compound with the negative form of the substrate. The low probability of the reaction is to be expected from the highly polar nature of the metal chelate, in which the negative carboxylate donors are concentrated near the active site of the metal ion which is available for combination with the ascorbate ion. The fact that an increase in the negative charge of the ligand attached to the Fe(III) ion correlates with a further increase in the negative value of the entropy of activation is in accord with this concept.

The slight differences in both the rates and entropies of activation for the CDTA and DTPA chelates are considered due to the characteristically different structure of CDTA. The rigidity imposed on the coordination sphere of Fe(III) by the presence of the cyclohexane ring in the CDTA ligand would be expected to make the entropy of activation for the Fe(III)–CDTA reactant somewhat more negative than that of the corresponding EDTA chelate, which occupies what is considered a more normal position in the series of chelates studied.

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# Isotopic Ligand-Exchange Studies on $[Re(amine)_4O_2]^+$-Type Ions

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**Abstract:** The rates of isotopic exchange of $[Re(amine)_4O_2]^+$ with amine are reported for amine = $^1/_2$(en), $CH_3NH_2$, and pyridine. With en and $CH_3NH_2$ the exchange follows the rate law $R = k[\text{complex}] + k_1[\text{complex}][OH^-]$. At 25° and $\mu = 0.10$, the values are $k = 8.5 \times 10^{-7}\ sec^{-1}$ and $k_1 = 6.9 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (en), and $k = 9.4 \times 10^{-6}\ sec^{-1}$ and $k_1 = 4.33 \times 10^2\ M^{-1}\ sec^{-1}$ ($CH_3NH_2$). With pyridine the rate $R$ is independent of $[OH^-]$ and of [py] and, at 25° and $\mu = 0.10$, $R = k[\text{complex}]$, where $k = 4.17 \times 10^{-5}\ sec^{-1}$. The rate of deuterium exchange on the amine hydrogens is extremely rapid. Exchange measurements have been made on the $CN^-$–$[Re(CN)_4O_2]^{3-}$ and $Cl^-$–$[ReCl_4O(OH_2)]^-$ systems. Both reactions are complete in less than 1 min under the conditions employed. A mechanism is postulated which includes two paths of exchange: (a) dissociation assisted by solvent and (b) amide formation followed by *trans* dissociation. Preliminary results are reported for the oxygen isotopic exchange $[Re(X)_4O_2]^n + H_2O$, where X = $^1/_2$(en), $CN^-$, and py.

Studies on the complexes of Re(III), Re(IV), and Re(V) have been expanding rapidly in recent years, but, although isotopic exchange studies are extremely valuable in the elucidation of reaction mechanisms, only a few exchange studies on these complexes have been reported.[2]

The study of the $[ReBr_6]^{2-}$–$Br^-$ exchange[2a] was limited to high HBr concentrations because of the instability of the complex at the high temperatures required for measurable exchange. The results showed that the over-all rate increased linearly with [HBr] above 4 *M* and with complex concentration. With the $[ReCl_6]^{2-}$–$Cl^-$ exchange,[2b] the observations paralleled those of the $Br^-$ system, and a mechanism involving acid and solvent assisted $Cl^-$ dissociation was suggested.

A study of the oxalate$^{2-}$ exchange with $[Re_2O(OH)_2(C_2O_4)_4]^{4-}$ and $[Re_2O(OH)_6(C_2O_4)_2]^{4-}$ was reported.[2c] In the former system no exchange was observed after 200 hr at 20°, but in the latter the exchange was independent of $[C_2O_4]^{2-}$ and decreased with increasing [complex]. No pH-dependent studies were made. The author does not explain the peculiar dependence of the rate on [complex] but deduces from the ligand independence and $E_a$ that an intermediate aquo complex is involved in the exchange. Since the structures of these ions are not known, this study is of little value in predicting the behavior of other rhenium complexes.

We have recently reported[3,4] some properties of $[Re(amine)_4O_2]^+$ ions (amine = $^1/_2$(en), $CH_3NH_2$, py). These complexes are of known *trans*-oxygen structure and are suitable for isotopic exchange studies since their rates are measurable over a wide range of conditions. Complexes containing the ligands en, $CH_3NH_2$, py, $CN^-$, and $Cl^-$ were chosen so the effects of a chelate ring, an aromatic ring, $\pi$ bonding, and the presence and absence of hydrogens on the coordinated nitrogens could be evaluated. The results of these studies and some oxygen exchange rates with $H_2O$ are reported in this paper.

## Experimental Section

**Materials.** $[Re(en)_2O_2]Cl$, $[Re(CH_3NH_2)_4O(OH_2)]Cl_3$, and $[Re(py)_4O_2]Cl$ were prepared by methods described[3,4] and had analyses as good or better than those previously reported. Their purity was also checked by ir and visible spectra measurements.

$K_3[Re(CN)_4O_2]$ was prepared by the following procedure. $[Re(en)_2O_2]Cl$ was refluxed with a tenfold excess of KCN in absolute methanol for 12 hr. The solid crude product was collected, washed repeatedly with absolute methanol, and recrystallized four times from $MeOH$–$H_2O$ mixtures. The bright orange crystals were dried under vacuum for 2 days at 60°, yield 50–60%. *Anal.*

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(1) National Science Foundation Postdoctoral Associate, 1964.

(2) (a) G. Schmidt and W. Herr, *Z. Naturforsch.*, **16a**, 748 (1961); (b) J. Casey and R. K. Murmann, *Inorg. Chem.*, **6**, 1053 (1967); (c) S. Wajda, "Theory and Structure of Complex Compounds," B. Jezowsha-Trzebiatowska, Ed., Pergamon Press Ltd., Oxford, England, 1964, pp 383–397.

