Following again the argument that correlation splitting is slight, it is reasonable to assume that the inactive A_{2u} and E_u modes will be close in frequency to the known A_{1g} and E_g modes. This is important in that restrictions are then placed upon interpretation of the combination bands at 464, 548, and 635 cm^{-1}. The only modes for which we now have absolutely no *direct* experimental evidence are the sole T_{1g}-T_{2u} pair associated with δ(ZnCN) motion. Jones placed this mode, ν_9, at 230 cm^{-1} on the basis of combination-band evidence. Such arguments can be very misleading, but we support this one mainly because it is difficult to find plausible alternatives to our assignment (Table II) for the 548-cm^{-1} band. This can arise from either or both of the combinations 320 cm^{-1} (E_g or T_{2g}) + 228 cm^{-1} (T_{1g}) although we are inclined to favor the T_{2g} label because of the observed *zz* component. Likewise, the 635-cm^{-1} band is most probably an overtone of that at 320 cm^{-1} with either or both symmetry species involved (since the products $E_g \times E_g$ and $T_{2g} \times T_{2g}$ both contain E_g).

The provenance of the 464-cm^{-1} band is less readily settled. Combinations 346 + 137 = 483 cm^{-1} and 320 + 161 = 481 cm^{-1} are improbable for two reasons: (i) they suggest an improbably high anharmonicity; (ii) the 464-cm^{-1} combination is not temperature sensitive but both the 137- and 161-cm^{-1} fundamentals are. We consider that it is the first overtone of the inactive T_{1g}-T_{2u} mode. Alternatively, it could be the first overtone of the T_{1g} part of this correlation doublet (but *not* their combination as $T_{1g} \times T_{2u}$ is not Raman active).

General Comments

Although he saw only three fundamentals directly, Jones located others from combinations. On this basis he conducted a normal-coordinate analysis. The difficulty with CZnC bending force constants is readily understood as our assignments for these modes are rather different from those which he had deduced.

Compared with $Ni(CO)_4$ there are major differences of intensity, as well as of interaction force constants (*e.g.*, separation of ν(CN) and ν(M-CN) modes is negligible compared with the analogous ν(CO) and ν(M-CO) modes). δ(MCO) modes are weak in the Raman effect: it was the extreme feebleness of ν_3(e)-δ(MCO) which long delayed completion of the assignment for $Ni(CO)_4$. In contrast, δ(ZnCN) appears to be quite intense. CMC bending modes are much higher for $[Zn(CN)_4]^{2-}$ than for $Ni(CO)_4$, although this may well be due to the constraints provided by interaction with potassium cations.

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Kinetic Studies of Oxygen Exchange between Oxocyanorhenate(V) Complex Ions and Solvent Water[1]

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The rates of oxygen exchange between *trans*-dioxotetracyanorhenate(V) and water have been determined in both acidic and basic media. At unit ionic strength the rate law is given by $R = k_1 [ReO(OH)(CN)_4{}^{2-}] + k_b[ReO_2(CN)_4{}^{3-}]$. In the presence of added cyanide ions, $k_b = k_2[CN^-]^{-0.90}$ and in the absence of added cyanide ions $k_b = k_3[OH^-]^{0.22}$. The value for k_1 at 35.0° is $(3.42 \pm 0.05) \times 10^{-2}$ sec^{-1}. The value for k_2 at 89.7° is $(4.16 \pm 0.23) \times 10^{-7}$ *M* sec^{-1} and the value for k_3 at 70.3° is $(4.23 \pm 0.04) \times 10^{-3}$ sec^{-1}. The Arrhenius activation energies for k_1 and k_3 are 23.3 ± 0.3 and 20.3 ± 0.1 kcal/mol, respectively. In acidic media a mechanism is proposed in which exchange of an oxo ligand is facilitated by protonation. The mechanism for exchange in basic media is proposed to involve solvent replacement of an equatorial cyano ligand with consequent axial oxo ligand labilization. The rates of oxygen exchange of the dimeric anion μ-oxo-bis[oxotetracyanorhenate(V)] have also been determined. At unit ionic strength the rate law for the terminal oxygens is given by $R = k_1[Re_2O_3(CN)_8{}^{4-}] + k_2[Re_2O_3(CN)_8{}^{4-}][H^+]$. At 50.0°, the values of k_1 and k_2 are $(1.11 \pm 0.07) \times 10^{-4}$ sec^{-1} and $(3.46 \pm 0.24) \times 10^{-2}$ *M* sec^{-1}, respectively. The Arrhenius activation energy for terminal oxo ligand exchange is 30.3 ± 0.9 kcal/mol. At 70.3° and $[H^+] = 2.0 \times 10^{-4}$ *M*, the rate of terminal oxo ligand exchange is 40 times faster than the rate of bridging oxo ligand exchange. A mechanism is proposed in which exchange of terminal oxo ligands is facilitated by association with $H_{aq}{}^+$.

Introduction

The existence of *trans*-dioxotetraligand(metal ion) complexes of second and third-row transition elements has been recognized for some time.[2] It is becoming increasingly clear that such complexes are of fundamental importance in the aqueous solution chemistry of $4d^2$ and $5d^2$ metal ions such as molybdenum(IV), ruthenium(VI), tungsten(IV), rhenium(V), and osmium(VI). It is only recently, however, that kinetic studies of ligand substitution reactions of these complex ions have been undertaken. In a survey study of several such rhenium(V) complexes Beard, *et al.*, reported[3] preliminary results of kinetic studies of oxo and equatorial ligand exchange of $ReO_2L_4{}^{n+}$ where L = CN^-, pyridine, or $^1/_2$ ethylenediamine (en). More recently Kriege and Murmann[4]

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[1] Taken in part from the Ph.D. dissertation of D. L. Toppen, University of Missouri, 1971.

[2] (a) N. Johnson, C. Lock, and G. Wilkinson, *Chem. Ind. (London)*, 333 (1963); (b) W. D. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 675 (1967); (c) W. D. Griffith and T. D. Wickins, *ibid.*, 400 (1967).

[3] J. Beard, C. Calhoun, J. Casey, and R. Kent Murmann, *J. Amer. Chem. Soc.*, 90, 3389 (1968).

[4] L. B. Kriege and R. K. Murmann, *J. Amer. Chem. Soc.*, 94, 4557 (1972).

have reported the results of a thorough study of the rates of oxo ligand exchange of $ReO_2(en)_2^+$ in aqueous and methanol-water solutions. They reported that R, the rate of oxygen exchange between $ReO_2(en)_2^+$ and solvent water, can best be expressed as a four-term rate law

$$R/[ReO_2(en)_2^+] = k_0 + k_1[enH_2^{2+}] + k_2[en] + k_3[OH^-]$$

Furthermore, the rate of oxo ligand exchange was found to depend upon the nature of the cation of the supporting electrolyte, upon the presence of acids and bases (including those other than H^+, OH^-, and the various protonated forms of en), and upon the partial substitution of methanol for water as solvent. The observed rate law was rationalized on the basis of an SN1cb type mechanism giving rise to the k_2 and k_3 terms, while direct solvent replacement and H_2en^{2+}-assisted solvent displacement give rise to the k_0 and k_1 paths, respectively.

This paper reports studies of the rates of exchange of oxygen between the *trans*-dioxotetracyanorhenate(V) complex, $ReO_2(CN)_4^{3-}$, and solvent water. Beard, *et al.*, reported[3] the half-time for oxygen exchange of this ion to be $(1.0\text{-}1.5) \times 10^4$ min at 25° in nonbuffered media containing excess ligand. Under similar conditions the half-times for oxygen exchange of $ReO_2(en)_2^+$ and $ReO_2(py)_4^+$ were reported to be 3×10^3 and 8×10^3 min, respectively. Thus the rate of oxo ligand exchange of *trans*-dioxorhenium(V) complexes appears to be greatly dependent upon the nature of the ligands in the equatorial plane of the complex ion, the rate decreasing as the π-bonding ability of the equatorial plane increases. The present work represents an attempt to explore further the role and scope of the equatorial ligands in the mechanism of oxo ligand exchange. During the course of these studies a hitherto unknown dimeric complex ion, $O{=}Re(CN)_4ORe(CN)_4{=}O^{4-}$, was discovered[5,6] in acidified solutions of $ReO_2(CN)_4^{3-}$. Consequently, the rates of aqueous solvent exchange of both the terminal and bridging oxo ligands of this species have been determined.

Experimental Section

Materials. $K_3[ReO_2(CN)_4]$ and $K_4[Re_2O_3(CN)_8]$ were prepared and characterized as previously described.[3,5] $K_3[Re^{18}O_2(CN)_4]$ was prepared by dissolving purified $K_3[ReO_2(CN)_4]$ in water containing *ca.* 4 times the natural abundance of ^{18}O. The resulting solution was maintained at 90° for 24 hr. Addition of acetone precipitated bright orange crystals which were recrystallized from methanol-water and dried under reduced pressure.

