Studies on the Rhenium(V)–Nitrate Ion Reaction

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Contribution from the Chemistry Department, University of Missouri, Columbia, Missouri. *Received June 17, 1969*

Abstract: The reaction of $[ReCl_4O(OH_2)]^-$ with NO_3^- in 10 *M* HCl solution is rapid and follows the equation $Re(V) + NO_3^- \rightarrow ReO_4^- + NO_2^-$. A further reaction with NO_2^- takes place more slowly according to the equation $5Re(V) + 2NO_2^- \rightarrow 3ReO_4^- + 2[ReCl_5NO]^{2-}$, and the overall equation is $7Re(V) + 2NO_3^- \rightarrow 5ReO_4^- + 2[ReCl_5NO]^{2-}$. Both the Re(V)–$NO_3^-$ and the Re(V)–NO_2^- reactions are described by second-order rate expressions, first order in each reactant. In 10 *M* HCl at 25°, $k = 2.19 \pm 0.13\ M^{-1}\ sec^{-1}$ for the NO_3^- reaction, and $k = 0.644 \pm 0.010\ M^{-1}\ sec^{-1}$ for the NO_2^- reaction. In $[ReCl_5NO]^{2-}$, the metal ion is octahedrally coordinated; the ion is a monomer and has one chloride ion more labile than the other four. Isotopic chloride ion-exchange rate studies gave the overall rate of exchange, $R_1 = 4.79 \pm 0.15 \times 10^{-7}$ and $R_4 = 3.14 \pm 0.05 \times 10^{-9}\ M\ sec^{-1}$ at 50° in 10 *M* HCl solution. A qualitative MO bonding scheme for $[ReCl_5NO]^{2-}$ is suggested.

During some previous studies[3] on the nature of rhenium(V) complexes in solution, it was noted that NO_3^- in acid media rapidly oxidized $[ReCl_4O(OH_2)]^-$ to ReO_4^-. This reaction was utilized as a sensitive analytical method for trace amounts of NO_3^- in water,[4] but neither the product analysis nor the stoichiometry of the primary reaction was studied in detail. Since rapid, low-temperature reductions of NO_3^- are not common, it seemed important to study this reaction in order to find the unique characteristics of the reductant which allow this rapid electron exchange to take place.

Rhenium(V) is not a powerful reductant, being stable for long periods in HCl solution in the presence of air and requiring strong oxidants for conversion to ReO_4^-. In strong HCl solution it appears to exist in the forms of $[ReCl_4O(OH_2)]^-$[5] or $[ReCl_4(OH)_2]^-$[6] and $[ReCl_5O]^{2-}$.[7] Both the water (or OH^-) and Cl^- are very labile, as suggested by isolation of $[ReBr_4O]^-$[5] and by $^{36}Cl^-$ exchange experiments.[6] The lability of the group (OH_2 or Cl^-) *trans* to the multiply bonded oxygen provides a path for N(V) coordination directly to Re(V), following which electron transfer may take place. This, combined with the two-electron compatibility of the reactants (both ReO_4^- and N(III) are often formed products), may explain the rather facile reaction rate.

The system is complicated by the unknown molecular and ionic structure of the various nitrogen species present as reactants and products in 10 *M* HCl. Since the molecular form and charge of the kinetically important oxidant from either NO_3^- or NO_2^- is not known, we will, in this paper, refer to them simply as NO_3^- and NO_2^-, with the understanding that potentially this includes forms such as HNO_3, NO_2^+, NO_2Cl and HNO_2, NO^+, NOCl, $H_2NO_2^+$, and nitrogen oxides present in relatively rapid equilibrium with the added ions.

In the preliminary studies a new negative ion of green color was generated. Upon standing, slight changes in its chemical properties and spectrum occurred, producing $[ReCl_5NO]^{2-}$ which was isolated as the cesium salt. For reasons cited later, the initial green product is thought to be very similar structurally to that isolated. In this paper, both substances will be referred to as $[ReCl_5NO]^{2-}$ with the understanding that the initially formed material differs slightly from this formula.

