at the same position or that one tautomer is present in much higher concentration than the others.

Derivatization reactions have been carried out by several authors,[2,3,6] using a variety of organic reactants. They found reaction only with the nitrile tautomer. We have carried out reactions of $LiCH_2CN$ with $MgCl_2$ and $HgCl_2$ and of $C_6H_5CH(Li)CN$ with $MgCl_2$. The infrared spectra of the magnesium compounds show absorptions near 1650 cm^{-1} (C═N) and 3300 cm^{-1} (N–H) with no absorption in the C≡N region. The mercury compound on the other hand shows a strong absorption at 2180 cm^{-1} (C≡N) and only very weak absorptions at 1632 and 3200 cm^{-1}. Magnesium chloride either preferentially reacts with one of the tautomers or rearranges to give a species with a C═N fragment; mercuric chloride, on the other hand, gives only the nitrile form.

The lithium derivatives of acetonitrile and phenylacetonitrile represent a unique class of organolithium compounds which do not have the typical electron-deficient framework. The general bonding scheme for $LiCH_2CN$ is one of intermolecular association with the lithium of one molecule interacting with the cyanide of an adjacent molecule. The lithium derivative of phenylacetonitrile is dimeric with the lithium of one molecule interacting with the cyanide of the other molecule. Studies of other nonelectron-deficient lithium compounds are currently underway.

Oxygen-18 Tracer Studies with the *trans*-Dioxobis(ethylenediamine)rhenium(V) Ion ($[Re(en)_2O_2]^+$)

Louis B. Kriege[1] and R. Kent Murmann*

Contribution from the Chemistry Department, University of Missouri, Columbia, Missouri 65201.
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Abstract: The rate of exchange of oxygen atoms between the *trans*-dioxobis(ethylenediamine)rhenium(V) ion and solvent water has been determined. The effect of changing the $[H^+]$, [ethylenediamine], ionic strength, temperature, supporting electrolyte, solvent, and the presence of other acids and bases on the rate has been investigated. The exchange has been studied over the $[H^+]$ concentration range from 4.17×10^{-5} *M* to 6.03×10^{-13} *M*. At pH 7.00, the concentration of total uncoordinated ethylenediamine present was varied from 0.0 to 0.4397 *M*. At 50.0° and $\mu = 1.50$ (KCl), the rate law is given by $R/[Re(en)_2O_2^+] = k_0 + k_{enh_2}[enH_2^{2+}] + k_{en}[en] + k_{oh}[OH^-]$. Values for k_0, k_{enh_2}, k_{en}, and k_{oh} at this temperature were found to be $7.86 \pm 1.52 \times 10^{-5}$ sec^{-1}, $6.47 \pm 0.37 \times 10^{-3}$ M^{-1} sec^{-1}, $1.42 \pm 0.10 \times 10^{-3}$ M^{-1} sec^{-1}, and $3.26 \pm 0.31 \times 10^{-1}$ M^{-1} sec^{-1}, respectively. The Arrhenius activation energies are 30.4 ± 2.7, 30.5 ± 0.4, 18.1 ± 3.5, and 24.2 ± 2.0 kcal/mol, respectively. The rate of oxygen exchange was found to be dependent upon the nature of the positive ion of the supporting electrolyte and appears to be general acid–base catalyzed. Partial substitution of methanol for water as the solvent increased the rate. When the *trans*-$[Re(en)_2O_2]^+$ ion is oxidized, a general feature is that the trans O═Re═O group of the rhenium(V) complex is transferred essentially intact to the product ReO_4^- ion. With ClO^- ion as the oxidant, 1.908 ± 0.043 of the oxygen atoms in ReO_4^- came from the rhenium(V) complex and 2.158 ± 0.024 came from solvent water. With MnO_4^- as the oxidizing agent, 1.706 ± 0.032 oxygen atoms were transferred. When O_3 was used to oxidize the complex, 1.953 ± 0.009 oxygen atoms were transferred to ReO_4^- and 1.620 ± 0.006 of the oxygen atoms came from the solvent water.

In order to perform oxygen-transfer experiments on the oxidation of $[Re(en)_2O_2]^+$ to ReO_4^-, it was necessary to know the rate equation for exchange of oxygen atoms between $[Re(en)_2O_2]^+$ and water. The rate law for the oxygen exchange between ReO_4^- and solvent water has been reported.[2] This paper reports the rate law for the exchange of oxygen atoms between $[Re(en)_2O_2]^+$ and solvent water and its dependence upon solvent composition and temperature. The results of oxygen-18 transfer experiments are reported for the oxidation of $[Re(en)_2O_2]^+$ to ReO_4^- using several oxidizing agents.

Experimental Section

The water used in these experiments was deionized on a double-bed column, distilled from acidic $K_2Cr_2O_7$ solution and from alkaline $KMnO_4$ in an all-glass apparatus.

Reagent grade ethylenediamine was purified by slow distillation at atmospheric pressure. The first and last thirds of the distillate were discarded and only the middle fraction boiling at 116.5–117.0° (uncorrected) was used.

The concentration of solutions of ethylenediamine was determined by pH titration with hydrochloric acid standardized ultimately against standard ACS potassium hydrogen phthalate.

Perrhenic acid obtained from S. W. Shattuck Chemical Co. was used without further purification.

Oxygen-18 water was obtained from YEDA, Rehovoth, Israel, and had an ^{18}O content of approximately 1.5 atom %.

Solutions of chromium(II) perchlorate were used to remove traces of oxygen from prepurified tank nitrogen and were prepared by dissolving chromium metal in 2.0–6.0 *M* perchloric acid. Mossy

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[1] Abstracted in part from the Ph.D. thesis of L. B. Kriege, University of Missouri, 1971.

[2] R. K. Murmann, *J. Phys. Chem.*, 71, 974 (1967).

zinc amalgam was always present in excess to keep the chromium ion in the reduced state.

Potassium hexachlororhenate(IV) was prepared by the method of Watt and Thompson[3] and was used without further purification in the preparation of $[Re(en)_2O_2]Cl$.

trans-Dioxobis(ethylenediamine)rhenium(V) chloride was prepared by the method of Murmann[4] and was purified by conversion to the slightly soluble $[Re(en)_2O_2]I$, which was washed several times with reagent grade acetone and vacuum dried. Reaction with freshly prepared silver chloride, free of acid and Cl^-, followed by removal of silver iodide on a filter gave a solution of the chloride salt which was precipitated with acetone. The complex was recrystallized twice from methanol–water mixtures and dried under vacuum at 56° for 24 hr. Yields were in the range 75–80% based on the amount of K_2ReCl_6 used.

Anal. Calcd for $ReO_2C_4H_{16}N_4Cl$: C, 12.85; H, 4.32; N, 14.99. Found: C, 12.71; H, 4.14; N, 14.76.

Physical Measurements. A Leeds and Northrup Model 7401 pH meter, standardized with appropriate buffers before and after each use, was used to measure the acidity of aqueous solutions of ethylenediamine.

A Beckman DU spectrophotometer was used to record visible and ultraviolet spectra and was equipped with a thermostated cell compartment (±0.05°). Infrared spectra were obtained on Nujol mulls with a Perkin-Elmer Model 237B instrument.

