller separation and greater covalent mixing for compounds of the other metals. The existence or nonexistence of different oxidation states of these metals in combination with various ligands can be qualitatively understood on the basis of the energies of predominantly M d and L p orbitals obtained from spectra or molecular cluster calculations (and to some extent from the M d and L p atomic orbital energies). Similarly, the coordination numbers and polyhedral distortions in the most stable polymorphs of these compounds are determined by the numbers of M d electrons and the extent of M d–L p covalent mixing. The adoption of structures with low M coordination numbers by compounds with filled M d shells and small M d–L p energy differences serves to lower the M d energy and reduce the destabilization due to M d–L p covalent mixing.

Introduction

Compounds of metals near the ends of the transition series often exhibit unusual structures even for binary phases.[1] For example, Cu_2O adopts the cuprite structure in which Cu^I is two-coordinate, CuO adopts the tenorite structure in which Cu^{II} is four-coordinate square planar, Cu_2S adopts the complex chalcocite structure in which the Cu exists in (distorted) three-coordination, and CuS adopts the very unusual covellite structure, in which the Cu is partly three-coordinate and partly four-coordinate and in which disulfide anions, S_2^{2-}, occur. Even the copper fluorides are not simple—solid CuF has apparently never been prepared and CuF_2, although it has the common rutile structure, has Cu in a highly distorted six-coordinate (or 4 + 2) site. Compounds of heavier elements in the Cu group also have unusual structures, e.g., the acanthite structure of Ag_2S contains both two- and four-coordinate Ag^I, and Au^I exists in two-coordination in AuI and CsAuO. Zn^{II} and Cd^{II} compounds show fairly simple structures although even in ZnO the observed coordination number of 4 differs from that of 6 expected on size criteria. For Hg^{II} compounds unusual structures are again common, for example the cinnabar structure of HgS in which Hg^{II} is two-coordinate. The existence of such complex structures (or their stability with respect to hypothetical simpler structures) has not yet been given an adequate quantum mechanical explanation.

Accurate direct quantum mechanical calculation of the total energies of such complex materials containing heavy atoms is still not possible nor is it likely for some time in the future. Nonetheless, some understanding of these structures can be achieved with use of the qualitative molecular orbital concepts which have been successfully applied to gas-phase molecules.[2] Such an approach relies upon the identification of one or a few orbitals and the investigation of their change in energy as a function of structure type. The basic principle of such a method is to minimize the product of orbital energy times occupation number, e.g., by distorting a symmetric structure in such a way as to stabilize filled orbitals and destabilize empty orbitals. Many such methods in the past have relied upon rather simple quantum mechanical methods such as that of extended Hückel theory.[3] In this work we rely upon orbital energies or ionization potentials obtained either by analysis of X-ray spectral data or from multiple-scattering self-consistent-field $X\alpha$ (MS–$X\alpha$) MO calculations,[4] which have been shown to yield accurate ionization potentials for a wide variety of transition-metal compounds. We feel that this is a critical methodological improvement for the systems under study since the energetic relations between metal (M) d and ligand (L) p orbitals are rather subtle and require rather accurate methods for their prediction. Indeed, for compounds of Au and Hg, consideration of relativistic effects may even be quite important. However, the principles which we finally derive will be qualitative in nature and will therefore not rely upon the detailed features of this computational method.

In the following section the analysis of the spectra and the computations to obtain information on the energies of predominantly M d or L p orbitals in sulfides and chlorides of the Cu and Zn group metals is described, in some cases referring to previous work. When spectral data do not exist, MS–$X\alpha$ calculations are employed to give approximate in-

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