Thus, this paper describes attempts to understand the oxidation of $[ReCl_4O(OH_2)]^-$ in 10 *M* HCl by N(V) (added as NO_3^-) and N(III) (added as NO_2^-).

Experimental Section

Materials. K_2ReCl_6 was prepared by the reduction of $KReO_4$ with hypophosphorous acid according to the method of Watt and Thompson.[8] The yield was greater than 90% of theoretical and of sufficient purity for further preparations.

$[Re(en)_2O_2]Cl$ was prepared by a reported procedure.[9] It was recrystallized from water–acetone and then from water–methanol and gave analyses as good as or better than previously reported.

$[ReCl_4O(OH_2)]^-$ was prepared in two ways. In method A, solid $[Re(en)_2O_2]Cl$ was added to 10 *M* HCl and the resulting solution heated at just below boiling for about 20 min, after which time the yellow solution had the proper spectrum for the complex ion. The desired concentration was then achieved by dilution in a volumetric flask. The spectrum has absorption maxima at 800 mμ (ε 21.9), 480 (27.0), and 410 (27.0), in agreement with an authentic analyzed sample of the Cs^+ or $(C_6H_5)_4As^+$ salt.[5,6] Solutions heated somewhat longer than 20 min had spectra whose extinction coefficients were slightly different from those given. Analysis of these solutions for ReO_4^-, after separation from the Re(V), showed that 3–5% of the total rhenium was present as ReO_4^-. Prolonged heating presumably facilitates air oxidation of Re(V) to ReO_4^-. The solutions used in reported studies contained less than 1% total rhenium as ReO_4^-.

In method B, a stoichiometric amount of freshly prepared standardized stannous chloride dissolved in concentrated HCl was added to a solution of $NaReO_4$ dissolved in 10 *M* HCl. The resulting solution of Re(V) was adjusted to the desired rhenium and acid concentrations and exhibited a spectrum in agreement with those previously reported.[5,6,10,11]

For the majority of the work reported, rhenium(V) solutions prepared by method A were used. However, the same stoichiometric results are obtained using Re(V) produced by either method.

The reduction of an aqueous solution of $NaNO_2$ by sodium amalgam[12] was used for preparation of sodium hyponitrite ($Na_2N_2O_2$).

Purification of sulfamic acid (HSO_3NH_2, Eastman practical) was accomplished by the method of Sisler, Butler, and Audrieth.[13]

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[1] This work comprises a portion of the Ph.D. Thesis of J. A. Casey, University of Missouri, 1969.

[2] Presented in part at the Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 1967.

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The ^{36}Cl-labeled HCl was obtained from Nuclear Science and Engineering Corp. as a solution containing 356 μCi/ml.

$NaNO_3$ was recrystallized from water before use. Reagent grade $NaNO_2$ was used without further purification as previous experience[4] demonstrated that careful purification did not have a noticeable effect. All other chemicals were reagent grade and used without further purification. Water was distilled and deionized by a double bed column.

Preparation of $Cs_2[ReCl_5NO]$. To a solution of 0.008 M Re(V) in 10 M HCl, made by method A, was added 1.00 ml of freshly prepared $NaNO_2$ solution such that the molar ratio $NO_2^-/Re(V) = 0.5$. The resulting solution was allowed to stand overnight, then heated to about 80° for 30 min. Solid CsCl was then added until a persistent cloudiness indicated that the complex was beginning to precipitate. The solution was heated until it was a clear green and allowed to cool slowly to room temperature. If too large an excess of CsCl is added or if precipitation is not allowed to proceed slowly, contamination by $CsReO_4$ is a serious problem. The resulting dark green crystalline product was collected on a filter, washed several times with absolute methanol, and dried under vacuum.

Anal. Calcd for $Cs_2[ReCl_5NO]$: Cs, 40.32; Re, 28.24; Cl, 26.89; N, 2.12. Found: C, 40.30; Re, 28.58; Cl, 26.84; N, 2.06.