$[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ were prepared by methods described in the literature.[7] KCN and KCl were of reagent grade and were further purified by crystallization prior to use.

Water used as solvent in all runs was doubly distilled, once from alkaline permanganate solution. Solutions prepared for kinetic runs at temperatures in excess of 50° were deaerated with Cr(II)-scrubbed nitrogen gas.

Equipment. Visible and uv spectral measurements were carried out on Beckman DU or Cary 14 spectrophotometers. Kinetic runs conducted at temperatures below 70° were carried out in a water-jacketed flask with a capacity of 25 ml and equipped with a Haake circulating-water thermostat. Samples were withdrawn with conventional pipets. Runs conducted at temperatures of 70° or above were carried out in a 50-ml glass vessel which was equipped with a Teflon stopcock. The vessel was immersed in a dewar flask containing ethylene glycol which was maintained at the desired temperature. The vessel was evacuated prior to use and filled by forcing the solution into the flask with deaerated nitrogen gas. At the elevated temperatures of the bath, the vapor pressure of the solvent and the pressure of nitrogen were sufficient to force solution from the vessel when the stopcock was opened. The construction and use of this bath has been described in detail.[1] Possible effects of light were obviated by shrouding the reaction vessel with foil throughout the course of the runs. Temperature control for both baths was ±0.05°.

A Nuclide RMS-16 ratio mass spectrometer was used for ^{18}O analysis of gas samples. The mass spectrometer was standardized at each use with a standard sample of CO_2 of natural ^{18}O abundance. The mass to charge ratio $46/(44 + 45)$ for this sample was arbitrarily assigned the value of 0.00400.

A Corning Model 12 Research pH meter equipped with a Sargent miniature combination electrode and a Moseley 5-mV strip chart recorder was used for the measurement of pH.

Purification of gas samples prior to mass spectral analysis was accomplished with a vapor-phase chromatograph of local construction. The chromatograph was equipped with a thermistor detector and a $^1/_4$-in. column, 6 ft in length containing 30% Dow 704 silicone oil on firebrick and having a liquid N_2 collection device. The chromatograph was operated at ambient temperature and CO_2, $(CN)_2$, and HCN were eluted in 1, 3, and 7 min, respectively.

$Re^{18}O_2(CN)_4$-H_2O Exchange Studies. Procedure. In a typical run, a total of 0.750 mmol of ^{18}O-labeled $K_3[ReO_2(CN)_4]$ was dissolved in 25 ml of a solution of the desired concentration of KCl and either KOH, KCN, or HCl. After deaeration, the solution was transferred to the sample vessel of the constant-temperature bath. At timed intervals approximately 3 ml of solution was withdrawn from the bath and quickly cooled to 0° in a stoppered vial. Sufficient solid $[Co(NH_3)_6]Cl_3$ to afford quantitative precipitation of Re(V) as $[Co(NH_3)_6][ReO^*_2(CN)_4]$ was added. The samples were washed, dried under reduced pressure, and transferred to Pyrex break-seal tubes, each of which contained *ca.* 150 mg of $Hg(CN)_2$.[8] After sealing, the samples were maintained at 425° for 4 hr, after which the contents were placed in the inlet system of the vapor-phase chromatograph. After purification, the carbon dioxide fraction was collected for oxygen isotopic analysis.

In exchange runs at 89.7°, an odor of ammonia was observed in aliquots taken for analysis but the visible spectrum of a deaerated solution which was 0.03 M in $ReO_2(CN)_4^{3-}$ and 0.20 M in KCN and was maintained at 89.7° was constant for a period of 5 days, indicating that the complex ion was stable under the stated conditions. Thus the ammonia was being produced by decomposition of cyanide ion. This loss of cyanide ion from solution is unavoidable, and a quantitative determination of the rate constants for cyanide hydrolysis was necessary for a proper treatment of the ^{18}O-exchange rate data (see below).

Treatment of Data. Preliminary studies indicated that the rate of exchange of oxygen between $ReO_2(CN)_4^{3-}$ and H_2O was inversely dependent upon $[CN^-]$ added. Furthermore, in experiments conducted under conditions where cyanide ion is not stable, *i.e.*, alkaline aqueous media at 90°, nonlinear McKay plots ($-\ln(1 - F)$ *vs.* time) were obtained, also suggesting that the rate of oxygen exchange is sensitive to the concentration of free cyanide ion.

In treating the kinetic data in a fashion which is consistent with these observations, it has been assumed that the exchange of oxygen between $ReO_2(CN)_4^{3-}$ and solvent water involves a preequilibrium process in which a cyano ligand is lost from the coordination sphere of Re(V). This assumption is consistent with the earlier observation that the rate constant for cyano ligand exchange is very large compared to the rate constant for oxygen exchange.[3]

$$\begin{tikzcd}
2H_2O + c^* \arrow[r, shift left, "K_{eq}"] & CN^- + a^* + H_2O \arrow[l, shift left] \arrow[d, "k_{exch}"] \\
H_2O + H_2O^* + c \arrow[r, shift left, "K_{eq}"] & CN^- + a + H_2O^* \arrow[l, shift left]
\end{tikzcd}$$

Here c* and a* respectively represent $ReO_2(CN)_4^{3-}$ and an intermediate, say, $ReO_2(CN)_3(OH_2)^{2-}$, for which the ^{18}O isotopic content is greater than that of the solvent. c and a represent these same species with an ^{18}O isotopic content equal to that of the solvent. In all runs the low excess ^{18}O abundance and low concentration of complex lead to only negligible perturbation of the ^{18}O:^{16}O ratio of the solvent during the course of a run.

If $d[CN^-]/dt = 0$ and if it is assumed that K_{eq} is very small and that $-d[c^*]/dt = k_{exch}[a^*]$, the integrated rate expression becomes

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(5) D. L. Toppen and R. K. Murmann, *Inorg. Nucl. Chem. Lett.*, 6, 139 (1970).

(6) R. Shandles, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, 10, 2785 (1971).

(7) J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, 2, 216 (1946).

(8) M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isotop.*, 4, 233 (1959).

$$-\ln (1 - F) = -\ln ((D^* - D^*_\infty)/(D^*_0 - D^*_\infty)) = k_{\mathbf{exch}}K_{\mathbf{eq}}[\mathrm{CN}^-]^{-1}t = k_{\mathbf{obsd}}t$$

where F is the fraction of labeled material which has undergone exchange and D^*_0, D^*_∞, and D^* represent the ^{18}O abundances of $[ReO_2(CN)_4]^{3-}$ at the starting time, infinite time, and time t, respectively. Under these conditions graphs of $-\ln (1 - F)$ *vs.* time were observed to be linear, with slope equal to $k_{\mathbf{obsd}} = k_{\mathbf{exch}}k_{\mathbf{eq}} \cdot [\mathrm{CN}^-]^{-1}$. Values of $k_{\mathbf{obsd}}$ were obtained by linear least-squares analysis, employing the IBM 360/65 at UMC.[9] R, the rate of oxygen exchange, was then calculated with the usual exchange rate law[10]

$$R = k_{\mathbf{obsd}}\frac{2[\mathrm{ReO_2(CN)_4}^{3-}][\mathrm{H_2O}]}{2[\mathrm{ReO_2(CN)_4}^{3-}] + [\mathrm{H_2O}]}$$

which, since $[H_2O] >> [ReO_2(CN)_4^{3-}]$, can be closely approximated by

$$R \simeq 2k_{\mathbf{obsd}}[\mathrm{ReO_2(CN)_4}^{3-}] = 2k_{\mathbf{exch}}K_{\mathbf{eq}}[\mathrm{CN}^-]^{-1} \times [\mathrm{ReO_2(CN)_4}^{3-}]$$

Under conditions where cyanide ion hydrolyzes and $d[CN^-]/dt = k_{\mathbf{cn}}[CN^-]$, the integrated rate expression becomes

$$-\ln (1 - F) = -\ln ((D^* - D^*_\infty)/(D^*_0 - D^*_\infty)) = k_{\mathbf{exch}}K_{\mathbf{eq}}[\mathrm{CN}^-]_0^{-1}k_{\mathbf{cn}}^{-1}(\exp(K_{\mathbf{cn}}t) - 1)$$

where $k_{\mathbf{cn}}$ and $[CN^-]_0$ are the first-order rate constant for hydrolysis of cyanide ion and the initial concentration of cyanide ion, respectively. Graphs of $-\ln (1 - F)$ *vs.* time were found to be nonlinear under these conditions, with slope increasing with time. This integrated rate equation is of the form $y = B_1(\exp(B_2x) - 1)$, where $y = -\ln (1 - F)$ and $x = t$, respectively. Treatment of the data by the method of nonlinear least squares gives values for B_1 and B_2 which are respectively $k_{\mathbf{exch}}K_{\mathbf{eq}}/[CN^-]_0k_{\mathbf{cn}}$ and $k_{\mathbf{cn}}$. Under conditions where $k_{\mathbf{cn}}$ could be evaluated independently, the value of B_1 was obtained holding B_2 fixed at the determined value of $k_{\mathbf{cn}}$ (see below). R, the overall rate of oxygen exchange at $[CN^-] = [CN^-]_0$, was then calculated using the expression

$$R = 2B_1k_{\mathbf{cn}}[\mathrm{ReO_2(CN)_4}^{3-}] = 2k_{\mathbf{exch}}K_{\mathbf{eq}}[\mathrm{CN}^-]_0^{-1} \times [\mathrm{ReO_2(CN)_4}^{3-}]$$

The parameters $k_{\mathbf{exch}}$ and $K_{\mathbf{eq}}$ are inseparable and their magnitudes cannot be individually determined from these measurements.