Oxygen-18 analysis of gas samples was performed on a Nuclide RMS isotopic ratio mass spectrometer.

Carbon dioxide samples were purified for mass spectral analysis by vapor-phase chromatography. The instrument employed has been described in detail[5] and was equipped with a $^1/_4$-in. column, 6 feet in length, packed with 30% by weight DOW 704 silicone oil on firebrick.

Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Isotopic exchange studies were carried out using a constant temperature bath (±0.05°). Two types of reaction vessels were used. The first consisted of a three-necked, 25-ml "Bantam-Ware" flask. Into one of the openings water-saturated O_2 and CO_2-free N_2 were passed through a capillary glass tube to the bottom of the vessel. The second opening, fitted with a ground glass stopper, was used to admit a solid sample of $[Re(en)_2O_2]Cl$ to start the exchange. The third opening contained a rubber serum cap and a hypodermic needle to vent nitrogen. Samples were removed through this serum cap with a hypodermic syringe and stainless steel needle. Wrapping the reaction vessel with aluminum foil stopped any light-caused exchange.

The second type of reaction vessel,[5] designed to prevent volatilization at the elevated temperatures used, was constructed from an inverted 50-ml Pyrex erlenmeyer flask joined at the neck to 1-mm capillary tubing. The capillary tubing was bent 180° at the point of connection to the flask and joined to a three-way Teflon stopcock of 1-mm bore. The capillary tubing connecting the erlenmeyer flask and the three-way Teflon stopcock was of sufficient length so that the entire erlenmeyer flask could be immersed in the bath and still allow the Teflon stopcock to remain above the bath liquid. This reaction vessel was used where the solvent consisted of methanol–water mixtures or when a volatile base such as 2,6-lutidine was present. An initial sample was discarded for each aliquot because of the temperature differential near the stopcock.

$[Re(en)_2O_2]^+$–H_2O Exchange. Samples of *trans*-dioxobis(ethylenediamine)rhenium(V) ion containing ^{18}O were prepared by allowing $[Re(en)_2O_2]Cl$ in enriched[6] water to stand at 50° for 24 hr. The complex was precipitated by adding an excess of reagent grade acetone, washed several times with acetone, and dried overnight under vacuum (10^{-3} Torr) at 56°.

The previous studies on the rate of oxygen exchange of $[Re(en)_2O_2]^+$ with solvent H_2O[7,8] showed that at 25°, 10^{-2} M complex, and in 0.10 M ethylenediamine solution the half-time for exchange was about 3000 min. When no excess ethylenediamine was present and the solution was buffered to a pH 6.04 with 4×10^{-2} M phthalate ion, the half-time for exchange decreased to 150 min. In order to obtain more convenient half-times for exchange, a temperature of 50.0° was chosen.

It was observed in preliminary runs that the half-time for exchange increased with increasing concentration of $[Re(en)_2O_2]^+$ and decreased with increasing $[en]_T$. McKay graphs were linear but the solution color decreased slightly during the exchange. Subsequent investigation of the ultraviolet and visible spectra of $[Re(en)_2O_2]^+$ revealed that in the presence of air some complex ion was oxidized to ReO_4^- (identified by its ultraviolet spectra[9]). No new species were found. Therefore, in all subsequent studies oxygen was excluded from the system with a slow stream of purified nitrogen. The half-time for exchange then became independent of the concentration of $[Re(en)_2O_2]^+$; however, it remained a function of $[en]_T$.

The majority of the exchange runs were conducted by adding approximately 0.40 mmol of ^{18}O-labeled $[Re(en)_2O_2]^+$ to 10 ml of a solution containing the proper amounts of KCl, ethylenediamine, and HCl at 50.0°. Before the addition of the $[Re(en)_2O_2]Cl$, a slow stream of purified nitrogen was bubbled through the reaction mixture for 60 min to remove oxygen from the system. The solid complex dissolved within 15 sec, and the stirring action of the bubbling nitrogen assured complete mixing. The time of addition of the $[Re(en)_2O_2]Cl$ was taken as (t_0). At timed intervals, 1-ml samples were removed, and the reaction was quenched by cooling to 0° with an ice bath. Excess solid sodium iodide was added to the sample to precipitate the slightly soluble $[Re(en)_2O_2]I$. After 5 min at 0°, the samples were collected on a filter, washed six times with reagent grade acetone, and dried under vacuum at room temperature.

For runs containing substances more volatile than water, the second reaction vessel was used. $[Re(en)_2O_2]Cl$ (0.80 mmol) was dissolved in 20.00 ml of a solution containing the appropriate amounts of KCl, ethylenediamine, base or methanol, and HCl at 0°. Purified nitrogen was slowly bubbled through this solution for at least 1 hr. The solution was allowed to enter the evacuated reaction flask and pressurized with purified nitrogen. The time of placement of the reaction vessel in the constant temperature water bath was taken as (t_0). In a separate experiment the solution reached bath temperature within 3 min. This time was insignificant since the half-time for exchange was 2–20 hr. At the temperature of the bath, the vapor pressure above the solution was high enough to force the solution from the flask when the stopcock was opened. Before a sample was taken, 1 ml of solution was withdrawn and discarded. This was three times the volume of the solution contained in the colder environment of the stopcock and capillary tube. Solid samples were obtained at timed intervals in the same manner as described previously.

Samples were analyzed for oxygen-18 content by a modification of the method of Anbar and Guttmann.[10] Each sample of $[Re(en)_2O_2]I$ was placed in a break-seal tube together with approximately 100 mg of mercuric cyanide that had been carefully dried for 24 hr at 10^{-3} Torr and 100°. Each sample was evacuated to at least 1×10^{-4} Torr for a minimum of 30 min at which time the tubes were sealed and maintained in an oven at 425 ± 25° for 4.5 hr. After cooling, the break-seal tubes were placed on the inlet system of the gas chromatograph. Carbon dioxide, cyanogen, and hydrogen cyanide were found as condensible gases and were placed on the column using a stream of purified helium. Carbon dioxide was quantitatively separated from the other gases and collected by means of a liquid nitrogen trap. The carbon dioxide was introduced into the ionization chamber of the mass spectrometer, which revealed only peaks characteristic of carbon dioxide to be present. The ratio of the 46/(44 + 45) ion beams was measured for each sample and for a standard CO_2 sample. The standard sample was arbitrarily set at 0.004000 and all samples measured were normalized to this value. The mass spectral response was shown to be linear with atomic fraction in the region used.

Experimental data were plotted as graphs of $-\ln(N - N_\infty)$ (where $N = 46/(44 + 45)$ *vs.* time). The slope (k_{obsd}) and intercept ($-\ln(N_0 - N_\infty)$) were evaluated by the use of a linear least-squares computer program[11] utilizing an IBM 306/65 computer. The over-

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[3] G. W. Watt and R. J. Thompson, *Inorg. Syn.*, 7, 189 (1963).

[4] R. K. Murmann, *ibid.*, 8, 173 (1966).

[5] D. L. Toppen, "Isotopic Oxygen Exchange Studies on Some Re(V) Complexes," Ph.D. Dissertation, The University of Missouri, Columbia, 1971.