(3) J. Beard, J. Casey, and R. K. Murmann, *Inorg. Chem.*, **4**, 797 (1965).

(4) R. K. Murmann, *Inorg. Syn.*, **8**, 173 (1966).

Calcd for $K_3ReO_2C_4N_4$: Re, 42.36; C, 10.93; N, 12.74. Found: Re, 42.09; C, 10.76; N, 12.82.

The ligands containing $C^{14}$ were obtained from the following sources. Ethylenediamine was prepared from dibromoethane (Volk Corp.) by reaction with liquid $NH_3$ and purified as previously described.[5] Methylamine hydrochloride was prepared by Zn–HCl reduction of $CH_3NO_2$ (Biological Chemistry Research Laboratories) and was purified by precipitation of the $PtCl_6^{2-}$ salt followed by conversion to the hydrochloride through the volatilization of $CH_3NH_2$ from basic solution. Pyridine-$C^{14}$ was obtained from Merck Sharpe and Dohme of Canada, KCN-$C^{14}$ was obtained from International Chemical and Nuclear Corp, and $HCl^{36}$ was obtained from Oak Ridge National Laboratory.[6a] They were of suitable purity to be used without purification. Water containing $O^{18}$ approximately eight times the natural abundance was obtained from YEDA[6b] and was redistilled from $KMnO_4$ before use. All compounds containing radioactive isotopes were diluted with a weighable amount of the same compound of AR quality before use in exchange measurements.

Reinecke's salt, $NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$, was obtained from Eastman Kodak Co. and was used after recrystallization. $NaClO_4$ was prepared from AR $HClO_4$ and $NaHCO_3$ followed by recrystallization. Ethylenediamine was redistilled from BaO at reduced pressure. A Model G.S. pH meter with calomel and lithium glass electrodes was standardized at pH 4 and 7 using standard buffers. All pH's were measured at 25.0°. Solvent water was distilled and passed through a double bed ion-exchange column. It was essentially free of metal ions but contained traces of organic materials from the resin. All other chemicals were of reagent grade.

**Equipment.** Spectral measurements were carried out on a temperature-controlled Beckman DU, or a Cary Model 12, spectrophotometer.

Isotopic exchange measurements were carried out in a constant-temperature water bath; ±0.02° at 25° and ±0.1° at 50°. Since the reactions are somewhat light sensitive, all measurements were carried out in covered flasks.

Radioactivity measurements were made with a Technical Associates DS-5B instrument equipped with a 2-in. thin window, 100-$\mu$g/cm$^2$ flow counter working in the porportional region using 90% Ar–10% methane. It was standardized before and after each series of samples with $C^{14}$ or $Cl^{36}$ standards. All samples were counted to 1% or better for one standard deviation.

$O^{18}$ content measurements were made on a Nuclide-RMS-16 instrument by measuring the 46/(45 + 44) ratio of samples of $CO_2$. The solid complexes were converted to $CO_2$ by the Anbar[7] method and purified by the method of Gordon.[8] The isotopic composition of $H_2O$ was determined by equilibration (3 days, 25°) with a known amount of standard $CO_2$, and from the 46/(44 + 45) ratio of the $CO_2$ the water $O^{18}$ content was calculated.[9] The per cent $O^{18}$ in $CO_2$ was calculated using the expression $\% \, O^{18} = (100/2)[R/(R + 1)]$, where $R = 46/(44 + 45)$. The mass spectrometer was shown to be linear with respect to % $O^{18}$ in both $CO_2$ and $O_2$ in the range used in this work using standard synthetic samples.

**Ligand-Exchange Experiments.** $[Re(en)_2O_2]^+$–en. The majority of the rate runs were conducted by adding 0.35 ±0.01 g of finely powdered $[Re(en^*)_2O_2]Cl$ to a thermostated mixture of the appropriate amounts of a standard solution of en, KCl, and HCl. The volume was adjusted to 25.00 ml with a few drops of water, and the mixture was placed in a thermostated bath. Solution was complete in 10–15 sec. At timed intervals, samples were injected into cold saturated NaI solutions; the precipitated $[Re(en)_2O_2]I$ was collected, washed with acetone, and filtered onto a thick filter matte giving uniform dispersion on a well-defined area, *ca.* 1 cm. After careful drying they were counted as infinitely thick samples. Rates measured using labeled en and normal complex were identical with the above procedure within stated limits.

$[Re(CH_3NH_2)_4O_2]^+$–$CH_3NH_2$. Solutions of methylamine and HCl in $H_2O$ at the proper pH were prepared and separated into two 10-ml portions. To one was added 10–100 $\mu$l of a 0.10 *M* $CH_3{}^*NH_2\cdot HCl$ solution and to the other *ca.* 0.160 g of $[Re(CH_3NH_2)_4O(OH_2)]Cl_3$. Both solutions were purged of air with argon to eliminate oxidation and equilibrated at the proper temperature. Initiation of the reaction was accomplished by mixing the solutions, and aliquots were taken at timed intervals. The complex was precipitated by a freshly prepared solution of Reinecke's salt in 2.5 *M* $HClO_4$. The precipitate was collected, washed with water and absolute MeOH, and collected as a matte on thick filter paper. The matte was uniformly distributed over a well-defined area, *ca.* 1 cm$^2$. Most samples were above infinite thickness, but those that were not were corrected to infinite thickness by a calibration graph. The pH of the reaction mixture was measured shortly after mixing, but in the range 3–6 it varied slightly during the exchange rate measurements owing to complex decomposition. Thus the precision of these measurements is somewhat lower than that reported for the en system.