$Re_2O_3(CN)_8^{4-}$-H_2O Exchange Studies. Procedure. In a typical run, 15.00 ml of 1.85 times ^{18}O-enriched H_2O, containing the requisite amounts of KCl and HCl, were placed in the thermostated bath and allowed to reach the desired temperature. A 176.9-mg amount of $K_4[Re_2O_3(CN)_8]$ of natural isotopic abundance was added and the solution was stirred. Dissolution of $K_4[Re_2O_3(CN)_8]$ required less than 5 sec. The time of addition of the Re(V) salt was taken as t_0 for the run. Aliquots were withdrawn at timed intervals and cooled to 0° and solid $[Co(en)_3]Cl_3$ was added, precipitating $[Co(en)_3]_4[Re_2O_3(CN)_8]_3$. ($^{18}O$-enriched samples of $Re_2O_3(CN)_8^{4-}$, precipitated rapidly from solution at 0° by addition of $Co(en)_3^{3+}$, were found to have undergone no exchange. Similarly, samples of $Re_2O_3(CN)_8^{4-}$ of normal isotopic composition, precipitated rapidly from highly enriched water, showed no apparent exchange. These results indicate that the $Co(en)_3^{3+}$ salt of $Re_2O_3(CN)_8^{4-}$ is anhydrous and that the precipitation process does not induce exchange.) The normalized ^{18}O content of individual samples was subsequently obtained by exactly the same procedure which has been described for $ReO_2(CN)_4^{3-}$.

A preliminary study[5] indicated that the exchange of two-thirds of the oxygens of $Re_2O_3(CN)_8^{4-}$ was complete within 1 hr at 25°. In the course of the present study it was shown that the exchange is not complete in 1 hr at 25° and that 50° is a more convenient temperature for study of the rates of terminal oxygen exchange. It was shown that the highly enriched nonrecrystallized $K_4[Re_2O_3(CN)_8]$ used in the previous study was contaminated with acid (pH of *ca.* 100 mg of enriched salt in 1.0 ml of H_2O was 5.8), offering a possible explanation for the more rapid rate of exchange of that material.

Treatment of Data. Letting N represent the isotopic ratio 46/(44 + 45), with N_∞ referring to the ratio at infinite time, the slope, $k_{\mathbf{obsd}}$, of a plot of $-\ln (N_\infty - N)$ *vs.* time was evaluated using a linear least-squares program. Since two of the oxygen ligands of $[Re_2O_3(CN)_8]^{4-}$ exchange more rapidly than the bridging oxo ligands, the expected value of N_∞, when only terminal oxo ligands had reached isotopic equilibrium with the solvent, was calculated using $N_\infty = {}^1/_3N_0 + {}^2/_3N_s$, where N_s is the isotopic ratio of the solvent and N_0 is the isotopic ratio of the complex ion before any exchange had occurred. The mass of oxygen in the solvent was in vast excess over the mass of oxygen in the complex ion, resulting in negligible ^{18}O dilution of the solvent during exchange. Rates of exchange were calculated using $R = k_{\mathbf{obsd}}ab/(a + b)$ where a is the concentration of exchanging coordinated ligands and b is the concentration of water. For the run conducted to determine the rate of bridging ligand exchange at 70.3°, the data were treated in an identical fashion, except that N_∞ was taken to have the value of N_s, the isotopic ratio of the solvent.

Cyanide Ion Hydrolysis Studies. Procedure. Solutions for the determination of the rate constants for cyanide ion hydrolysis were prepared and deaerated in exactly the same manner as solutions prepared for the study of oxygen exchange of $ReO_2(CN)_4^{3-}$. The solutions were forced with deaerated nitrogen into the high-temperature sample vessel and placed in the 89.7° bath. Samples (6 ml) were withdrawn at timed intervals and rapidly cooled to 25°. A 5.00-ml aliquot of each sample was placed in an erlenmeyer flask to which had been added 5 ml of H_2O, 1 ml of concentrated ammonia, and *ca.* 100 mg of solid potassium iodide. These solutions were titrated with standardized silver nitrate solution to the turbidimetric (AgI) end point. The concentration of cyanide ion present was calculated from the volume of silver(I) solution required to complex all available cyanide as $Ag(CN)_2^-$. These experiments were conducted with initial concentrations of potassium cyanide of 0.100 and 0.200 *M*. The ionic strength was maintained at 1.0 *M* (KCl). (Chloride ion has no effect on the end point of the titration.) The presence of $ReO_2(CN)_4^{3-}$ was shown to have no effect on the rate of cyanide ion hydrolysis.

Treatment of Data. For all kinetic studies graphs of $-\ln (C/C_0)$ *vs.* time were linear, where C is the concentration of cyanide ion remaining in solution at the time of sampling and C_0 is its initial concentration. The slopes of these graphs, $k_{\mathbf{cn}}$, were evaluated by linear least-squares analysis.

$ReO_2(CN)_4^{3-}$-Acid Association Constant. The equilibrium constant for the association of $ReO_2(CN)_4^{3-}$ with hydrogen ion could not be determined by a conventional potentiometric titration, due to the secondary reaction which occurs quickly following the addition of acid, *i.e.*, the formation of $Re_2O_3(CN)_8^{4-}$. The method employed took advantage of the fact that the protonation reaction is much faster than the dimerization reaction. By using rapid mixing and rapid pH measurement the two reactions could be separated. For the conjugate base of a weak acid, the addition of 0.5 equiv of hydrogen ion gives a solution of pH equal to log $K_{\mathbf{eq}}$, where $K_{\mathbf{eq}}$ is the equilibrium constant for association of the base with hydrogen ion.

The measurement of $K_{\mathbf{eq}}$ for $ReO_2(CN)_4^{3-}$ was conducted at 0.0, 25.0, and 50.0°. In each case duplicate determinations were made. In a typical measurement 10.00 ml of a solution which was 0.020 *M* in $ReO_2(CN)_4^{3-}$ and 0.88 *M* in KCl ($\mu = 1.0$) was placed in a stirred, thermostated container. Upon equilibration, the response of the glass electrode to the injection of 100 μl of 1.000 *N* HCl was recorded on the strip chart recorder. The reproducibility and accuracy of this rapid procedure were demonstrated by determining the value of the equilibrium constant for association of $H_2PO_4^-$ with H^+, a reaction for which the value of $K_{\mathbf{eq}}$ at 25.0° is[11] log $K_{\mathbf{eq}} = 2.160$ (found: 2.181, 2.187, 2.186). For $ReO_2(CN)_4^{3-} + H^+ \rightleftarrows ReO(OH)(CN)_4^{2-}$, log $K_{\mathbf{eq}}$ values found at various temperatures are as follows: 0.0°, 3.68, 3.60, 3.58; 25.0°, 3.71, 3.70; 50.0°, 3.96, 3.95. Here $K_{\mathbf{eq}}$ is defined as $[ReO(OH)(CN)_4^{2-}]/[ReO_2(CN)_4^{3-}][H^+]$.

Results

Kinetics of $ReO_2(CN)_4^{3-}$-H_2O Exchange. Preliminary Study. The preliminary study of the exchange of oxygen between $ReO_2(CN)_4^{3-}$ and H_2O was conducted at 25.1°, in the presence of 0.20 *M* potassium cyanide. The results of those experiments, which are presented in Table I, indicate that (1) under these conditions, no significant exchange occurred in 75 hr; (2) since the starting material and the reprecipitated salts were of essentially the same isotopic com-

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(9) All least-squares analyses were performed using a local modification of program ANME208, obtained from Argonne National Laboratory. This program is based on Report LA-2367, Los Alamos Scientific Laboratory.

(10) H. A. C. McKay, *Nature (London)*, **142**, 997 (1938).