[6] The term enrichment is defined as the mass ratio 46/(44 + 45). The sample of carbon dioxide used as a standard was of natural isotopic abundance. The ratio 46/(44 + 45) for this sample was arbitrarily assigned the value of 0.004000.

[7] R. K. Murmann, *J. Inorg. Nucl. Chem.*, 18, 226 (1961).

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

[9] J. B. Headridge, *Analyst*, 83, 690 (1958).

[10] M. Anbar and S. Guttmann, *Int. J. Appl. Radiat. Isotopes*, 4, 233 (1959).

[11] R. H. Moore and R. K. Ziegler, "The Solution of the General

all rate of exchange, R, was calculated using the McKay[12] expression

$$R = k_{\mathrm{obsd}} \frac{(2)([\mathrm{Re(en)_2O_2}^+])([\mathrm{H_2O}])}{(2)([\mathrm{Re(en)_2O_2}^+]) + ([\mathrm{H_2O}])}$$

in M sec^{-1} which reduces to $R = k_{\mathrm{obsd}}(2)([\mathrm{Re(en)_2O_2}^+]$ since in all cases studied the $[\mathrm{H_2O}] >>>$ than that of $[\mathrm{Re(en)_2O_2}]^+$.

Tracer Studies on the Oxidation of $[\mathrm{Re(en)_2O_2}]^+$ to $\mathrm{ReO_4}^-$. A previous study[7] indicated that when $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$ was oxidized to $\mathrm{ReO_4}^-$ using $\mathrm{Br_2}$ in basic media, the transfer of oxygen from $[\mathrm{Re(en)_2O_2}]^+$ to $\mathrm{ReO_4}^-$ was essentially complete. However, the precision of these results was somewhat limited. The purpose of the tracer studies was to determine more precisely the origin of the oxygen atoms in $\mathrm{ReO_4}^-$ when $[\mathrm{Re(en)_2O_2}]^+$ was oxidized to $\mathrm{ReO_4}^-$ with a variety of oxidizing agents. The number of oxidizing agents that could be used was limited, however, since the oxidation had to take place rather rapidly in neutral or slightly basic solution where $[\mathrm{Re(en)_2O_2}]^+$ and $\mathrm{ReO_4}^-$ water exchange is slow. For example, $\mathrm{H_2O_2}$ oxidized $[\mathrm{Re(en)_2O_2}]^+$ to $\mathrm{ReO_4}^-$, but the reaction was too slow to avoid a great deal of oxygen exchange on both $[\mathrm{Re(en)_2O_2}]^+$ and $\mathrm{ReO_4}^-$.

For the $[\mathrm{Re(en)_2O_2}]^+$–ClO^- reaction, 4 ml of 2.5% NaClO solution at pH 9.9 and at 0° was added to 0.045-g samples of $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$. Solution was rapid and after 10 min, solid CsCl was added to precipitate $\mathrm{CsReO_4}$. After 20 min at 0° it was collected on a filter, washed four times with acetone, and dried under vacuum. The samples were analyzed for $^{18}\mathrm{O}$ content in the same manner as has been described for $[\mathrm{Re(en)_2O_2}]\mathrm{I}$. The water used as solvent was analyzed for $^{18}\mathrm{O}$ by distilling a few milligrams under vacuum into a break-seal tube that contained approximately 100 mg of $\mathrm{Hg(CN)_2}$. $\mathrm{CO_2}$ was obtained and purified in the usual manner.

The $[\mathrm{Re(en)_2O_2}]^+$–ClO^- reaction was also carried out using normal complex and ClO^- in enriched water. Anbar and Taube[13] have found that the rate of oxygen exchange between ClO^- and $\mathrm{H_2O}$ is Cl^- catalyzed so the ClO^- sample was freed of Cl^-.

The removal of Cl^- from the sodium hypochlorite solution was handled by adding 1 M $\mathrm{AgNO_3}$ solution to a 5% solution of NaClO until $\mathrm{Ag_2O}$ began to form. The filtered solution was diluted with approximately eight times enriched $^{18}\mathrm{O}$ water. The pH of the solution was adjusted to 11.6 by the addition of 1 M NaOH. This solution (4 ml) at 0° was added to 0.045-g samples of normal $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$, shaken briefly, and kept at 0°. After 20 min solid CsCl was added, and 10 min later the $\mathrm{CsReO_4}$ precipitate was collected on a filter, washed four times with acetone, and dried under vacuum.

For the $[\mathrm{Re(en)_2O_2}]^+$–$\mathrm{MnO_4}^-$ reaction, room temperature was used since preliminary experiments had shown the rate of oxidation to be too slow at 0°.

Samples of $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$, 0.045 g, were dissolved in 2 ml of normal water at room temperature and 2 ml of 0.1 N $\mathrm{KMnO_4}$ was added. Solution and mixing was very rapid. The pH of the solution at the time of mixing was 9.40, and 15 min after mixing it had increased to 9.50. At this time, the $\mathrm{MnO_2}$ that had formed was removed by centrifugation and solid CsCl was added. After 10 min at 0° the $\mathrm{CsReO_4}$ which had precipitated was collected, washed four times with acetone, and dried under vacuum.

The reaction of $[\mathrm{Re(en)_2O_2}]^+$ (0.045 g in 4 ml of normal water) with $\mathrm{O_3}$ was carried out at 0°. CsCl was present, and a slow stream of ozonated oxygen, $\sim$0.5% $\mathrm{O_3}$, was passed through the samples for 30 min. The pH of the solutions changed from 7.5 to 8.3 during the course of the reaction. The $\mathrm{CsReO_4}$ which had formed was collected on a filter, washed four times with acetone, and dried under vacuum. The $^{18}\mathrm{O}$ content of the ozone was taken to be the same as that of the oxygen from which it was produced. The $\mathrm{CsReO_4}$ was converted to $\mathrm{CO_2}$ by reaction with $\mathrm{Hg(CN)_2}$ in the usual manner and the isotopic ratio for $^{18}\mathrm{O}$ determined with the $\mathrm{CO_2}$.

The $[\mathrm{Re(en)_2O_2}]^+$–$\mathrm{O_3}$ reaction was also carried out using normal complex, normal ozone, and oxygen-18 enriched water. $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$, 0.045 g, was dissolved in 2 ml of water approximately eight times enriched in $^{18}\mathrm{O}$ containing CsCl. The pH of the solution, before the addition of ozone, was about 7.5 initially and 8.3 finally. Ozonated oxygen was passed through the solution for 30 min at 0°. The $\mathrm{CsReO_4}$ which had formed was collected on a filter, washed with acetone, and dried under vacuum. Also, samples of the solvent water taken before and after the reaction were analyzed.

Stoichiometry of the $[\mathrm{Re(en)_2O_2}]^+$–$\mathrm{O_3}$ Reaction. In order to determine the stoichiometry of the $[\mathrm{Re(en)_2O_2}]^+$–$\mathrm{O_3}$ reaction, two cells were constructed of glass and Teflon and connected in series. The ozone–oxygen mixture was passed through them until a steady state was reached and then, after isolation, a bulb was broken releasing complex solutions into the ozone. An excess of complex was always present. Also, the ozone in the second cell was flushed into an I^- solution for analysis.[14] The reaction was allowed to proceed for 24 hr during which time the cell and its contents were shaken periodically. The solution of $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$ was then removed and its concentration determined by measuring its absorbance at 440 mμ. The volume of the reaction cells was determined by filling them with water and weighing. The liberated iodine was titrated with standard sodium thiosulfate solution. The concentration of ozone was assumed to be the same in both cells.