A complex which appears to have the same properties as the above $Cs_2[ReCl_5NO]$ has recently been prepared by an entirely different method in which $ReNOCl_3$ is an intermediate.[14] An aqueous solution of this product gives absorption maxima at 640 mμ (ϵ 34.6), 305 (5890), 250 (1860), and 210 (5130); the infrared spectrum has a sharp peak at 1710 cm^{-1}. These properties are in close agreement with the compound we have prepared by NO_2^- reduction (see Results section).

As will become evident, the complex ion, $[ReCl_5NO]^{2-}$, is also produced by reaction between Re(V) and nitrate ion but in poorer yield.

Attempts to Produce $[ReCl_5NO]^{2-}$ from Other Nitrogen Oxidation States. The complex is not produced, as discerned by spectral measurements, by bubbling NO gas through a solution of Re(V) in 10 M HCl, at either room temperature or at about 50° over a period of 12 hr. Addition of solid $Na_2N_2O_2$ to a solution of Re(V) in 10 M HCl produced no visible reaction other than the formation of N_2O.

Attempted Preparation of ^{36}Cl-Labeled $Cs_2[ReCl_5NO]$. The above procedure for preparation of the complex was used with two modifications. In order to get a larger fraction of the available ^{36}Cl into the complex, a high concentration of Re(V) was used (0.02 M). Also, to avoid addition of chloride ion after formation of the complex and the possibility of unequal labeling, a solution of Cs_2CO_3 was used to precipitate the complex. The resulting green crystalline compound was not the one desired, as shown by a slight variation in its visible spectrum, its decomposition in dilute acid, and its markedly different exchange properties. Analysis for Cl and Re gave a Cl:Re ratio of 4.02 ± 0.06 (average deviation, two determinations).

Physical Measurements. Visible and ultraviolet spectral measurements were made on a Beckman DU spectrophotometer; some preliminary spectral studies were recorded on a Cary Model 12. A Perkin-Elmer Model 237B was used to record infrared spectra using Nujol mulls. X-Ray data were recorded on film using Cu Kα radiation. A Nuclide-RMS-16 mass spectrometer was used for analysis of gas samples. Radioactivity measurements were made on a Technical Associates DS-5B instrument equipped with a 2-in. (100 μg/cm^2) window, flow counter working in the proportional region.

$[ReCl_5NO]^{2-}$–Cl^- Exchange. A 100-ml volumetric flask containing 10 M HCl to which 0.5 ml of stock $H^{36}Cl$ solution had been added was brought to 50.0 ± 0.1° in a constant-temperature bath. To this, 50 mg of finely ground $Cs_2[ReCl_5NO]$ was quickly added. Solution was complete in about 3 min. At appropriate time intervals, approximately 11-ml aliquots were removed and cooled to $\sim$20°. A 10.00-ml sample was pipetted onto excess solid CsCl, cooled to 0°, centrifuged, and decanted. The solid sample was washed with methanol, then quantitatively transferred to a filter as a methanol slurry, again washed with methanol, and sucked to dryness. The resulting mat was uniformly distributed over a well-defined area suitable for counting. Samples were stored over $CaSO_4$. There was no evidence of decomposition under these conditions as shown by spectral measurements on solutions of the solid on the mat.

The exchange data were evaluated by graphing ln (cpm* − cpm$_t$) as a function of time. The slope of this line is the observed rate constant for exchange, k_{obsd}, and was evaluated on the computer using a linear least-squares program. The overall rate, R, was calculated using $R = k_{obsd}ab/(a + b)$, where a is the concentration of the complex times the number of exchangeable ligands per molecule and b is the concentration of the free ligand.

Stoichiometric Studies. Preliminary experiments were conducted in which aqueous solutions of $NaNO_3$ were added to solutions of Re(V) in 10 M HCl to give molar NO_3^-:Re(V) ratios from 0.05 to 1.00. Complex ion concentrations were determined spectrally as described later. In every case, the total rhenium content was accounted for in three forms: ReO_4^-, $[ReCl_5NO]^{2-}$, and excess $[ReCl_4O(OH_2)]^-$. The molar NO_3^-:Re(V) ratio at which all Re(V) was consumed varied from about 0.3 to 0.6, and amounts of $[ReCl_5NO]^{2-}$ and ReO_4^- produced were also variable.