(11) R. G. Bates, *J. Res. Nat. Bur. Stand.*, **47**, 127 (1951).

Table I. Preliminary Study of the Rate of Isotopic Oxygen Exchange of $ReO_2(CN)_4^{3-}$ (25.1°, $\mu = 0.38$)

Time, hr	Atom % of ^{18}O[a]	Time, hr	Atom % of ^{18}O[a]
0[b]	0.7350	40	0.7431
0[c]	0.7315	75	0.7483
20	0.7517		

[a] The atom % of ^{18}O in samples of natural origin is approximately 0.20. [b] Solid sample of the $K_3[ReO^*_2(CN)_4]$ starting material. [c] Dissolved and reprecipitated immediately.

position, the process of precipitation does not lead to exchange; and (3) the primary coordination number of Re(V) does not change in such a way as to incorporate more or less than 2 equiv of oxo ligands in solution. This last observation suggests that the linear O-M-O geometry which has been demonstrated for solid $K_2Re(O_2)(CN)_4$ is retained in solution.[12,13]

Cyanide Dependence. The effect of added potassium cyanide on the rate of oxygen exchange between $ReO_2(CN)_4^{3-}$ and H_2O was studied at 89.7°. Studies in these alkaline, nonbuffered media were complicated by accompanying hydrolysis of cyanide ion. Values of B_1 and B_2, evaluated by least-squares analysis of $-\ln(1 - F)$ *vs.* time data for each run (example in Figure 1), are presented in Table II. Values for R, the rate of oxygen exchange, as well as average values of k_{cn}, the first-order rate constant for hydrolysis of cyanide ion determined under the exact conditions of each run also appear in Table II. For runs at $[CN^-]_0 \geqslant 0.10\,M$, where k_{cn} could be directly determined, the values of the cyanide hydrolysis rate constant determined directly (k_{cn}) and indirectly (B_2) are identical within experimental error.

The order of the $[CN^-]_0$ term in the exchange rate law was evaluated by determining the weighted least-squares slope of a graph of $\log R$ *vs.* $-\log[CN^-]_0$, Figure 2. The experimental order with respect to $[CN^-]_0$ for the runs in Table II is -0.90 ± 0.13 (error is 2σ).

Hydrogen Ion Dependence. In acidic media, the rates of oxygen exchange between $ReO_2(CN)_4^{3-}$ and H_2O were considerably more rapid than in alkaline media. Consequently, those studies were conducted at 35.0°. The concentration of hydrochloric acid added to the exchanging solutions was varied from 3.73×10^{-5} to $2.00 \times 10^{-3}\,M$. Linear McKay graphs were obtained for all runs.

The equilibrium constant for the association of $ReO_2(CN)_4^{3-}$ with the hydrogen ion is $6.3 \times 10^3\,M^{-1}$ at 35° (see above). Thus, under the conditions of these runs, essentially all added hydrogen ion is associated with the complex ion (assumedly $ReO(OH)(CN)_4^{2-}$). Results indicating the dependence of the observed rate, R, upon the concentration of $ReO(OH)(CN)_4^{2-}$ are shown in Table III, where the values of R_a have been corrected for the small amount of exchange carried by the acid-independent terms.

A graph of R *vs.* $[ReO(OH)(CN)_4^{2-}]$ was found to be linear in the region from 3.71×10^{-5} to $5.95 \times 10^{-4}\,M$ in $ReO(OH)(CN)_4^{2-}$, Figure 3. The weighted least-squares slope and intercept of the plot are $(3.42 \pm 0.05) \times 10^{-2}$ sec^{-1} and $(3.63 \pm 0.60) \times 10^{-7}\,M$ sec^{-1}, respectively. Above a concentration of $[ReO(OH)(CN)_4^{2-}] = 6.0 \times 10^{-4}\,M$, only a minimal increase in R with increasing acid occurs. In these more acidic experiments, furthermore, slow color changes were observed, as well as the appearance of the 3000-Å absorption maximum characteristic of $Re_2O_3(CN)_8^{4-}$, indicating significant decomposition of the monomeric species.

Table II. Effect of Cyanide Ion on the Oxygen Exchange between $ReO_2(CN)_4^{3-}$ and H_2O (0.03 M $ReO_2(CN)_4^{3-}$, 89.7°, $\mu = 1.00$ (KCl))

$[CN^-]_0$, M	$10^2 B_1$[a]	$10^6 B_2$,[a] sec^{-1}	$10^6 k_{cn}$,[a,b] sec^{-1}	$10^8 R$,[a,c] M sec^{-1}
0.200	9.95 ± 0.12	9.05 ± 0.47	8.88 ± 0.13	5.30 ± 0.14
0.200	10.48 ± 0.12	8.80 ± 0.30	8.88 ± 0.13	5.58 ± 0.14
0.200	9.21 ± 0.10	9.17 ± 0.35	8.88 ± 0.13	4.91 ± 0.13
0.100	15.5 ± 0.5	8.98 ± 0.33	9.45 ± 0.05	8.79 ± 0.36
0.100	17.8 ± 0.6	9.35 ± 0.52	9.45 ± 0.05	10.09 ± 0.42
0.100	17.7 ± 0.3	9.28 ± 0.25	9.45 ± 0.05	10.04 ± 0.24
0.065	22.5 ± 0.4	10.58 ± 0.30		14.29 ± 0.66
0.050	26.1 ± 0.9	11.17 ± 0.61		18.37 ± 1.56
0.050	26.6 ± 0.5	11.92 ± 0.30		18.72 ± 1.26
0.050	26.7 ± 0.8	11.72 ± 0.47		18.79 ± 1.50

[a] Errors represent two standard deviations. B_1 and B_2 are obtained from least-squares analysis of $-\ln(1 - F)$ *vs.* time. [b] k_{cn} obtained independently. $[CN^-]_0$ was 0.200 or 0.100 M. [c] R is the rate of exchange of oxygen between $ReO_2(CN)_4^{3-}$ and H_2O.

Table III. Effect of Added Acid on the Rate of Oxygen Exchange between $ReO_2(CN)_4^{3-}$ and H_2O (35°, $\mu = 1.0$ (KCl), $[Re(V)]_T = 0.0200\,M$)

$10^5[H^+]$, M	$10^5[ReO(OH)(CN)_4^{2-}]$,[a] M	$10^6 R$,[b] M sec^{-1}	$10^6 R_a$,[b,c] M sec^{-1}
3.730	3.710	1.64 ± 0.01	1.27 ± 0.08
11.20	11.10	4.16 ± 0.06	3.80 ± 0.12
20.00	19.80	7.45 ± 0.30	7.08 ± 0.37
28.00	27.80	9.61 ± 0.40	9.25 ± 0.46
40.00	39.70	14.79 ± 0.08	14.43 ± 0.14
60.00	59.50	20.86 ± 0.03	20.50 ± 0.09
76.00	75.40	22.73 ± 0.16	22.37 ± 0.22
100.0	99.20	25.71 ± 0.40	25.35 ± 0.41
200.0	198.0	25.99 ± 0.16	25.63 ± 0.22

[a] Concentration of $ReO(OH)(CN)_4^{2-}$ calculated with $\log K_w$ (35°) = −13.68 and $\log K_a[ReO(OH)(CN)_4^{3-}]$ (35°) = −3.8. [b] Errors represent two standard deviations. [c] R_a is the contribution to R from the acid-dependent path. R_a is defined as $R_a = R - \{R_b([Re(V)_T - [ReO(OH)(CN)_4^{2-}])/[Re(V)]_T\}$, where R_b is the value of the hydroxide-catalyzed contribution to the rate at 35.0° when $[ReO(OH)(CN)_4^{2-}] = 0.0$ ($3.63 \times 10^{-7}\,M$ sec^{-1}).

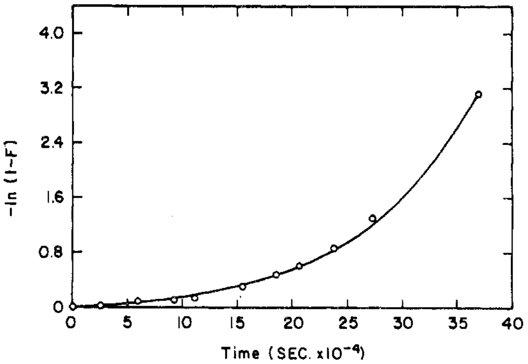

Figure 1. $-\ln(1 - F)$ *vs.* time for $ReO_2(CN)_4^{3-}$–H_2O exchange. [Complex] = 0.03 M, $[CN^-] = 0.20$, $T = 89.7°$; nonlinear least-squares curve.

No further runs at higher acidities were attempted.