$[Re(py)_4O_2]^+$–py. A solution of pyridine at the proper acidity containing $[Re(py)_4O_2]I$ or $[Re(py)_4O_2]ClO_4$ was added to a solution of py* at the same acidity. Both solutions were temperature equilibrated before mixing. Samples were taken at timed intervals and precipitated with saturated $NaClO_4$ solution. The solid was washed with cold $NaClO_4$ solution and water and dried as a uniform, well-defined (*ca.* 1 cm$^2$) matte under vacuum. All samples were of infinite thickness (>30 mg/cm$^2$) and were counted at constant geometry. Measurements of pH were made during the entire period of the rate measurement. Only with solutions above a pH of 7 did the pH decrease because of hydrolysis of the complex.

$[ReCl_4O(OH_2)]^-$–$Cl^-$. This complex is difficult to prepare in a pure state in a form which is soluble in HCl solutions. Thus it was generated in the presence of en · 2HCl and used without purification. It is now known that 2–5% $ReO_4^-$ is also generated during this reaction. The rate was followed in 5–10 *M* HCl since hydrolysis occurs below 5 *M*.

Treatment of $[Re(en)_2O_2]^+Cl^-$ with 8 *M* HCl* at 50° for 6 hr generated $[ReCl_4{}^*O(OH_2)]^-$. The excess solvent and HCl were removed by gentle heating in a stream of $N_2$. The solid residue was brought into solution with 5 or 10 *M* HCl at the proper temperature, and at timed intervals a saturated CsCl solution was added to aliquots to precipitate $Cs[ReCl_4O(OH_2)]$. The solid was collected as a uniform matte of well-defined area. It was washed, dried, weighed, and counted. The weight of the sample was constant (±3%).

$[Re(CN)_4O_2]^{3-}$–$CN^-$. A solution of 0.100 g of $K_3[Re(CN)_4O_2]$ and 0.050 g of KCN was approximately neutralized with 0.10 *M* HCl and diluted to 25.00 ml. After temperature equilibration, 0.100 ml of 0.10 *M* KCN* was added and aliquots were taken at timed intervals. The complex ion was precipitated at 0° with a saturated solution of $[Co(NH_3)_6]Cl_3$, collected on a filter, washed with acetone, and dried under vacuum. It formed a uniformly distributed matte of constant (*ca.* 1 cm$^2$) area. The radioactivity was counted at infinite thickness. The pH was measured on the final solution after the counting samples had been taken, but no complex decomposition which would alter the pH was observed.

In each system the exchange data were evaluated by graphing $\ln (1 - F)$ as a function of time and the $t_{1/2}$ obtained from the slope of the straight line. Except where specified, the graph was a straight line within experimental error for at least the middle 80% of the reaction. Exchange induced by precipitation was less than 5%. The over-all rate, *R*, was evaluated with the usual expression

$$R = \frac{\ln 2}{t_{1/2}} \frac{[ab]}{[a + b]}$$

where $a$ is the [complex$_T$] × number of ligands per molecule and $b$ is the [free ligand$_T$]. The rate constants $k$ and $k_1$ were evaluated as explained in the Results section using the general expression $R = k[\text{complex}] + k_1[\text{complex}][OH^-]$.

**Deuterium Exchange on Amine Nitrogens in $[Re(en)_2O_2]^+$.** $[Re(en)_2O_2]Cl$ (0.10 g) was dissolved in 2.0 ml of 99.5% $D_2O$ at 0° (pH 6.8), and $[Re(en)_2O_2]I$ precipitated at 0.5-min intervals with solid NaI. Solution was complete in 0.1 min, precipitation was essentially instantaneous, and the first sample was taken at 0.4 min. The samples were immediately collected by filtration, washed with absolute acetone, and dried under vacuum.

In a modified version the $[Re(en)_2O_2]Cl$ was isolated by vacuum drying at 0–2° which took about 1 min.

Deuterium content was determined by ir spectra in KBr pellets using normal and completely deuterated samples as standards. The normal complex absorbed at 6.2 $\mu$ and the deuterated complex at 4.1 $\mu$ with no interference at these points. The usual difficulties

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[5] R. W. Gaver and R. K Murmann, *J. Inorg. Nucl. Chem.*, **26**, 881 (1964).

[6] (a) We are indebted to Dr. W. R. Fleming for this solution. (b) YEDA—Research and Development Co., Ltd., Weizmann Institute of Science, Rehovoth, Israel.

[7] M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, **4**, 233 (1959).

[8] B. Z. Shakhashiri and G. Gordon, *Talanta*, 13, 142 (1966).

[9] D. Samuel in "Oxygenases," O. Hayaishi, Ed., Academic Press Inc., New York, N. Y., 1962, p 67.

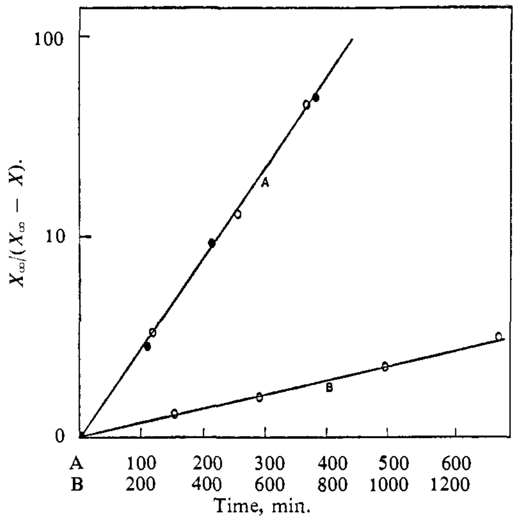

Figure 1. $[Re(en)_2O_2]^+$-en exchange at 50.0°: (A) pH 9.20, [en] = 0.033 *M*, duplicate run; (B) pH 7.29, [en] = 0.20 *M*.

encountered in a quantitative evaluation of composition from ir spectra were not applicable here since all samples gave only the deuterated spectra. The estimated threshold limit for the normal complex in the deuterated complex was 5%.