During these studies, the evolution of a gas was often detected. The gases produced from the reaction carried out on degassed solutions were analyzed by mass spectrometry. This showed NO to be the only gaseous product. Since nitrite ion had previously been detected in the Re(V)–NO_3^- reaction,[4] the acid decomposition of NO_2^- seemed a likely source of NO, according to the reaction $3NO_2^- + 2H^+ \rightleftarrows NO_3^- + 2NO + H_2O$.[15] The NO_3^- produced would react with more Re(V) and the NO_3^-:Re(V) ratio at which Re(V) was completely consumed would depend on the amount of NO which escaped. Furthermore, since NO reacts rapidly with O_2 and H_2O ultimately producing NO_2^- and NO_3^-

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + H_2O \rightleftarrows HNO_2 + H^+ + NO_3^-$$

this would also lower the stoichiometric NO_3^-:Re(V) ratio and would contribute to its variability.

The production of nitrite ion in the Re(V)–NO_3^- reaction solutions was reconfirmed. In order to eliminate the Re(V)–NO_2^- reaction which is comparable in rate to the NO_3^- reaction, sulfamic acid was used as a scavenger for NO_2^-. The reaction $HSO_3NH_2 + NO_2^- \rightarrow HSO_4^- + N_2 + H_2O$[16,17] is very rapid under the conditions used. An experimental procedure was designed to reduce the complicating reactions of product NO_2^-, to keep the maximum amount of NO gas in solution, to eliminate its oxidation by molecular oxygen, and to remove NO_2^- as it was formed and prevent its reaction with Re(V). Under these conditions, the only observable rhenium-containing product is ReO_4^-.

The Re(V)–NO_3^- Reaction. In a 50-ml volumetric flask were placed 20.00 ml of 0.01 M Re(V), 8.0 ml of 10.2 M HCl, and 20.00 ml of a freshly prepared solution of 0.20 M HSO_3NH_2 in 10.2 M HCl. The resulting solution was cooled to 0° and N_2 was bubbled through it for 45 min. To this was added 1 ml of aqueous $NaNO_3$ solution, N_2 was passed over the top, and the flask was tightly stoppered. Solutions were carefully mixed and allowed to warm to room temperature. After several hours, they were diluted to volume and absorbance was measured at 800 mμ, an absorbance maximum for $[ReCl_4O(OH_2)]^-$, ϵ 21.9.

The Re(V)–NO_2^- Reaction. Since nitrite ion reacts with rhenium(V) and was found as a product in the reaction between Re(V) and NO_3^-, it was helpful to study the reaction between Re(V) and NO_2^-. The final procedure for determination of the NO_2^-:Re(V) ratio which consumed all of the rhenium(V) was as follows. In a 50-ml volumetric flask were placed 20.00 ml of 0.01 M Re(V) and 28.00 ml of 10.2 M HCl. The solution was cooled to 0° and N_2 was bubbled through it for 45 min. To this was added 1.00 ml of freshly prepared $NaNO_2$ solution, N_2 was passed over the top, and the flask was tightly stoppered. The solutions were mixed and allowed to warm to room temperature. The flask was placed in a 50° bath overnight to convert the initial forms of the Re–NO complex to the final $[ReCl_5NO]^{2-}$ for which ϵ's are known. It was subsequently cooled to room temperature and diluted to volume. Absorbance was measured at 800 mμ, an absorbance maximum for $[ReCl_4O(OH_2)]^-$, and at 645 mμ, an absorbance maximum for $[ReCl_5NO]^{2-}$. Values for concentrations of these two complex ions were then obtained by solution of two simultaneous equations of