The experimental order with respect to $[ReO(OH)(CN)_4^{2-}]$ was determined by obtaining the weighted least-squares slope of a graph of $-\log R_a$ *vs.* $-\log[ReO(OH)(CN)_4^{2-}]$, where R_a represents the rate of oxygen exchange carried by the $ReO(OH)(CN)_4^{2-}$ path and is calculated for each run using the expression $R_a = R - \{R_b([Re(V)]_T - [ReO(OH)(CN)_4^{2-}])/[Re(V)]_T\}$, where R_b is the value of the hydroxide ion catalyzed contribution to the rate at 35.0° when $[ReO(OH)(CN)_4^{2-}] = 0.0$ (the value of the intercept of Figure 3 is $3.63 \times 10^{-7}\,M$ sec^{-1}). The experimental order with respect to $[ReO(OH)(CN)_4^{2-}]$ was found to be 1.00 ± 0.01.

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(13) R. K. Murmann and E. O. Schlemper, *Inorg. Chem.*, 10, 2352 (1971).

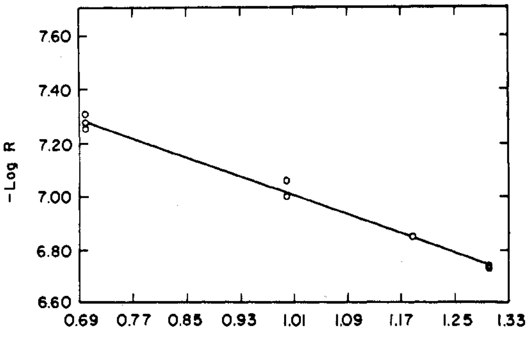

Figure 2. Cyanide ion dependence of overall rate R for $ReO_2(CN)_4{}^{3-}$-H_2O exchange. [Complex] = 0.03 M, $\mu = 1.00$ (KCl), $T = 89.7°$.

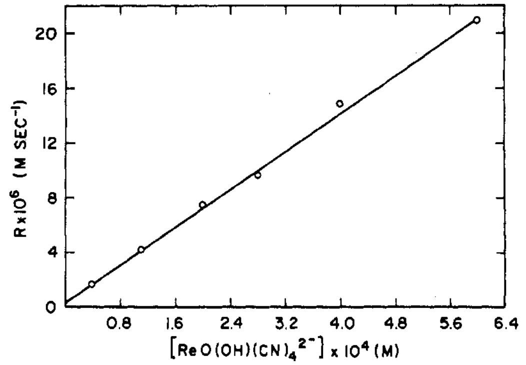

Figure 3. $[Re(O)(OH)(CN)_4{}^{2-}]$ dependence for $Re(O_2)(CN)_4{}^{3-}$-H_2O exchange. $[Re(V)]_T = 0.020\ M$, $\mu = 1.00$ (KCl), $T = 35.0°$.

Hydroxide Ion Dependence. The effect of hydroxide ion on the rate of $ReO_2(CN)_4{}^{3-}$-H_2O exchange was studied at 70.3°, in the absence of added potassium cyanide. The concentration of added KOH was varied from 0.88 to $5.90 \times 10^{-6}\ M$. The effect was not dramatic, as is shown in Table IV. R, the observed rate of oxygen exchange, decreases regularly as the concentration of hydroxide ion decreases. The rate begins to increase, however, below a hydroxide concentration of $1.00 \times 10^{-4}\ M$. This is due to the contribution to the rate from the path dependent upon the concentration of $ReO(OH)(CN)_4{}^{2-}$. The magnitude of R_a, the contribution to the rate arising from exchange of the protonated form of the complex was calculated using $R_a = k_1[ReO(OH)(CN)_4{}^{2-}]$, where k_1 was estimated from the value of k_1 at 35.0° ($3.42 \times 10^{-2}\ sec^{-1}$) and the activation energy of 23.3 kcal/mol to be 1.7 sec^{-1} at 70.3°. $[ReO(OH)(CN)_4{}^{2-}]$ was calculated using $\log K_a(ReO(OH)(CN)_4{}^{2-})(70°) = -4.0$. R_b, the hydroxide-dependent portion of the rate of exchange was calculated using $R_b = R - R_a$. A plot of $-\log R_b$ *vs.* $-\log [OH^-]$ is linear in the range of hydroxide ion concentration from 0.100 to $1.00 \times 10^{-5}\ M$, Figure 4. Deviation from linearity above 0.100 M may be due to ionic media effects, since total substitution of KOH for KCl was necessary. Below $10^{-5}\ M$, the deviation from linearity can be attributed to errors in the estimation of R_a, the acid-dependent exchange rate.

The slope of the linear region of the above plot of $-\log R_b$ *vs.* $-\log [OH^-]$ is the experimental order with respect to hydroxide ion. The order is found to be 0.22 ± 0.02. Such fractional terms can arise from the composite effects of two terms with different hydroxide dependencies, *e.g.*, $R_b = (k + k'[OH^-])[Re(V)]$. In this case, however, the data are not adequately explained by such terms; *i.e.*, a graph of R_b *vs.* $-[OH^-]$ is markedly curved.

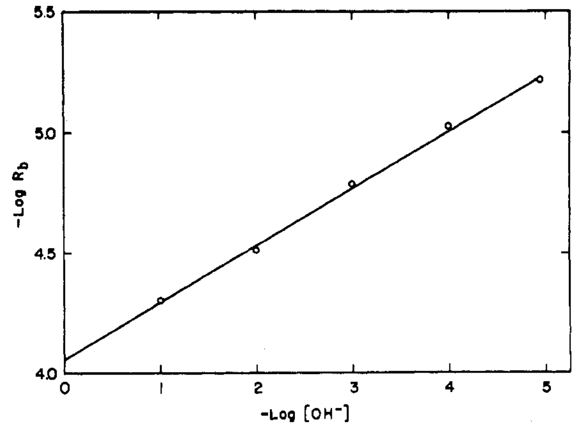

Figure 4. $[OH^-]$ dependence for $ReO_2(CN)_4{}^{3-}$-H_2O exchange. [Complex] = 0.02 M, $\mu = 1.00$ (KCl), $T = 70.3°$.

Table IV. Effect of Hydroxide Ion on the Oxygen Exchange between $ReO_2(CN)_4{}^{3-}$ and H_2O (0.02 M $ReO_2(CN)_4{}^{3-}$, 70.3°, $\mu = 1.00$ (KCl))

$-\log [OH^-]_{added}$	$10^5 R$,[a] $M\ sec^{-1}$	$10^5 R_a$,[b] $M\ sec^{-1}$	$10^5 R_b$,[c] $M\ sec^{-1}$
0.0556	6.80 ± 0.13		6.80
1.00	5.01 ± 0.03		5.01
2.00	3.09 ± 0.15		3.09
3.00	1.64 ± 0.07		1.64
4.00	1.03 ± 0.02	0.09	0.94
4.96	1.50 ± 0.03	0.89	0.61
5.23	1.83 ± 0.03	1.7	0.13

[a] Errors represent two standard deviations. [b] R_a calculated using the expression $R_a = k_1[ReO(OH)(CN)_4]$, where k_1 is estimated to have the value 1.72 sec^{-1} at 70.3°. [c] R_b defined as $R_b = R - R_a$.

$[ReO_2(CN)_4{}^{3-}]$ Dependence. The effect of the concentration of Re(V) upon the rate of oxygen exchange was investigated in basic and acidic media, at 70.3 and 35.0°, respectively. In the basic region $[ReO_2(CN)_4{}^{3-}]$ was varied from 0.020 to 0.060 M. Potassium cyanide was not added. $[OH^-]$ was maintained at $1.0 \times 10^{-4}\ M$ by addition of KOH. The results of these experiments appear in Table V. k', the rate constant for exchange, is defined as $k' = R/[ReO_2(CN)_4{}^{3-}]$. The relatively constant value of $(5.27 \pm 0.14) \times 10^{-4}\ sec^{-1}$ obtained for k' demonstrates the unitary dependence of the rate on $[ReO_2(CN)_4{}^{3-}]$ in the alkaline region. $[Re(V)]_T$, the sum of the concentrations of $ReO(OH)(CN)_4{}^{2-}$ and $ReO_2(CN)_4{}^{3-}$, for runs conducted in acidic media, was varied from 0.020 to 0.060 M. The relative concentrations of $ReO(OH)(CN)_4{}^{2-}$ and $ReO_2(CN)_4{}^{3-}$ were held constant by addition of HCl. The results are presented in Table VI. The relatively constant value of $(2.05 \pm 0.03) \times 10^{-4}\ sec^{-1}$ obtained for k' is evidence for the first-order dependence of the rate on $[Re(V)]_T$.