## Results

**$[Re(en)_2O_2]^+$-en Exchange.** Most of the rate data on this system were obtained at 50° and $\mu = 0.25$ with KCl as a substituting salt. Figure 1A gives a representative rate run and a duplicate, and Figure 1B shows a run at another pH. The standard error of the slope was about ±4% and duplicate runs agreed within ±6%. The rate constant, $k = R/[\text{complex}]$, was independent of complex concentration and of free ligand concentration but was a function of pH as shown in Figure 2A. In the pH region 4–7, the rate constant was essentially independent of pH, but at higher values it assumed a slope or order of approximately 1. Assuming this to indicate a two-term rate law, the constant value of $9.0 \times 10^{-4}$ min$^{-1}$ at 50° was subtracted from the over-all rate constants giving the line B in Figure 2. Over the pH range 7–13, the residual values form a straight line of graphical slope +0.95. The scatter at the lower pH's is due primarily to the fact that $k_{\text{residual}}$ is the difference between two nearly equal numbers.

Several measurements were made at lower pH's. For example, at pH 2.0, $k = 4.7 \times 10^{-7}$ sec$^{-1}$, and at pH 7.0, $k = 1.5 \times 10^{-5}$ sec$^{-1}$ at 50°. In this region the rate of exchange became very slow and nonlinear, and a chemical change took place in the solutions which involved replacing one en molecule by chloride ions and/or water molecules. The reduced rate of exchange observed under these conditions is due to a chemical replacement of en by 2 $Cl^-$'s. A partially dissociated en molecule can either isotopically exchange or irreversibly react. When the latter becomes significant, a reduced rate of isotopic exchange would be observed.

Figure 3 shows the temperature dependence at pH 10.30 and 8.06. This gave apparent activation energies of 20.4 and 21.7 kcal/mole, respectively. However, both of these are composite values of the two paths. Solution of the simultaneous equations gave an $E_a$ for $k$ of 22.3 and an $E_a$ for $k_1$ of 20.3 kcal/mole. Thus at 25° $k = 8.5 \times 10^{-7}$ sec$^{-1}$, $k_1 = 6.9 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$, and $k = 1.8 \times 10^{10}e^{-22{,}300/RT}$ sec$^{-1}$, $k_1 = 5 \times 10^{13}e^{-20{,}300/RT}$ $M^{-1}$ sec$^{-1}$.

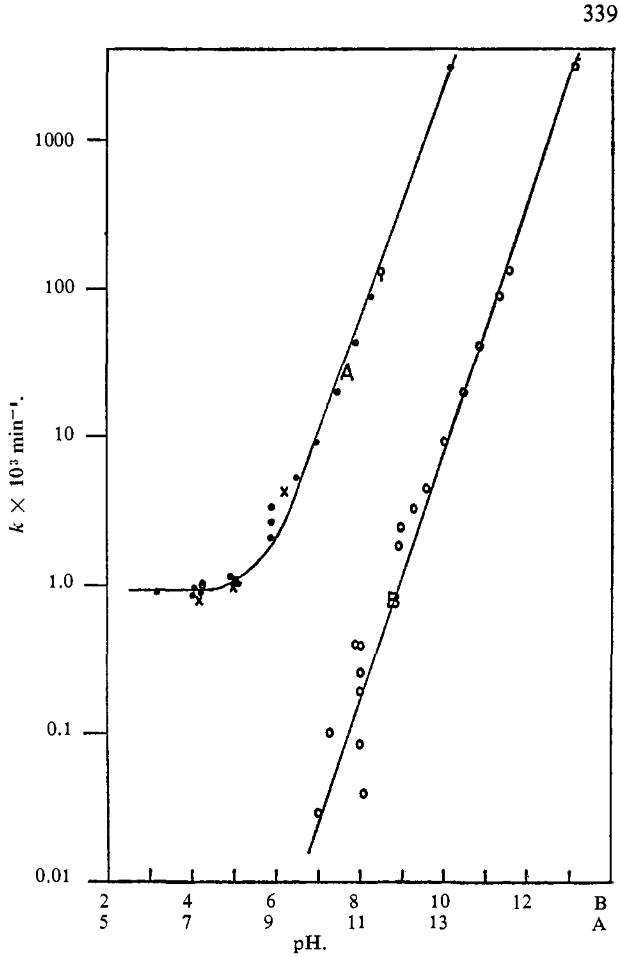

Figure 2. $[Re(en)_2O_2]^+$-en exchange at 50° *vs.* pH, $\mu = 0.25$, $[Re(en)_2O_2^+] = 0.025$ *M*. [en]: ○ = 0.017, × = 0.033, ● = 0.067, ♀ = 0.133, ⊙ = 0.20 *M*.