As previously noted, solutions of $[\mathrm{Re(en)_2O_2}]^+$ were not entirely stable. Since exchange kinetics may be quite sensitive to impurities, a more careful study was made of the absorption characteristics of this ion. The visible spectrum has been reported by several authors.[15-17] Considerable disagreement existed. Using samples of $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$ giving excellent C, H, and N analyses and showing identical ir spectra to samples previously prepared, freshly prepared solutions gave as the major band (440 nm) ϵ's of 22.7, 22.0, and 21.9 for concentrations of 6.48, 16.20, and 40.49 $\times$ 10^{-3} M. The absorption at 440 nm changed gradually with time to a nearly constant ϵ of 21, and an absorption appeared between 225 and 254 nm. This change was prevented when the solution was maintained under a nitrogen atmosphere. The species absorbing in the uv was $\mathrm{ReO_4}^-$, as shown by its ion exchange behavior and spectral identification. In the absence of $\mathrm{O_2}$ the ϵ at 440 nm for $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$ was found to be 22.6 ± 0.2 and for $[\mathrm{Re(en)_2O_2}]\mathrm{I}$, 22.3 ± 0.2 agreeing with ref 16.

Results

Table I shows the results of the complex dependence studies. Plots of $-\ln(N - N_\infty)$ *vs.* time were linear over greater than 95% of the reaction, and the average standard deviation in the slope was approximately 1%. Each run consisted of from five to eight individual points. Duplicate runs also gave slopes differing by approximately 1%. A plot of $-\log R$ *vs.* $-\log[\mathrm{Re(en)_2O_2}^+]$ gave an order with respect to complex of 1.03 ± 0.01. (± values will refer to one standard deviation unless otherwise indicated.)

Table I. $[\mathrm{Re(en)_2O_2}]^+$ Dependence[a]

$[\mathrm{Re(en)_2O_2}]^+$, M	$10^4 k_{\mathrm{obsd}}$,[b] sec^{-1}
0.020	2.59 ± 0.01
0.020	2.58 ± 0.02
0.030	2.60 ± 0.03
0.040	2.66 ± 0.02
0.050	2.56 ± 0.06
0.060	2.68 ± 0.03

[a] Conditions: $[\mathrm{en}]_{\mathrm{Total}} = 0.4375$ M, $\mu = 1.50$ (KCl), pH 7.00, 50.0°. [b] $k_{\mathrm{obsd}} = 0.693/t_{1/2}$.

The results of the ethylenediamine dependence studies are shown in Table II. The pH dependence data showed that the increase in rate with increasing total ethylenediamine concentration was due mainly to the increase in concentration of the doubly protonated form of ethylenediamine. Consequently, the data in Table II were fitted to a rate law of the form

$$R = k_0[\mathrm{Re(en)_2O_2}^+] + k_{\mathrm{enh_2}}[\mathrm{Re(en)_2O_2}^+][\mathrm{enH_2}^{2+}]$$

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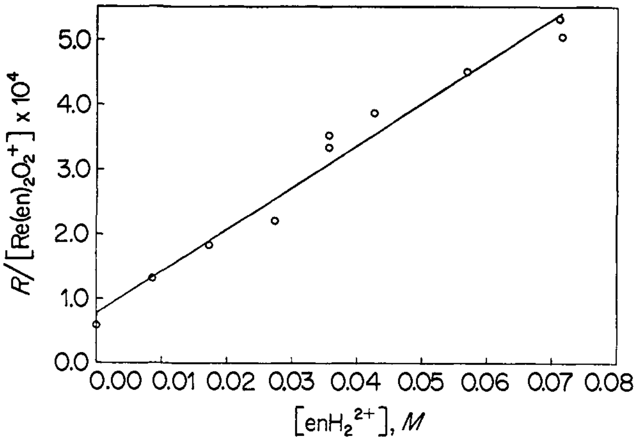

Figure 1. Rate constants of ^{18}O exchange at 50° sec^{-1}.

Figure 1 shows a plot of $R/[Re(en)_2O_2^+]$ *vs.* $[EnH_2^{2+}]$ which is relatively linear. The concentrations of enH_2^{2+} at 50.0° and other temperatures were calculated from the acid association constants reported by Fernelius, *et al.*[18] Each individual run in Figure 1 was weighted with its calculated standard deviation. A least-squares analysis gave values for k_0 and k_{enh_2} of 7.86 ± 1.52 × 10^{-5} sec^{-1} and 6.47 ± 0.37 × 10^{-3} M^{-1} sec^{-1}, respectively.

Table II. Ethylenediamine Dependence[a]

[en],[b] M	$[enH_2^{2+}]$, M	k_{obsd}, sec^{-1} [c]
	50.0° (k Values × 10^4)	
0.4397	0.0715	2.52 ± 0.06
0.4375	0.0711	2.66 ± 0.02
0.3497	0.0569	2.26 ± 0.02
0.2618	0.0426	1.93 ± 0.02
0.2188	0.0356	1.76 ± 0.07
0.2188	0.0356	1.67 ± 0.03
0.1687	0.0274	1.11 ± 0.02
0.1066	0.0173	0.92 ± 0.05
0.0530	0.0086	0.66 ± 0.02
0.0530	0.0086	0.66 ± 0.04
0.0000	0.0000	0.30 ± 0.007
	40.1° (k Values × 10^5)	
0.3497	0.0839	6.68 ± 0.16
0.2618	0.0628	5.50 ± 0.22
0.1687	0.0405	3.59 ± 0.10
0.0000	0.0000	0.794 ± 0.032
	30.0° (k Values × 10^5)	
0.3497	0.1333	2.10 ± 0.05
0.2618	0.0998	1.79 ± 0.04
0.1687	0.0643	1.11 ± 0.03
0.0000	0.0000	0.225 ± 0.009

[a] Conditions: $[Re(en)_2O_2]^+$ = 0.040 M, μ = 1.50 (KCl), pH 7.00. [b] Represents the sum total of all non-rhenium-coordinated forms of ethylenediamine present. [c] $k_{obsd} = 0.693/t_{1/2}$.

The temperature dependence of k_0 and k_{enh_2} was determined using data in Table II: 50.0, 40.1, and 30.0°. The total concentration of ethylenediamine was varied from 0.0 to 0.440 M. Each point in graphs similar to Figure 1 was weighted with the standard deviation calculated for that run. The values obtained for k_0 and k_{enh_2} at 40.1 and 30.0° are shown in Table III, along with the activation parameters.