Temperature Dependence. The temperature of runs conducted in the basic region was varied from 49.8 to 89.7°. The results are given in Table VII. The activation energy, E_{act}, was determined using the Arrhenius equation, $\ln k_{obsd} = \ln A - E_{act}/RT$, where k_{obsd} is the observed rate constant for isotopic exchange, and A is the Arrhenius factor. Weighted least-squares analysis of a graph of $-\log k_{obsd}$ *vs.* $1/T$ gives values of 20.3 ± 0.2 kcal/mol and 9.32 ± 0.05 for E_{act} and $\log A$, respectively.

In acidic media, where exchange is carried by oxygen exchange of $ReO(OH)(CN)_4{}^{2-}$, the temperature was varied from 25.0 to 50.0°. The results appear in Table VIII. The weighted slope and intercept of a graph of $-\log k_{obsd}$ *vs.* $1/T$ yield values of 23.3 ± 0.3 kcal/mol and 12.8 ± 0.2 for E_{act} and $\log A$, respectively. Units of A are sec^{-1}.

Table V. $[ReO_2(CN)_4{}^{3-}]$ Dependence of the Oxygen Exchange of $ReO_2(CN)_4{}^{3-}$ in Basic Media ($[OH^-] = 1.00 \times 10^{-4}$ *M*, 70.3°, $\mu = 1.00$ (KCl))

$[ReO_2(CN)_4{}^{3-}]$, *M*	10^5R,[a] *M* sec^{-1}	$10^4k'$,[a] sec^{-1}
0.02	1.03 ± 0.02	5.15 ± 0.10
0.04	2.16 ± 0.14	5.40 ± 0.35
0.06	3.16 ± 0.12	5.26 ± 0.20

[a] Errors represent two standard deviations; k' is defined as $k' = R/[ReO_2(CN)_4{}^{3-}]$. The weighted mean of the k' values is $(5.27 \pm 0.14) \times 10^{-4}$ sec^{-1}.

Table VI. [Rhenium(V)] Dependence of the Oxygen Exchange of $ReO(OH)(CN)_4{}^{2-}$ (35.0°, $\mu = 1.00$ (KCl))

$[Re(V)]_T$,[c] *M*	$10^4 [H^+]_{added}$,[d] *M*	10^6R,[a] *M* sec^{-1}	$10^4k'$,[a,b,e] sec^{-1}
0.02	1.12	4.16 ± 0.06	2.08 ± 0.03
0.04	2.24	8.07 ± 0.08	2.02 ± 0.02
0.06	4.48	12.35 ± 0.40	2.06 ± 0.07

[a] Errors represent two standard deviations. [b] k' is defined as $k' = R/[Re(V)]_T$. [c] $[Re(V)]_T$ is the sum of the concentrations of all rhenium(V) species present; *i.e.*, $[Re(V)]_T = [ReO_2(CN)_4{}^{3-}] + [ReO(OH)(CN)_4{}^{2-}]$. [d] Under these conditions 0.55% of $Re(V)_T$ is in the form of $ReO(OH)(CN)_4{}^{2-}$. However, 91% of *R*, the rate of exchange, is due to the term dependent on $[ReO(OH)(CN)_4{}^{2-}]$. Percentages calculated from the data presented in Table III. [e] The weighted mean of the k' values is $(2.05 \pm 0.03) \times 10^{-4}$ sec^{-1}.

Table VII. Effect of Temperature on the Rate of Oxygen Exchange of $ReO_2(CN)_4{}^{3-}$ (0.02 *M* $ReO_2(CN)_4{}^{3-}$, 1.00×10^{-4} *M* OH^-, $\mu = 1.00$ (KCl), $[CN^-]_{added} = 0.0$)

Temp, °C	10^4k_{obsd},[a] sec^{-1}	Temp, °C	10^4k_{obsd},[a] sec^{-1}
49.8	0.390 ± 0.008	70.3	2.57 ± 0.05
59.9	1.01 ± 0.02	89.7	12.45 ± 0.33

[a] Errors represent two standard deviations.

Table VIII. Effect of Temperature on the Rate of Oxygen Exchange of $ReO(OH)(CN)_4{}^{2-}$ (0.02 *M* $ReO_2(CN)_4{}^{3-}$, 2.00×10^{-4} *M* HCl, $\mu = 1.00$ (KCl), $[CN^-]_{added} = 0.0$)

Temp, °C	10^4k_{obsd},[a,b] sec^{-1}	Temp, °C	10^4k_{obsd},[a,b] sec^{-1}
25.0	0.493 ± 0.008	50.0	10.37 ± 0.27
35.0	1.86 ± 0.08		

[a] Errors represent two standard deviations. [b] 95% of exchange is carried by exchange of $ReO(OH)(CN)_4{}^{2-}$ (estimated from the relative rates shown in Table III).

The Rate Expression. The rate of oxygen exchange between $[ReO_2(CN)_4]^{3-}$ and H_2O has been shown to be first order in $[Re(V)]_T$ under all conditions studied. In the acidic region, where $ReO(OH)(CN)_4{}^{2-}$ is primarily responsible for oxygen exchange, the rate has been shown to be first order in $[ReO(OH)(CN)_4{}^{2-}]$, $R = k_1 [ReO(OH)(CN)_4{}^{2-}]^{1.00 \pm 0.01}$, where the value of k_1 (evaluated from the slope of a graph of *R vs.* $[ReO(OH)(CN)_4{}^{2-}]$) is $(3.42 \pm 0.05) \times 10^{-2}$ sec^{-1} (35.0°). The rate expression could also be written as $R = k_1'[ReO_2(CN)_4{}^{3-}][H^+]$, where $k_1' = k_1K_{eq}$ and K_{eq} is the acid association constant for $ReO_2(CN)_4{}^{3-}$. Since the protonated form of the complex is clearly present in these solutions, it has been decided to formulate the rate as a function of $[ReO(OH)(CN)_4{}^{2-}]$.

In basic media, in the presence of cyanide ion, the empirical rate law for exchange has been shown to be $R = k_2[ReO_2(CN)_4{}^{3-}][CN^-]^{-0.90 \pm 0.13}$, where k_2 has the value $(4.16 \pm 0.23) \times 10^{-7}$ *M* sec^{-1} at 89.7°. In the absence of added cyanide ion, the empirical rate law is $R = k_3[ReO_2(CN)_4{}^{3-}] \cdot [OH^-]^{0.22 \pm 0.02}$, where k_3 has the value $(4.23 \pm 0.04) \times 10^{-3}$ sec^{-1}.

The absence of $[CN^-]$ in the rate law in the acidic region was demonstrated by conducting a single run in the presence of HCN. At 35.0°, $[ReO(OH)(CN)_4{}^{2-}] = 1.98 \times 10^{-4}$ *M*, and, $\mu = 1.0$ *M*, the rates of oxygen exchange in the presence of 0.0133 *M* HCN and in the absence of HCN were $(5.97 \pm 0.11) \times 10^{-6}$ and $7.08 \pm 0.37 \times 10^{-6}$ *M* sec^{-1}, respectively. The slightly lower rate in the presence of HCN is not considered sufficient to suggest an exchange mechanism involving loss of coordinated cyano ligands in acidic media.

The overall rate law can now be written: $R = k_1[ReO(OH)(CN)_4{}^{2-}] + k_b[ReO_2(CN)_4{}^{3-}]$, where in the presence of added cyanide ion $k_b = k_2[CN^-]_0{}^{-0.90}$ and in the absence of added cyanide ion $k_b = k_3[OH^-]^{0.22}$. The value for k_1 at 35.0° is $(3.42 \pm 0.05) \times 10^{-2}$ sec^{-1}. The value for k_2 at 89.7° is $(4.16 \pm 0.23) \times 10^{-7}$ *M* sec^{-1}. The value for k_3 at 70.3° is $(4.23 \pm 0.04) \times 10^{-3}$ sec^{-1}. (The rate expression is presented in this split form since the effects of $[CN^-]$ and $[OH^-]$ were studied independently, under differing conditions.)

Exchange of Oxygen between $Re_2O_3(CN)_8{}^{4-}$ and H_2O. Hydrogen Ion Dependence. The effect of added hydrogen ion on the rate of exchange of $Re_2O_3(CN)_8{}^{4-}$ was studied at 50.0°. Added HCl was varied from 1.87×10^{-4} to 6.93×10^{-3} *M*. $[Re_2O_3(CN)_8{}^{4-}]$ was constant at 0.015 *M*. Ionic strength was maintained at unity by addition of KCl. Linear graphs of $-\ln(1 - F)$ were obtained for all runs, the results of which are shown in Table IX. No spectral changes which could be attributed to complex decomposition or association with H^+ were observed, even at the highest acidities employed on long-term exposure to elevated bath temperatures.

A graph of *R vs.* $[H^+]$ added, Figure 5, was found to be linear, with slope and intercept of $(5.18 \pm 0.36) \times 10^{-4}$ sec^{-1} and $(1.67 \pm 0.11) \times 10^{-6}$ *M* sec^{-1}, respectively. The nonzero intercept suggests the existence of an exchange path which does not require the presence of added hydrogen ion.