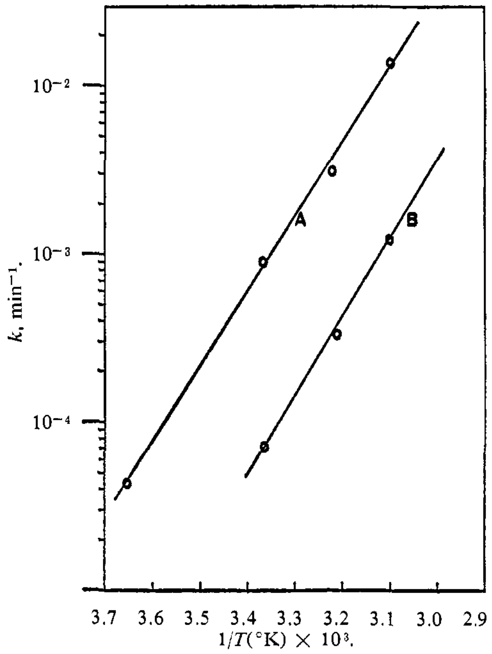

Figure 3. Temperature dependence of $[Re(en)_2O_2]^+$-en exchange, $\mu = 0.25$: (A) pH 10.30; (B) pH 8.06.

**$[Re(CH_3NH_2)_4O_2]Cl$-$CH_3NH_2$ Exchange.** The over-all rate, $R$, as a function of pH at constant [complex]

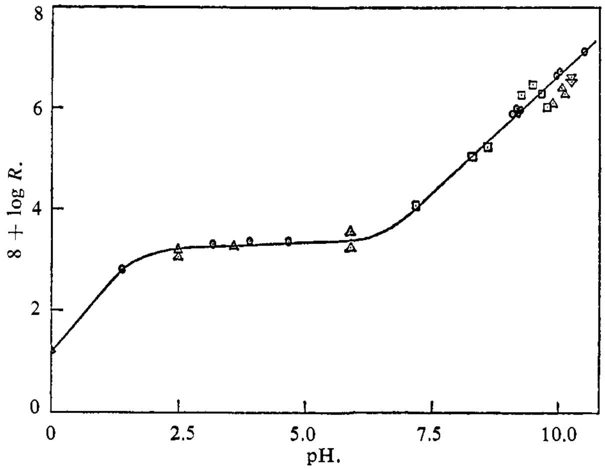

Figure 4. $[Re(CH_3NH_2)_4O_2]^+$–$CH_3NH_2$ exchange, *R vs.* pH, 25.0°, $\mu$ = [complex] = $1.76 + 0.01 \times 10^{-3}$ *M*. $[CH_3NH_2]$: ⊙ = 1.0, ⊡ = 0.50, ▽ = 0.20, △ = 0.10, ◇ = 0.02 *M*.

is shown in Figure 4. Below a pH of 3 the apparent rate decreased, presumably owing to the formation of $[Re(CH_3NH_2)_4O(OH)]^{2+}$ and $[Re(CH_3NH_2)_4O(OH_2)]^{3+}$. The loss of complexed methylamine is not likely since that rate is very slow in acidic media. The first acid dissociation constant is −0.4,[3] and the second can be estimated from the en complex[3] to be about 3. In the pH region 3.5–6, a level portion is observed followed by a linear increase with increasing pH. By analogy with the en system we interpret this in terms of a two-term rate law, $R = k[\text{complex}] + k_1[\text{complex}][OH^-]$ with a decreased rate in the acidic region due to the slower exchange of the protonated complex compared to the dioxo species. The $CH_3NH_2$ dependence is small, but at low $[CH_3NH_2]$ and high $[OH^-]$ *R* is consistently slower. This is due to a small amount of decomposition which is observed under these conditions and explains the smaller apparent *R*.

Figure 5 shows the dependence of *R* on $[Re(CH_3NH_2)_4O_2^+]$ at constant pH and $[CH_3NH_2]$. Although the scatter is large, the best interpretation involves a first-order dependence on $[Re(CH_3NH_2)_4O_2^+]$.

Rate measurements at a temperature of 0 and 25° in the pH ranges 9.6–9.7 and 5.1–5.3 gave the following values for *k* and $k_1$ from which the activation energy was calculated.

| | 25° | 0° |
|---|---|---|
| $k$, sec$^{-1}$ | $9.4 \times 10^{-6}$ | $3.5 \times 10^{-7}$ |
| $k_1$, $M^{-1}$ sec$^{-1}$ | $4.33 \times 10^{-2}$ | $4.25 \times 10^{1}$ |

Decomposition was so rapid at or above 35° that no accurate values could be obtained. From these values the over-all rate from pH 3.0 to 10.5 is governed by the rate constants: $k = 2.0 \times 10^{10}e^{-20,900/RT}$ sec$^{-1}$, $k_1 = 4 \times 10^{13}e^{-15,000/RT}$ $M^{-1}$ sec$^{-1}$.

**$[Re(py)_4O_2]^+$–py Exchange.** Table I lists the rate constants obtained at 25°. There is considerable scatter to the data reflecting the difficulty in obtaining reproducible disks satisfactory for counting. Below a pH of 3 and above 10, the amount of decomposition becomes appreciable compared to the rate being measured. This decomposition involves replacing coordinated pyridine with $H_2O$ or $Cl^-$ and $OH^-$, respectively. In both pH extremes the observed rate becomes appreciably slower than in the neutral region. This can be rationalized by assuming the pyridines independently dissociate and exchange is observed only when they are reassociated. If $Cl^-$, $H_2O$, or $OH^-$ compete irreversibly for the intermediate, then the observed rate of appearance of py* in the complex will be decreased. The rate constant is independent of the source of the complex ion; $I^-$, $Cl^-$, $ClO_4^-$, and several different preparations of the $I^-$ salt showed identical behavior. Preliminary experiments indicated that the rate was accelerated by about a factor of 2 in laboratory lighting, and thus the reactions were carried out in a darkened container. In the pH region 3–10 the observed rate constant is essentially independent of pH. The weighted average value of *k* is $4.17 \times 10^{-5}$ sec$^{-1}$ with a negligible slope of $-1.85 \times 10^{-7}$ sec$^{-1}$ pH$^{-1}$. From the total data the rate is essentially independent of [py] in the concentration range 1.2–7.1 $\times 10^{-2}$ *M*. Temperature-dependence studies at 0, 15, 25, and 35° gave an activation energy of 26 ± 1 kcal/mole. The rate of exchange is given by the expression $R = k[Re(py)_4O_2^+]$, where $k = 2.0 \times 10^{10}e^{-26,000/RT}$.