Table III. Temperature Dependence,[a] $[Re(en)_2O_2]^+$–H_2O Exchange

Temp, °C	10^5k_0, sec^{-1} [b]	$10^3k_{enh_2}$, M^{-1} sec^{-1} [b]
50.0[c]	7.86 ± 1.52	6.47 ± 0.37
40.1	1.58 ± 0.49	1.42 ± 0.08
30.0	0.453 ± 0.362	0.290 ± 0.04

[a] Conditions: $[Re(en)_2O_2^+]$ = 0.040 M, μ = 1.50 (KCl), pH 7.00. [b] k_0 and k_{enh_2} are defined as $R = k_0[Re(en)_2O_2^+] + k_{enh_2}\cdot[Re(en)_2O_2^+][enH_2^{2+}]$. [c] Using a weighted linear least-squares analysis, E_a for the k_0 term was 30.4 ± 2.7 kcal with log A = 16.5 ± 1.9 and for the k_{enh_2} term they were 30.5 ± 0.4 kcal and 18.4 ± 0.3.

Four rate determinations were conducted to determine the effect of increasing the concentration of potassium chloride on the rate of oxygen exchange. Table IV lists the results found where the ionic strength varied from 0.17 to 1.50. An appreciable increase in rate constant occurred with increasing ionic strength.

Table IV. Ionic Strength Effect,[a] KCl

μ (KCl)	10^5k_{obsd},[b] sec^{-1}
1.500	6.61 ± 0.16
1.000	6.12 ± 0.08
0.500	5.41 ± 0.10
0.172	4.44 ± 0.02

[a] Conditions: ionic strength maintained with KCl, $[Re(en)_2O_2]^+$ = 0.040 M, $[en]_{Total}$ = 0.0530 M, pH 7.00, 50.0°. [b] $k_{obsd} = 0.693/t_{1/2}$.

In order to determine if the electrolyte concentration dependence was a general or specific effect, the alkali metal ion was changed. The ionic strength was maintained at 1.50 M in each case and the total concentration of chloride ion remained constant. The results are shown in Table V. The value for k_{obsd} reported for K^+ was calculated from the ethylenediamine dependence data at 50.0°. k_{obsd} increases from 2.192 ± 0.048 × 10^{-4} sec^{-1} with LiCl to 2.450 ± 0.025 × 10^{-4} sec^{-1} with CsCl. The increase is regular and directly related to the size of the cation although some of the values overlap within the experimental error.

Table V. Effect of Alkali Metal Ions[a]

Metal ion[b]	10^4k_{obsd},[c] sec^{-1} [d]
Li^+	2.192 ± 0.048
Na^+	2.276 ± 0.054
K^+ [e]	2.366 ± ~0.020
Cs^+	2.450 ± 0.025

[a] Conditions: $[Re(en)_2O_2]^+$ = 0.040 M, $[en]_{Total}$ = 0.3611 M, μ = 1.50, pH 7.00, 50.0°. [b] All metal ions were added as chloride ion salts. [c] $k_{obsd} = 0.693/t_{1/2}$. [d] Errors represent one standard deviation. [e] Calculated from the ethylenediamine dependence at 50.0° where the supporting electrolyte was KCl.

Table VI shows the effect of changing the anion from Cl^- to NO_3^-. A very small change is noted.

Since it is known[19] that solutions of ethylenediamine decompose, the effect of the age of solutions on the rate of oxygen exchange was determined, Table VI. The values agree within experimental error and show that

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(18) G. H. McIntyre, Jr., B. P. Block, and W. C. Fernelius, *J. Amer. Chem. Soc.*, **81**, 529 (1959).

(19) G. L. Putman and K. A. Kobe, *Trans. Electrochem. Soc.*, **74**, 609 (1938); *Chem. Abstr.*, **32**, 5707 (1938).

Table VI. Effect of Anion Change[a]

10^4k_{obsd},[b] sec^{-1}	Salt used to maintain ionic strength
2.05 ± 0.02[c]	KCl
1.96 ± 0.09	KCl
1.73 ± 0.01	NaCl
1.63 ± 0.01	$NaNO_3$

[a] Conditions: $[Re(en)_2O_2]^+$ = 0.040 M, $[en]_{Total}$ = 0.0707 M, μ = 1.50, pH 10.69, 50.0°. [b] $k_{obsd} = 0.693/t_{1/2}$. [c] This run was done using a 1-year-old solution of ethylenediamine. Others used immediately after distillation.

any decomposition of the ethylenediamine used in this study had no observable effect on the rate of oxygen exchange. It should be emphasized that the solutions of ethylenediamine were stored in the dark in Teflon-stoppered flasks.

The results of the acidity studies are shown in Table VII. The pH covered the range of 4.38–12.22 with the total concentration of ethylenediamine at 0.0707 M. Solutions below a pH of 6.02 exhibited a spectral change with time, becoming much darker. This had been previously observed and is due to the replacement of one or more complexed ethylenediamine molecules by chloride ions and/or water molecules.[8] Due to this decomposition no useful information could be obtained in acidic media.

Table VII. Calculated and Observed Values for the pH Dependence of the $[Re(en)_2O_2]^+$–H_2O Exchange Reaction[a]

pH	10^4k_{obsd}, sec^{-1}	$10^4R/[Re(en)_2O_2^+]_{calcd}$, sec^{-1}	$10^4R/[Re(en)_2O_2^+]_{obsd}$, sec^{-1}
4.38[b]	5.53 ± 0.28		
5.19[b]	4.68 ± 0.17		
5.44[b]	4.34 ± 0.14		
5.68[b]	3.51 ± 0.10		
6.02[b]	2.52 ± 0.02		
6.18	2.02 ± 0.02	3.49	4.04
6.54	1.22 ± 0.01	2.51	2.45
7.00	0.714 ± 0.007	1.57	1.43
7.58	0.559 ± 0.010	1.04	1.12
7.94	0.494 ± 0.006	0.932	0.989
8.62	0.468 ± 0.007	0.995	0.936
9.28	0.542 ± 0.004	1.35	1.08
9.59	0.711 ± 0.009	1.58	1.42
9.84	0.911 ± 0.002	1.80	1.82
10.10	1.16 ± 0.01	2.07	2.31
10.34	1.45 ± 0.04	2.42	2.91
10.68	2.05 ± 0.02	3.31	4.11
11.28	3.95 ± 0.08	8.00	7.90
11.56	6.27 ± 0.05	13.6	12.5
11.85	12.8 ± 0.2	24.9	25.6
12.22	31.7 ± 0.8	55.9	63.3

[a] Conditions: $[Re(en)_2O_2^+]$ = 0.040 M, $[en]_{Total}$ = 0.0707 M, μ = 1.50 (KCl), 50.0°. [b] Some decomposition; linear McKay graph, however.

Figure 2 shows a Calcomp graph of log $R/[Re(en)_2O_2^+]$ *vs.* pH, using the calculated parameters. Several important details are apparent in this curve: (1) the rate of oxygen exchange is essentially first order in hydroxide ion above a pH of ~11; (2) there is a minimum in the rate at approximately pH 8.5; (3) the rate increases with acidity from pH 8.5 but the increase is not first order in hydrogen ion; and (4) the rate increases as the pH increases above pH 8.5 but does not become first order in hydroxide ion until about pH 11. Obviously the rate equation must consist of several terms and it is likely that no unambiguous rate equation can be established. Within that framework we have attempted to obtain a simple, reasonable rate equation which satisfies the data within the anticipated error.