$[Re_2O_3(CN)_8{}^{4-}]$ Dependence. The concentration of $Re_2O_3(CN)_8{}^{4-}$ was varied from 0.015 to 0.045 *M*. μ and $[H^+]$ were held constant at 1.00 and 1.87×10^{-4} *M*, respectively, Table X. The constant k' is defined as $k' = R/[Re_2O_3(CN)_8{}^{4-}]$. The relatively constant value of k' ($(1.24 \pm 0.04) \times 10^{-4}$ sec^{-1}) demonstrates the first-order dependence of the rate on $[Re_2O_3(CN)_8{}^{4-}]$ for the path requiring added H^+.

Temperature Dependence. The temperature was varied from 40.0 to 60.0°. μ, $[H^+]$, and $[Re_2O_3(CN)_8{}^{4-}]$ were constant at 1.00, 1.87×10^{-4}, and 0.015 *M*, respectively. The activation parameters E_{act} and *A* were obtained from a least-squares analysis of a graph of $-\log k_{obsd}$ *vs.* $1/T$. The values of E_{act} and $\log A$ are respectively 30.3 ± 0.9 kcal/mol and 16.2 ± 0.6. (Units of A are sec^{-1}.) These are composite activation parameters, with contributions from both the acid-dependent and -independent paths.

The Rate Expression. The linearity and nonzero intercept of the graph of *R vs.* $[H^+]$, Figure 5, indicate that an empirical rate law for exchange of the terminal oxo ligands of $Re_2O_3(CN)_8{}^{4-}$ can be written as $R = k_1[Re_2O_3(CN)_8{}^{4-}] + k_2[Re_2O_3(CN)_8{}^{4-}][H^+]$. The first-order dependence in complex of the k_2 term has been demonstrated. The first-order dependence on $[Re_2O_3(CN)_8{}^{4-}]$ in the k_1 term is assumed. The values of k_1 and k_2 at 50.0°, evaluated from the intercept and slope of Figure 5, respectively, are $(1.11 \pm 0.07) \times 10^{-4}$ sec^{-1} and $(3.46 \pm 0.24) \times 10^{-2}$ M^{-1} sec^{-1}.

Exchange of the Bridging Oxo Ligand. One run was conducted at 70.3° to determine the rate at which the bridging oxo ligand undergoes exchange with the solvent. For this run, where $[H^+] = 2.00 \times 10^{-4}$ *M* and $\mu = 1.00$ *M* (KCl), the first sample was withdrawn after 1 hr, known from previous

Table IX. Rates of Terminal Oxygen Exchange of $O{=}Re(CN)_4ORe(CN)_4{=}O^{4-}$ ($\mu = 1.00$ (KCl), $[Re_2O_3(CN)_8{}^{4-}] = 0.015$ *M*)

Temp, °C	$10^4[H^+]_{added}$, *M*	10^6R,^{a} *M* sec^{-1}
50.0	1.87	1.86 ± 0.07
50.0	3.47	1.85 ± 0.09
50.0	17.3	2.53 ± 0.03
50.0	34.7	3.59 ± 0.07
50.0	69.3	5.25 ± 0.07
40.0	1.87	0.406 ± 0.004
60.0	1.87	7.20 ± 0.11
70.3	2.00	0.727 ± 0.010^b

^{a} Errors represent two standard deviations. ^{b} *R* is the rate of exchange of the bridging oxo ligand.

Table X. $[Re_2O_3(CN)_8{}^{4-}]$ Dependence of the Rate of Terminal Oxygen Exchange of $Re_2O_3(CN)_8{}^{4-}$ ($[H^+] = 1.87 \times 10^{-4}$ *M*, 50°, $\mu = 1.00$ (KCl))

$[Re_2O_3(CN)_8{}^{4-}]$, *M*	10^6R,^{a} *M* sec^{-1}	$10^4k'$,^{a,b} sec^{-1}
0.015	1.86 ± 0.07	1.24 ± 0.05
0.030	3.80 ± 0.10	1.27 ± 0.03
0.045	5.43 ± 0.19	1.21 ± 0.04

^{a} Errors represent two standard deviations. ^{b} k' is defined as $k' = R/[Re_2O_3(CN)_8{}^{4-}]$.

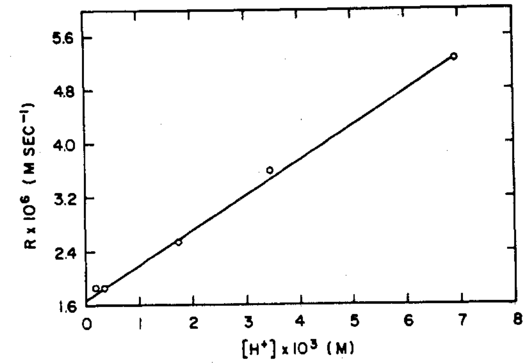

Figure 5. Hydrogen dependence for $Re_2O_3(CN)_8{}^{4-}$–H_2O exchange (terminal oxygens). [Complex] = 0.015 *M*, $\mu = 1.00$ (KCl), $T = 50.0°$.

experiments to be sufficient time for virtually complete terminal oxo ligand exchange (the half-time for terminal oxo ligand exchange is calculated from the above data to be 709 sec at 70.3° and $[H^+] = 1.87 \times 10^{-4}$ *M*). A graph of $-\ln(1 - F)$ *vs.* time was strictly linear. The rate of bridging oxo ligand exchange was found to be 7.27×10^{-7} *M* sec^{-1}. Under these same conditions, the rate of terminal oxo ligand exchange would be 3.0×10^{-5} *M* sec^{-1}. Thus, the rate of exchange of the terminal oxo ligands is approximately 40 times faster than bridging ligand exchange under these conditions.

Discussion

$ReO_2(CN)_4{}^{3-}$-H_2O Exchange. Any mechanism proposed for oxygen exchange of $ReO_2(CN)_4{}^{3-}$ must be consistent with the following: (1) the complex ion maintains a tetragonally distorted octahedral geometry in solution, (2) acidified solutions of $ReO_2(CN)_4{}^{3-}$ contain $ReO(OH)(CN)_4{}^{2-}$, and (3) the overall rate expression is $R = k_1[ReO(OH)(CN)_4{}^{2-}] + k_b[ReO_2(CN)_4{}^{3-}]$ where $k_b = k_2[CN]_0{}^{-0.90}$ or $k_b = k_3[OH^-]^{0.22}$ in the presence or absence of added potassium cyanide, respectively.

In acidic media, where the k_1 pathway is responsible for exchange, it is reasonable to propose that protonation of an oxo ligand increases the lability of that ligand. This effect has also been observed[14] in the acid-catalyzed aquation reactions of other octahedral complex ions containing basic ligands, *e.g.*, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5(CO_3)^+$, $Co(NH_3)_5ONO^{2+}$, and $Co(en)_2F_2{}^+$, where protonation of F^-, $CO_3{}^{2-}$, and ONO^- ligands is presumed effective in increasing the lability of the leaving ligands.

The proposed mechanism for oxygen exchange of $ReO_2(CN)_4{}^{3-}$ in acidic media, then, consists of rapid formation of $ReO(OH)(CN)_4{}^{2-}$ in equilibrium concentrations, followed by replacement of the labile hydroxo ligand by a water molecule. Hydrogen bonding between the entering and leaving groups may facilitate exchange. It is impossible, on the basis of the data, to distinguish between an exchange path involving unassisted dissociation of the hydroxo ligand, followed by entry of a water molecule into the vacant coordination site, or an exchange path involving interchange of the hydroxo ligand with a solvent molecule, during which process there is significant Re-O bonding to both the entering and leaving groups. The magnitude of the activation energy for the k_1 path (23.3 kcal/mol) suggests that appreciable bond cleavage is involved in the rate-determining process.

Protonation of the analogous $ReO_2(en)_2{}^+$ ion has been shown to effect a simultaneous increase in the ReOH stretching frequency and a decrease in the Re=O stretching frequency.[15] This is interpreted as a decrease in the strength of the Re–O bond upon protonation, and when coupled with the suggestion that the *trans*-dioxo ligands exert a strong trans-labilizing effect on one another, it provides additional support for the mechanism proposed.

No evidence for exchange pathways involving generation of the dimeric $Re_2O_3(CN)_8{}^{4-}$ ion was observed. The determinations of the dependence of the rate on $[ReO(OH)(CN)_4{}^{2-}]$ and on $[Re(V)]_T$ were carried out specifically to test for a path of this type. The formation of $Re_2O_3(CN)_8{}^{4-}$ and its subsequent dissociation, reactions which would lead to exchange, occur too slowly to compete with the other paths for exchange.