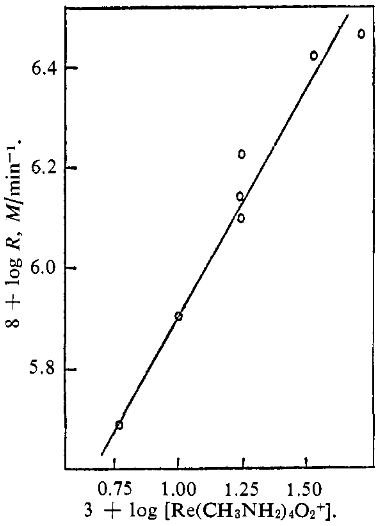

Figure 5. $[Re(CH_3NH_2)_4O_2]^+$–$CH_3NH_2$ exchange, complex dependence, pH 9.50 ± 0.05, $[CH_3NH_2]$ = 0.562 ± 0.002 *M*, 25°.

Table I. Rates of py–$[Re(py)_4O_2]I$ Exchange[a]

| pH | $k \times 10$ sec$^{-1}$ [e] | pH | $k \times 10$ sec$^{-1}$ |
|---|---|---|---|
| 2.94 | 4.40 ± 0.53 | 5.38[b] | 4.11 ± 0.13 |
| 3.02 | 3.75 ± 0.14 | 5.48[d] | 4.34 ± 0.01 |
| 3.50 | 4.39 ± 0.07 | 5.50[b] | 4.00 ± 0.16 |
| 3.90 | 4.54 ± 0.16 | 5.62[c] | 4.09 ± 0.03 |
| 4.15 | 3.56 ± 0.09 | 6.30 | 4.48 ± 0.02 |
| 4.80 | 4.35 ± 0.05 | 6.72 | 3.71 ± 0.05 |
| 5.00 | 3.41 ± 0.02 | 6.73[c] | 3.64 ± 0.05 |
| | | 7.31[b] | 4.01 ± 0.12 |
| 1.92 | 0.18 ± 0.04 | 8.48 | 4.47 ± 0.27 |
| 2.50 | 1.84 ± 0.10 | 9.86 | 4.00 ± 0.08 |
| 10.90 | 2.99 ± 0.24 | 10.15 | 3.86 ± 0.07 |
| 11.00 | 2.89 ± 0.49 | | |
| 11.18[b] | 2.05 ± 0.59 | | |

[a] [Complex] = $4.88 \pm 0.03 \times 10^{-3}$ *M*, [py] = $3.55 \times 10^{-2}$ *M*. [b] $[Re(py)_4O_2]ClO_4$. [c] py = $7.09 \times 10^{-2}$ *M*. [d] $[Re(py)_4O_2]Cl$. [e] Errors listed are one standard deviation.

**$[Re(CN)_4O_2]^{-3}$–$CN^-$ Exchange.** Table II shows the results of attempts to measure the $CN^-$ exchange rate with $[Re(CN)_4O_2]^{3-}$. The data can be interpreted in terms of either a very fast exchange rate not measurable by this technique or by induced exchange during precipitation. Since other separating methods having suitable properties were not found, this ambiguity could not be resolved.

Table II. $[Re(CN)_4O_2]^{3-}$–$CN^-$ Exchange

| pH 7.65[a] | | pH 10.35[b] | | pH 5.15[c] | |
|---|---|---|---|---|---|
| Time, min | Counts/min | Time, min | Counts/min | Time, min | Counts/min |
| 0.0 | 0 | 0.0 | 0 | 0.00 | 0 |
| 1.5 | 120 | 0.5 | 2807 | 0.25 | 1915 |
| 10 | 132 | 1.0 | 2944 | 1.00 | 1870 |
| 20 | 124 | 2.0 | 2825 | 10.0 | 1820 |
| 90 | 115 | 4.0 | 3080 | ∞ (calcd) | 1850 |
| ∞ (calcd) | 127 | ∞ (calcd) | 2570 | | |

[a] $[Re(CN)_4O_2{}^{3-}] = 9.6 \times 10^{-3}$ *M*, $[CN^-] = 3.0 \times 10^{-2}$ *M*, 28.0°. [b] $[Re(CN)_4O_2{}^{3-}] = 3.6 \times 10^{-2}$ *M*, $[CN^-] = 4.0 \times 10^{-2}$ *M*, 0°. [c] $[Re(CN)_4O_2{}^{3-}] = 8.4 \times 10^{-3}$ *M*, $[CN^-] = 1.23 \times 10^{-2}$ *M*, 0°.