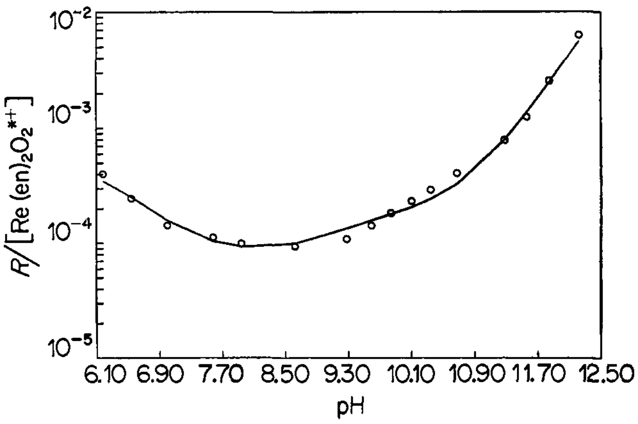

Figure 2. Rate constants of ^{18}O exchange at 50° sec^{-1}.

During the course of this study, numerous reasonable rate equations were fitted to the data. None gave a better fit than the one to be described but some gave a fit judged to be about equal. The rate equation suggested has the smallest number of terms, all of which are reasonable. The following is a rationalization of that selection.

The increase in rate at pH 7.00 with increasing concentration of total ethylenediamine is best explained by including a term in the rate law which is first order in enH_2^{2+}. Justification for this comes from the fact that at pH 7.00 the two main species of ethylenediamine present are enH^+ and enH_2^{2+}. The first and second acid dissociation constants for ethylenediamine are approximately 5×10^{-7} and 5×10^{-10} which give the pH of maximum $[enH^+]$ of approximately 8. As can be seen from Figure 2, this is close to the minimum in k_{obsd}. Thus, a $[enH^+]$ term does not contribute strongly to the observed rate. It is reasonable to suggest, however, that if enH_2^{2+} is effective then an enH^+ term should also be present but of smaller magnitude.

The minimum in Figure 2 can be explained by a term independent of acidity which corresponds to the k_0 term suggested during the preliminary studies at pH 7.00.

The only species that is increasing in concentration in the region pH 8.5–11, other than hydroxide ion, is free ethylenediamine. Assuming each term is first order in complex ion, the rate law becomes

$$R/[Re(en)_2O_2^+] = k_0 + k_{enh_2}[enH_2^{2+}] + k_{en}[en] + k_{oh}[OH^-]$$

A nonlinear least-squares computer program was used to obtain the best values for k_{enh_2}, k_{en}, and k_{oh}. All experimental points were used except where noted and each point was weighted using its calculated standard deviation. In the computer program k_0 was set at 7.86×10^{-5} sec^{-1} (the value calculated from the ethylenediamine dependence data at pH 7.00) and the concentrations of the en species were calculated. The values calculated for the individual rate constants were found to be $k_{\mathrm{enh_2}} = 6.79 \pm 0.46 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, $k_{\mathrm{en}} = 1.42 \pm 0.10 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_{\mathrm{oh}} = 3.26 \pm 0.31 \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$. The value for $k_{\mathrm{enh_2}}$ from the pH dependence data can be compared to that found from the ethylenediamine dependence data at pH 7.00, which was $6.47 \pm 0.37 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, in reasonable agreement.

Figure 2 shows a graph of log $R/[\mathrm{Re(en)_2O_2}^+]$ *vs.* pH showing the experimental points and the calculated least-squares line. The experimental data fit the proposed rate law sensibly, considering the restrictive constants k_0, K_1, and K_2 for en. Table VII contains values for $R/[\mathrm{Re(en)_2O_2}^+]_{\mathrm{obsd}}$ and $R/[\mathrm{Re(en)_2O_2}^+]_{\mathrm{calcd}}$ for each point shown in Figure 2.

The Arrhenius activation energy for k_{en} and k_{oh} was obtained by conducting two runs at 39.9° and two at 30.0°. The k_0 and $k_{\mathrm{enh_2}}$ terms were subtracted from the overall rate and solution of the simultaneous equations gave values for k_{en} and k_{oh} at these temperatures. Plots of ln k *vs.* $1/T$ gave an E_a of 18.1 ± 3.5 kcal/mol with $\log A = 9.4 \pm 2.4$ for k_{en} and 24.2 ± 2.0 kcal/mol with $\log A = 15.8 \pm 1.4$ for k_{oh}.

Experiments designed to determine if other bases increased the rate of oxygen exchange of $[\mathrm{Re(en)_2O_2}]^+$ are presented in Table VIII. Values for k_{estd} were calculated from the pH-dependence studies.

Table VIII. Effect of Added Bases[a]

pH	Base used	$[\mathrm{Base}]_{\mathrm{Total}}$	10^4k_{obsd}, sec^{-1} [b]	10^4k_{estd}, sec^{-1} [c]
10.18	Ethylenediamine	0.1414	1.79 ± 0.02	1.12
7.02	2,6-Lutidine	0.103	1.06 ± 0.01	0.780
9.90	2,6-Lutidine	0.103	0.959 ± 0.020	0.960
7.44	*tert*-Butylamine	0.100	0.687 ± 0.004	0.598
10.62	*tert*-Butylamine	0.100	2.10 ± 0.05	1.88

[a] Conditions: $[\mathrm{Re(en)_2O_2}^+] = 0.040\ M$, $[\mathrm{en}]_{\mathrm{Total}} = 0.0707\ M$, $\mu = 1.50$ (KCl), 50.0°. [b] $k_{\mathrm{obsd}} = 0.693/t_{1/2}$. [c] Estimated value for k_{obsd} without additional added base present.

The results in methanol–water mixtures are shown in Table IX. Since the complex is not very soluble in methanol, high methanol to water ratios could not be used. Also, in these solvents there exists a problem in knowing the pH of the solutions and its meaning. For this reason the studies were carried out using the same amount of ethylenediamine and HCl in each run so that the pH of the solutions would be 8.68 if no methanol were added. At this pH the effects of a change in acidity are minimized since there is little contribution to the exchange rate except by the k_0 path.

Table IX. Rates of Exchange in $\mathrm{CH_3OH}$–$\mathrm{H_2O}$ Mixtures[a]

$\mathrm{CH_3OH}$ (ml) added per 100-ml total vol	10^5k_{obsd},[b] sec^{-1}
0.00	3.13 ± 0.01
10.00	3.39 ± 0.03
20.00	4.12 ± 0.02
30.00	5.27 ± 0.05

[a] Conditions: $[\mathrm{Re(en)_2O_2}]\mathrm{Cl} = 0.040\ M$, $[\mathrm{en}]_{\mathrm{Total}} = 0.0707\ M$, $\mu = 0.118$, pH (with no added $\mathrm{CH_3OH}$) 8.68, 50.0°. [b] $k_{\mathrm{obsd}} = 0.693/t_{1/2}$.

Table IX shows that as the methanol to water ratio increases the rate constant of oxygen exchange increases.