The form of the rate expression in basic media suggests that exchange occurs only after replacement of an equatorial cyano ligand by a solvent water molecule or hydroxide ion. This is consistent with the observation[3] that the cyano ligands of $ReO_2(CN)_4{}^{3-}$ exchange rapidly with free cyanide ion in solution. A plausible mechanism involves water (or OH^-) replacement of a coordinated cyano ligand in an equilibrium process: $ReO_2(CN)_4{}^{3-} + H_2O \rightleftarrows ReO_2(CN)_3(OH_2)^{2-} + CN^-$. (The observations that the visible-uv spectrum of $ReO_2(CN)_4{}^{3-}$ is not dependent upon the presence of cyanide and that solutions of $ReO_2(CN)_4{}^{3-}$ may be acidified without loss of HCN suggest that the equilibrium constant for this reaction is quite small.)

The explanation for the necessity of replacement of a cyano ligand by a solvent molecule prior to exchange probably involves the unoccupied, antibonding, π orbitals of the cyano ligand, which are capable, through metal to ligand electron donation, of accommodating some of the d-electron density of a metal ion upon coordination. The loss of a cyano ligand from the equatorial plane and its replacement by an aquo or hydroxo ligand are expected to result in a weakening of the Re-O bonds, due to the diminished accommodation of Re-O bonding electron density in the equatorial plane.

The exact nature (*i.e.* oxo, hydroxo, or aquo) of the equatorial solvent ligand in the species proposed above is unknown. However, the relative abilities of aquo and hydroxo ligands in assisting substitution reactions of other octahedral

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[14] R. K. Murmann and D. R. Foerster, *J. Phys. Chem.*, 67, 1383 (1963).

[15] D. E. Grove and G. Wilkinson, *J. Chem. Soc. A*, 1224 (1966).

complex ions have been studied; for example, the rate of aquation of *cis*-$Co(en)_2Cl(OH)^+$ is 7500 times faster than the rate of aquation of the corresponding aquo complex[16] while *trans*-$Co(en)_2Cl(OH)^+$ aquates 640 times faster than the corresponding aquo complex. These results indicate the superior ability of the hydroxo ligand (particularly in the cis position) to labilize other ligands in the coordination sphere of Co(III).

The mechanism proposed for oxo ligand exchange of $ReO_2(CN)_4^{3-}$ in basic media consists of initial formation of the proposed intermediate species, $ReO_2(CN)_3(OH_2)^{2-}$. Association of an axial ligand with a solvent proton or transfer of a proton from equatorial aquo ligand to one of the axial oxo ligands is then assumed to occur. The equatorial ligand thereby becomes a hydroxo ligand and is expected to exert a strong cis-labilizing effect on the axial ligands. The axial ligand is now a hydroxo ligand and for the same reasons discussed for acid-dependent exchange is expected to be labile with respect to substitution by solvent. Whether the exchange process is primarily associative or interchange in nature is once again unknown. As in the case of acid dependent exchange, however, the large activation energy observed for exchange (20.3 kcal/mol) suggests appreciable Re-O bond breaking in the rate-controlling process for exchange.

The rate of oxo ligand exchange depends upon the concentration of added hydroxide ion ($R = k[OH]^{0.22}$). This dependence may simply be due to a medium effect. Alternately, the intermediate species may exist in a hydroxide concentration dependent equilibrium: $ReO_2(CN)_3OH_2^{2-} + OH^- \rightleftarrows ReO_2(CN)_3OH^{3-} + H_2O$. At high $[OH^-]$, the presumed intermediate is expected to favor the hydroxo form and the cis axial ligands are expected to be correspondingly labilized. The ability of the axial ligands to be labilized by proton association is diminished, however, at high $[OH^-]$. Similarly, at low $[OH^-]$, where the intermediate is expected to increasingly favor $ReO_2(CN)_3OH_2^{2-}$, the cis-labilizing effect of the equatorial ligands is diminished while the possibility of axial labilization by proton association is increased. The fractional power dependence of the rate on $[OH^-]$ may reflect these competitive trends. The order with respect to $[OH^-]$ being greater than zero suggests that the labilizing effect of the cis hydroxo ligand is the more important effect.

$Re_2O_3(CN)_8^{4-}$-H_2O Exchange. The rate law observed for terminal oxygen exchange of the $Re_2O_3(CN)_8^{4-}$-H_2O system is $R = k_1[Re_2O_3(CN)_8^{4-}] + k_2[Re_2O_3(CN)_8^{4-}][H^+]$. This ion has been shown to consist of two tetragonally distorted octahedra, sharing a bridging oxo ligand. The mechanism for exchange by the k_2 path is proposed to involve labilization of the terminal oxo ligands upon association with hydrogen ion. This is analogous to the mechanism proposed for acidic exchange of $ReO_2(CN)_4^{3-}$. Unlike that ion, however, $Re_2O_3(CN)_8^{4-}$ was not observed to undergo proton association. $Re_2O_3(CN)_8^{4-}$ is expected to be less basic than $ReO_2(CN)_4^{3-}$ because of the inability of the dimeric ion to accommodate an increased multiple bonding of the ligand trans to the protonated oxo ligand.

If the $Re_2O_3(CN)_8^{4-}$ complex ion is considered to be $ReO(OH)(CN)_4^{2-}$ in which the $-Re(CN)_4{=}O$ entity has replaced the hydroxyl proton, a comparison of pathways for (terminal) oxo ligand exchange of $ReO_2(CN)_4^{3-}$ and $Re_2O_3(CN)_8^{4-}$ can be made. The rate constant, k_{obsd} for exchange of $Re_2O_3(CN)_8^{4-}$ at 40°, $[H^+]_{added} = 1.87 \times 10^{-4}$ *M*, and $\mu = 1.0$, was 6.93×10^{-6} sec^{-1}. This can be compared to the value of 1.77×10^{-4} sec^{-1} found for exchange of $ReO_2(CN)_4^{2-}$ at 35°, $[H^+] = 2.0 \times 10^{-4}$ *M*, and $\mu = 1.0$. The rate of oxo ligand exchange of $Re_2O_3(CN)_8^{4-}$ is considerably slower under similar conditions. This comparison of rate constants may be deceptive, however, because of the differing basicities of these ions. A more meaningful comparison is found in the values of the activation energies. E_{act} for exchange of $ReO_2(CN)_4^{3-}$ in acidic media is 23.3 kcal/mol, whereas E_{act} for terminal oxo ligand exchange of $Re_2O_3(CN)_8^{4-}$ is 30.3 kcal/mol. The higher activation energy for acidic exchange of the dimeric ion is consistent with the prediction that association of an oxo ligand with an electron-withdrawing group (*i.e.*, $-Re(CN)_4{=}O$) will increase the multiple bonding of the oxo ligand in the trans position. This increased multiple bonding is expected, if bond cleavage is a kinetically significant process, to increase the energy of activation.

Little can be said about the exchange path (k_1) which carries exchange in the absence of added acid. The slow exchange in neutral media may result from processes involving formation and dissociation of the dimeric ion, since $ReO_2(CN)_4^{3-}$ and $Re_2O_3(CN)_8^{4-}$ are known to exist in a slow, acid-dependent equilibrium.

The elucidation of the most plausible mechanism for exchange of the bridging oxo ligand in $O{=}Re(CN)_4ORe(CN)_4{=}O^{4-}$ requires more data than are presently available. Speculation as to the mechanism can be made here, however. The rate of exchange of the bridging oxo ligand at 70.3° and $[H^+] = 2.00 \times 10^{-4}$ *M* is approximately $^1/_{40}$th as fast as the rate of exchange of the terminal oxo groups. Under conditions of higher acidity the rate of exchange of the bridging oxo ligand decreases while the rate of exchange of the terminal oxo groups increases. This reaffirms the suggestion that $Re_2O_3(CN)_8^{4-}$ exists in an acid-dependent equilibrium with $ReO_2(CN)_4^{3-}$, lower concentrations of hydrogen ion favoring the formation of $ReO_2(CN)_4^{3-}$. This is not unexpected, since the acid-induced formation of $Re_2O_3(CN)_8^{4-}$ from $ReO_2(CN)_4^{3-}$ is reversible upon addition of base. Exchange of the bridging oxygen could be due, then, to H^+-catalyzed exchange of small amounts of $ReO_2(CN)_4^{3-}$ generated in solutions of $Re_2O_3(CN)_8^{4-}$.

Registry No. $K_3ReO_2(CN)_4$, 19439-48-6; $K_4Re_2O_3(CN)_8$, 39046-39-4; $Re(O)(OH)(CN)_4^{2-}$, 39046-40-7; H_2O, 7732-18-5; CN^-, 57-12-5; O_2, 7782-44-7.

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[16] M. L. Tobe, *Sci. Progr. (London)*, 48, 484 (1961).