**$[ReCl_4O(OH_2)]^-$–$Cl^-$ Exchange.** Several experiments conducted at 25° showed complete exchange within the time of the first sample (10 min). At 0° the data in Table III were obtained and are representative of several other runs. Other measurements showed that solid $Cs[ReCl_4O(OH_2)]$ was *ca.* 50% exchanged with one quick washing with 10 *M* HCl solution at 0° The conclusion that this exchange is very rapid is reasonable from these data, but again exchange could be induced at the solid–liquid interface.

Table III. $Cl^-$ Exchange with $[ReCl_4O(OH_2)]^-$

| Time, min | Counts/min (over background) of $Cs[ReCl_4O(OH)_2]$ |
|---|---|
| 3.0 | 4.0 |
| 3.5 | 4.4 |
| 4.5 | 2.8 |
| ∞ (calcd) | 4.0 |
| 0 | 960 |

**Rates of Oxygen Exchange.** Under the conditions, 25°, $10^{-2}$ *M* complex, no excess ligand, and buffered with $4 \times 10^{-2}$ *M* phthalate ion, the half-times in Table IV were obtained. Half-times were also obtained in an unbuffered system containing excess ligand. With $[Re(CN)_4O_2]^{3-}$ in the pH region of 5, the exchange graph was not linear, and within 10 min marked spectral changes had occurred suggesting appreciable conversion to the tri- or dicyano complex. Each half-time was determined by four to five separate points and had an estimated error of 10–15%.

Table IV. Half-Times of $O^{18}$ Exchange

| | $t_{1/2}$, min | $t_{1/2}$, min (unbuffered) |
|---|---|---|
| $[Re(en)_2O_2]^+ + H_2O^{18}$ | 150 (pH 6.04) | 3,000[a] |
| $[Re(py)_2O_2]^+ + H_2O^{18}$ | 8000 (pH 6.07) | 8,000[a] |
| $[Re(CN)_4O_2]^{3-} + H_2O^{18}$ | Dec (pH 5.36) | 10-15,000[a] |

[a] [en], [py], $[CN^-] = 0.10$ *M*, respectively. Thus these solutions were basic.

Obviously a complete $O^{18}$ study of each of the complexes must be made including ligand and $H^+$ dependence in order to make meaningful mechanistic suggestions. However, a few conclusions can be stated from the above data: (a) en rate > $CN^-$ rate at a pH of about 6 and py > $CN^-$ in the basic region; (b) with the en complex the rate increases with acidity. Unfortunately, it is extremely difficult to get pure $CO_2$ from these complexes for mass spectral analysis which has held back more quantitative work.

**Deuterium Exchange, Amine Nitrogens.** Only $[Re(en)_2O_2]^+$ could be studied since $[Re(CH_3NH_2)_4O_2]^+$ is somewhat unstable in the absence of excess $CH_3NH_2$. The experiments showed that deuterium exchange was complete within 0.4 min at 0° when $[Re(en)_2O_2]^+$ was isolated as the iodide. Since exchange could have been induced during precipitation with $I^-$, the isolation was carried out by volatilization of the solvent under vacuum. In these experiments the exchange was complete in 1 min at 0°. Thus it is clear that the amine hydrogens of $[Re(en)_2O_2]^+$ are labile in water solution at a pH of about 7.

## Discussion

The results of the kinetic studies on isotopic ligand exchange are summarized in Table V. The rate law for en and $CH_3NH_2$ exchange with their respective complexes is: $R = k[\text{complex}] + k_1[\text{complex}][OH^-]$. The $k_1$ term could be expressed as inverse $H^+$ dependence. It is clear from a comparison of the basicity of these complexes[3] that, in the pH range studied, protonation of the yl oxygens does not enter into the rate expression. The py exchange with $[Re(py)_4O_2]^+$ follows the rate law, $R = k[\text{complex}]$, with no hydroxide ion term.

Table V. Isotopic Exchange Rates

$[ReCl_4O(OH_2)]^- + Cl^- \rightleftarrows$ very rapid[a]

$[Re(CN)_4O_2]^{3-} + CN^- \rightleftarrows$ very rapid[b]

$[Re(en)_2O_2]^+ + en \rightleftarrows k = 1.8 \times 10^{10}e^{-22,300/RT}\ \text{sec}^{-1};\ k_1 = 5 \times 10^{13}e^{-20,3000/RT}\ M^{-1}\ \text{sec}^{-1}$

$[Re(CH_3NH_2)_4O_2]^+ + CH_3NH_2 \rightleftarrows k = 2.0 \times 10^{10}e^{-20,900/RT}\ \text{sec}^{-1};\ k_1 = 4 \times 10^{13}e^{-15,000/RT}\ M^{-1}\ \text{sec}^{-1}$

$[Re(py)_4O_2]^+ + py \rightleftarrows k = 2.0 \times 10^{10}e^{-26,000/RT}\ \text{sec}^{-1}$

$[Re(en)_2O(OH_2)]^{3+} \longrightarrow k_1 = 6.5 \times 10^{13}e^{-25,000/RT}\ \text{sec}^{-1};\ k_2 = 5 \times 10^{13}e^{-25,000/RT}\ \text{sec}^{-1}$[c]

[a] In 5 *M* HCl solution. [b] In basic media. [c] See ref 3. Rate expressions for successive dissociation of en in 10 *M* HCl solution.

Rapid exchange of the $Cl^-$ and $CN^-$ species was anticipated on the basis of the known tendency of $[ReCl_4O(OH_2)]^-$ to hydrolyze rapidly in 1 *M* HCl and on the reports[10] of the existence of cyano complexes of Re(V) of coordination number greater than six. The rapid exchanges reflect a rapid equilibrium between species containing different numbers of exchanging ligands.