The results of the tracer studies on the oxidation of $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$ to $\mathrm{ReO_4^-}$ using enriched complex, normal $\mathrm{H_2O}$, and normal Cl $\mathrm{O^-}$ are shown in Table XA. The number of oxygens transferred to the perrhenate ion from $[\mathrm{Re(en)_2O_2}]^+$ was calculated by using the formula

$$4N_{\mathrm{ReO_4^-}} = XN_{[\mathrm{Re(en)_2O_2}]^+} + (4 - X)N_{\mathrm{H_2O}}$$

where $N = 46/(44 + 45)$ mass ratio measured for the indicated sample and X is the number of oxygens transferred. The average number of oxygens transferred to $\mathrm{ReO_4^-}$ was 1.908 ± 0.043.

Table X. Tracer Studies on the $[\mathrm{Re(en)_2O_2}]^+$–$\mathrm{ClO^-}$ Reaction[a]

Sample	Enrichment[b]	No. of oxygens in $\mathrm{ReO_4^-}$ from $[\mathrm{Re(en)_2O_2}]^+$
	A	
$\mathrm{H_2O}$	0.003991[c]	
$[\mathrm{Re(en)_2O_2}]^+$	0.021828[d]	
$\mathrm{ReO_4^-}$	0.012346	1.874
$\mathrm{ReO_4^-}$	0.012827	1.981
$\mathrm{ReO_4^-}$	0.012419	1.890
$\mathrm{ReO_4^-}$	0.012405	1.887
		Av = 1.908 ± 0.043
		No. of oxygens in $\mathrm{ReO_4^-}$ from solvent
	B	
$\mathrm{ClO^-}$	0.003991[c]	
$\mathrm{H_2O}$	0.015872[c]	
$[\mathrm{Re(en)_2O_2}]^+$	0.004067[e]	
$\mathrm{ReO_4^-}$	0.010475	2.171
$\mathrm{ReO_4^-}$	0.010426	2.154
$\mathrm{ReO_4^-}$	0.010326	2.121
$\mathrm{ReO_4^-}$	0.010518	2.185
		Av = 2.158 ± 0.024

[a] Conditions: 0.045 g of $[\mathrm{Re(en)_2O_2}]\mathrm{Cl}$ per sample, 2.5% NaClO solution at pH 9.9 (A), 11.6 (B), 0°. [b] The enrichment of the "normal" carbon dioxide sample used as a standard was arbitrarily set at 0.004000. [c] Average of 4 determinations. [d] Average of 18 determinations. [e] Average of 10 determinations.

The oxidation of $[\mathrm{Re(en)_2O_2}]^+$ to $\mathrm{ReO_4^-}$ with $\mathrm{ClO^-}$ was also carried out using normal complex, normal $\mathrm{ClO^-}$, and enriched $\mathrm{H_2O}$.

The number of oxygens found in the perrhenate ion that came from the solvent was calculated from the formula

$$4N_{\mathrm{ReO_4^-}} = XN_{\mathrm{H_2{}^{18}O}} + 1.908N_{[\mathrm{Re(en)_2O_2}]^+} + (2.092 - X)N_{\mathrm{ClO^-}}$$

Table XB shows that the number of oxygens found in the perrhenate ion that came from the solvent was 2.158 ± 0.024. The value found is slightly greater than 2.0 apparently due to a small exchange of the ions with the solvent. No appreciable O transfer from $\mathrm{ClO^-}$ to rhenium occurred.

The results of the oxidation of enriched $[\mathrm{Re(en)_2O_2}]^+$ to $\mathrm{ReO_4^-}$ using normal $\mathrm{MnO_4^-}$ and normal $\mathrm{H_2O}$ are shown in Table XI. The number of oxygens transferred to the perrhenate ion was found to be 1.706 ± 0.032. The manganese product appeared to be $\mathrm{MnO_2}$.

The number of oxygens transferred to the perrhenate ion when normal ozone is used to oxidize enriched $[\mathrm{Re(en)_2O_2}]^+$ in normal water is shown in Table XIIA. It was found to be 1.953 ± 0.009.

Table XI. Tracer Studies on the $[Re(en)_2O_2]^+$–MnO_4^- Reaction[a]

Sample	Enrichment[b]	No. of oxygens in ReO_4^- from $[Re(en)_2O_2]^+$
H_2O	0.003921[c]	
$[Re(en)_2O_2]^+$	0.021828[d]	
ReO_4^-	0.011422	1.676
ReO_4^-	0.011794	1.759
ReO_4^-	0.011472	1.687
ReO_4^-	0.011530	1.700
		Av = 1.706 ± 0.032

[a] Conditions: 0.045 g of $[Re(en)_2O_2]Cl$ per sample, $[KMnO_4]$ = 0.1 *N*, pH 9.4, room temperature. [b] The enrichment of the "normal" carbon dioxide sample used as a standard was arbitrarily set as 0.004000. [c] Average of 4 determinations. [d] Average of 18 determinations.

Table XII. Tracer Studies on the $[Re(en)_2O_2]^+$–O_3 Reaction[a]

Sample	Enrichment[b]	No. of oxygens in ReO_4^- from $[Re(en)_2O_2]^+$
	A	
$[Re(en)_2O_2]^+$	0.021828[c]	
H_2O	0.003921[d]	
O_3	0.004012[e]	
ReO_4^-	0.012637	1.947
ReO_4^-	0.012716	1.965
ReO_4^-	0.012632	1.946
		Av = 1.953 ± 0.009
		No. of oxygens in ReO_4^- from $H_2{}^{18}O$
	B	
O_3	0.004012[e]	
$H_2{}^{18}O$	0.034708[d]	
$[Re(en)_2O_2]^-$	0.004067[f]	
ReO_4^-	0.016480	1.620
ReO_4^-	0.016401	1.610
ReO_4^-	0.016507	1.624
ReO_4^-	0.016526	1.627
		Av = 1.620 ± 0.006

[a] Conditions: 0.045 g of $[Re(en)_2O_2]Cl$ in 2.00 ml of solution, pH 7.5, 0°. [b] The enrichment of the "normal" carbon dioxide sample used as a standard was arbitrarily set as 0.004000. [c] Average of 18 determinations. [d] Average of 4 determinations. [e] Average of 2 determinations. [f] Average of 10 determinations.

The $[Re(en)_2O_2]^+$–O_3 oxidation reaction was also carried out using normal complex, normal ozone, and enriched water. The exchange of oxygen atoms between ozone and water is slow[20] under the conditions of this experiment. The results of this study are shown in Table XIIB.

The average number of oxygens found in ReO_4^- that were derived from the solvent was 1.620 ± 0.006. The number of oxygens derived from the ozone is then 0.427.

The purpose of the stoichiometry experiments was to determine how many ozone molecules were required for each complex ion. This information also indicates if molecular oxygen is one of the reaction products. In the first trial 9.00 ml of a solution, 0.01805 *M* in $[Re(en)_2O_2]Cl$ and 0.0345 *M* in free ethylenediamine, was allowed to react with 105.1 ml of an oxygen–ozone gas mixture that contained 1.46×10^{-4} mmol of O_3/ml. It was found that 0.01648 mmol of complex reacted with this amount of ozone, giving a ratio of 1.08 mol of complex/mol of O_3. In a second trial with no excess ethylenediamine it was found that the ratio was 1.03.

Discussion

Aqueous Formula of the $[Re(en)_2O_2]^+$ Ion. A single-crystal X-ray diffraction study[21] has shown that the $[Re(en)_2O_2]^+$ ion has distorted octahedral geometry in the solid state with a linear O═Re═O *trans*-dioxo grouping. This work shows that samples of ^{18}O-enriched $[Re(en)_2O_2]Cl$ can be dissolved in normal water and precipitated as $[Re(en)_2O_2]I$ with less than 1% exchange. This shows that the $[Re(en)_2O_2]^+$ ion retains the essentially octahedral configuration in solution which it has in the solid state. The solution structure, based on spectral interpretation by Basu and Basu,[17] cannot be correct.

Kinetics of $[Re(en)_2O_2]^+$–H_2O Exchange. The rate expression which best describes the rate of oxygen exchange of $[Re(en)_2O_2]^+$ at 50.0° and μ = 1.50 (KCl) is given by

$$R/[Re(en)_2O_2]^+ = k_0 + k_{enh_2}[enH_2{}^{2+}] + k_{en}[en] + k_{oh}[OH^-]$$

While many other rate equations were tried this form gives the best fit while minimizing the complexity of the equation. It has also been found that: (1) ions such as $enH_2{}^{2+}$, 2,6-lutidineH$^+$, and *tert*-butylamineH$^+$ increase the rate; (2) bases such as ethylenediamine and *tert*-butylamine increase the rate of oxygen exchange; (3) the rate increases with ionic strength and with the size of the cation of the supporting electrolyte at constant ionic strength; and (4) the rate increases when methanol is partially substituted for water or the solvent.

The Arrhenius activation energies found for k_0, k_{enh_2}, k_{en}, and k_{oh} were 30.4 ± 2.7, 30.5 ± 0.4, 18.1 ± 3.5, and 24.2 ± 2.0 kcal/mol, respectively. The similarity of the activation energies for k_0 and k_{enh_2} suggests that similar mechanisms may be involved. The high activation energies found for the k_0 and k_{enh_2} terms suggest that rhenium–oxygen bond breaking is more important in the oxygen exchange process than is rhenium-to-oxygen bond formation with the incoming exchanging species.

Toppen[5] has recently determined the rate of oxygen exchange of $[Re(CN)_4O_2]^{3-}$ with solvent water. He found that at 35.0° and μ = 1.00 (KCl) that the rate of oxygen exchange is described by

$$R = k_1'[Re(CN)_4O_2{}^{3-}][H^+] + k_4[Re(CN)_4O_2{}^{3-}][OH^-]^{0.22}[CN^-]^{-0.90}$$

where $k_1' = k_1K_{eq}$ (K_{eq} is the acid association constant for $[Re(CN)_4O_2]^{3-}$). Values for k_1 and k_4 at 35.0° were found to be $3.42 \pm 0.05 \times 10^{-2}$ sec^{-1} and $2.15 \pm 0.30 \times 10^{-12}$ M^{-1} sec^{-1}, respectively. The activation energies for the k_1 and k_4 paths were 23.3 ± 0.3 and 20.3 ± 0.1 kcal/mol, respectively. It was also found that the rate of oxygen exchange increased with ionic strength.

With $[ReO_2(CN)_4]^{3-}$ no path corresponding to the k_0 path found in this study was seen. This may be rationalized on the basis of the empty, antibonding π orbitals which CN$^-$ but not en has. Thus CN$^-$ is capable of accommodating some of the electron density placed on

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the rhenium atom by the oxo ligands. This oxygen-to-rhenium-to-cyanide transfer of electron density has the effect of strengthening both the rhenium–oxygen bonds and the rhenium–cyanide bonds.[15] Thus the oxygen exchange paths, which are predominately bond breaking in nature, will be considerably slower with the cyanide ion complex.

The $k_{\mathrm{enh_2}}$ term in the rate law for oxygen exchange of $[Re(en)_2O_2]^+$ is similar to the k_1' term in the rate law found with $[Re(CN)_4O_2]^{3-}$ except that a H_{aq}^+ has taken the place of enH_2^{2+}. The activation energies for the two paths (23.3 0.3 kcal/mol for $[Re(CN)_4O_2]^{3-}$ and 30.5 0.4 kcal/mol for $[Re(en)_2O_2]^+$) probably reflect a combination of their relative ability to weaken the rhenium–oxygen bond and the original Re–O bond strength.

A SN1CB type of mechanism[22] is suggested for the exchange in the basic region which involves the k_{en} and k_{oh} terms in the rate law. This mechanism was also suggested by Murmann[8] for the ethylenediamine ligand exchange for $[Re(en)_2O_2]^+$. The amido group in the equatorial plane of the molecules is able to multiple bond to the rhenium causing a weakening of the *trans*-rhenium–oxygen bonds since the rhenium would now be less able to accommodate the electron density from the oxygens.

Although the charge type of the ions $[ReO_2(CN)_4]^{3-}$ and $[Re(en)_2O_2]^+$ is quite different, the salt effect and sensitivity to the size of the positive ion of the salt are about the same. This may be a general phenomenon for *trans*-dioxo complexes paralleling their basic behavior with respect to acids (logs K_1) for the first-acid association constants for $[ReO_2(CN)_4]^{3-}$ and $[Re(en)_2O_2]^+$ are 3.26 ± 0.02 and 3.71 ± 0.15, respectively (25°).

A general feature of the oxidation of $[Re(en)_2O_2]^+$ to ReO_4^- is, on the basis of these first results, that the two oxygen atoms of $[Re(en)_2O_2]^+$ are almost completely transferred to ReO_4^-. If the oxidations take place by one-electron steps the Re^{6+} species must exchange its oxygens more slowly than it is oxidized to ReO_4^-. A two-electron transfer is, however, just as probable. The extent of oxygen atom transfer sets the upper limits for $2e^-$ oxidation.

The oxidation of $[Re(en)_2O_2]^+$ to ReO_4^- with MnO_4^-, however, shows incomplete oxygen transfer which may suggest the formation of 6+ rhenium and its partial exchange before oxidation in one of the steps. However, experimental difficulties due to the slowness of this reaction may be the cause of this apparent low value due to reactant and product solvent exchange.

The results of the oxygen transfer studies on the oxidation of $[Re(en)_2O_2]^+$ by ozone show that 1.953 ± 0.009 of the oxygens in the ReO_4^- product come from $[Re(en)_2O_2]^+$, 1.620 ± 0.006 come from the solvent water, and, consequently by difference, approximately 0.43 of the oxygens in ReO_4^- comes from the ozone. The stoichiometry of this reaction is 1.06 ± 0.04 $[Re(en)_2O_2]^+/O_3$ and thus molecular oxygen is produced.

While the general feature, retention of the -yl oxygens, is retained, the partial introduction of an ozone–oxygen into the coordination sphere of rhenium is not easily explained by a mechanism capable of being tested. The fraction transferred is highly reproducible, however, which will facilitate future more detailed mechanistic studies. At present no information is available concerning the intermediates or activate state(s) of this process. A similar situation exists in the oxidation of Pu(III) to PuO_2^{2+} by O_3.[23] In this case the number of oxygens derived from ozone reaches a limiting value of one in 1.0 M H^+.

Acknowledgment. The use of the Calcomp plotting computer program written by Dr. David L. Toppen is gratefully acknowledged.

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