It is useful to consider the kinetic results in terms of a bonding picture of the following type. Electron transfer from the multiply bound *trans* oxygens places appreciable electron density on the metal atom which (with non-π-bonding ligands) weakens the binding of the equatorial ligands. With π-bonding ligands such

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(10) R. Colton, R. D. Peacock, and G. Wilkinson, *J. Chem. Soc.*, 1374 (1960).

as pyridine or $CN^-$, the excess electron density can be withdrawn to these ligands strengthening both the equatorial and axial bonds. The kinetic results presented here as well as other properties of these ions appear to agree with this qualitative bonding scheme.

Considering the first-order term, $k$, the preexponential terms are nearly identical for the en, $CH_3NH_2$, and py complexes suggesting a similar mechanism. The activation energies are in the order py > en > $CH_3NH_2$. The higher $E_a$ for en compared to $CH_3NH_2$ is expected on the basis of the chelate effect and is also suggested by the fact that only the $CH_3NH_2$ complex decomposes in aqueous solution. The high activation energy for the py analog suggests appreciable $\pi$ bonding of it to the metal ion, the direction of which is metal $e^-$'s → ligand. This is also suggested by the oxygen exchange experiments and other characteristics given below.

With the $k_1$ term, again the preexponential is nearly constant for the en and $CH_3NH_2$ systems, and $E_a$ is smaller in the latter case. With the $[Re(py)_4O_2]^+$–py exchange this term does not exist presumably because no amine protons are available for ionization. This suggests a mechanism of the SN1-CB type which has been well established by Basolo and Pearson[11] and others. A necessary consequence of this mechanism is that the amine hydrogens must be labile to solvent protons under the appropriate conditions. Such was found to be the case with $[Re(en)_2O_2]^+$ by deuterium experiments and it is presumed, although because of chemical difficulties it could not be proved, that $[Re(CH_3NH_2)_4O_2]^+$ also exchanges its amine protons rapidly. Thus the facts are consistent with the $k_1$ arising from the following set of equations

$$[Re(en)_2O_2]^+ + HO^- \rightleftharpoons [Re(en)(en\text{-}H)O_2]^0 + H_2O$$

$$[Re(en)(en\text{-}H)O_2]^0 + en^* \rightleftharpoons [Re(en^*)(en\text{-}H)O_2]^0 + en$$

where the amido group labilizes the en opposite it. The rate-determining step would be the dissociation of an ethylenediamine from $[Re(en)(en\text{-}H)O_2]^0$ and would be followed by rapid addition of a labeled en molecule.

In neither the $k$ nor $k_1$ term can any distinction be made between a complete dissociation of en or a half-bonded intermediate.

Table V gives the rate expression for the dissociation of en from $[Re(en)_2O(OH_2)]^{3+}$ in 10 $M$ HCl. The detailed mechanism is not known, but $E_a$ is higher than that of the exchange of en with $[Re(en)_2O_2]^+$ where the linear oxygen field is present. For equatorial ligands which cannot accept metal electrons, it appears that the activation energy is raised upon protonation of the *trans* oxygens.

Although the $O^{18}$-exchange experiments are only preliminary and the rate equation is not known, $\pi$-bonding ligands in the equatorial positions of the complex ion cause slow rates of oxygen exchange with $H_2O$. The $t_{1/2}$'s quoted here are upper limits since oxygen protonation or hydrolysis increases the rate. With $[Re(en)_2O_2]^+$, the half-time is appreciably shorter in the more acidic region (where some O protonation takes place, $pK_a = 3.3$) suggesting that $[Re(en)_2O(OH)]^{2+}$ has a much greater oxygen exchange rate than $[Re(en)_2O_2]^+$. Since protonation would lessen the multiple bonding of the oxygens the exchange rate would be expected to increase.

If electron density is transferred from the oxygens, through the metal to $\pi$-bonding equatorial ligands, the yl oxygens should be less basic compared to complexes with non-$\pi$-bonding equatorial ligands. Such an effect has been noted.[3] For $[Re(en)_2O_2]^+$ and $[Re(CH_3NH_2)_4O_2]^+$, $pK_a = 3.3 \pm 0.3$, while for $[Re(py)_4O_2]^+$, $pK_a = -0.6$. The value given for $[Re(CN)_4O_2]^{3-}$ is 4.2 which is not unexpected because of the ion's large negative charge.

Spectral evidence also is in agreement with this picture. Considering the molecule as a distorted octahedron with short axial positions which give the metal ion a near-linear field the d levels are $d_{z^2} > d_{x^2-y^2} > d_{xz}, d_{yz} > d_{xy}$, and the two electrons are paired in the $d_{yx}$ orbital in agreement with the compound's near diamagnetism. Protonation of the yl oxygens should lessen the linear field resulting in less CFSE and a shift in visible absorption spectra to lower energies. This is a general phenomenon in these complexes. The energy of the visible absorption band of lowest energy has the order CN ≫ py > en > $MeNH_2$ = $NH_3$ > Cl. This is in qualitative agreement with a strengthening of the linear field with $\pi$-bonding ligands.

In summary, the kinetic studies of isotopic amine exchange with $[Re(amine)_4O_2]^+$ follow the rate law $R = k[\text{complex}] + k_1[\text{complex}][OH^-]$. The second term is absent when the amine does not have an ionizable hydrogen attached to the nitrogen. The activation energies suggest that pyridine and $CN^-$ are able to accept metal electrons and strengthen the M–O bond. This interpretation is in agreement with visible spectral changes with different equatorial ligands and spectral changes with oxygen protonation, and with the base strength of the yl oxygens.

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(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967.