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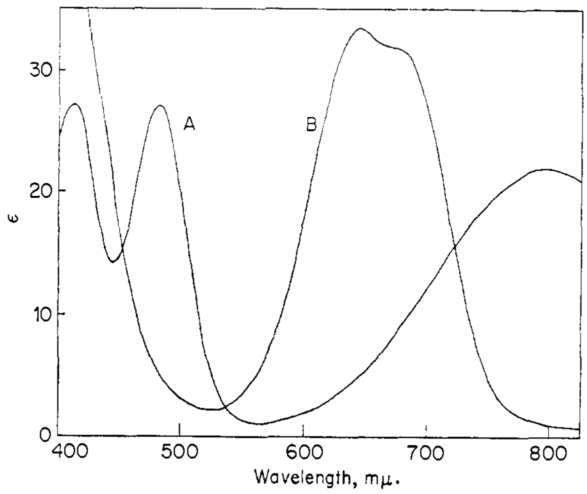

Figure 1. Spectra of (A) $[ReCl_4O(OH)_2]^-$ and (B) $[ReCl_5NO]^{2-}$

the form $A_\lambda = \epsilon_{a\lambda}10c_a + \epsilon_{b\lambda}10c_b$, where A is absorbance at wavelength λ, $\epsilon_{a\lambda}$ is the molar extinction coefficient of species a at λ, 10 is the path length in cm, and c_a is the concentration of a; the second term applies analogously to the other absorbing species, b. For a = $[ReCl_4O(OH_2)]^-$, $\epsilon_{a,645} = 5.02$ and $\epsilon_{a,800} = 21.9$; for b = $[ReCl_5NO]^{2-}$, $\epsilon_{b,645} = 32.9$ and $\epsilon_{b,800} = 0.6$ (see Figure 1 for spectra).

The ReO_4^- was separated by applying an aliquot of the solution to Dowex 1 × 4 anion-exchange resin, which retained the Re(V) and Re–NO complex ions but allowed ReO_4^- to be eluted by 12 column volumes of 10 M HCl. The concentration of ReO_4^- was determined by the α-furildioxime method.[18] It was determined that 3% of the ReO_4^- was retained by the resin in this procedure and a correction was applied to the results. An independent experiment showed that the ethylenediamine present in these solutions does not interfere with the ReO_4^- analysis.

The Composite Reaction. To confirm its stepwise nature, the reaction between Re(V) and NO_3^- was studied with no nitrite ion scavenger present. The procedure was the same as that given for the Re(V)–NO_2^- reaction with replacement of $NaNO_2$ solutions by solutions of $NaNO_3$. The products again were ReO_4^- and $[ReCl_5NO]^{2-}$, so these two ions were determined along with $[ReCl_4O(OH_2)]^-$.

Kinetics of the Re(V)–NO_2^- Reaction. The desired volume of Re(V) stock solution and 10.2 M HCl were placed in a 10-cm cell. A stream of N_2 was bubbled through the solution for about an hour: 1.00 ml of appropriate concentration of freshly prepared $NaNO_2$ solution was added, the cell capped, and solution mixed. Absorbance at 800 mμ, a maximum for $[ReCl_4O(OH_2)]^-$, was measured as a function of time.

Kinetics of the Re(V)–NO_3^- Reaction. The desired volume of Re(V) stock solution and 10.2 M HCl were placed in a 2-cm cell, 0.1 ml of appropriate concentration of aqueous $NaNO_3$ was injected, and the cell was capped and shaken vigorously. Absorbance at 800 mμ, a maximum for $[ReCl_4O(OH_2)]^-$, was followed as a function of time.

Results

Characterization of Products. The products of the reactions between rhenium(V) in 10 M HCl and either NO_3^- or NO_2^- were found to be ReO_4^-, $[ReCl_5NO]^{2-}$, and small varying amounts of NO gas. The ReO_4^- was separated by ion exchange techniques and detected by colorimetric methods; the NO gas was detected by mass spectral analysis of samples of gas collected from above degassed solutions mixed under vacuum. No N_2, N_2O, NO_2, or Cl_2 could be found.

The visible–ultraviolet spectrum of $[ReCl_5NO]^{2-}$ shows the following absorption maxima in 10 M HCl: 680 mμ (ε 31.7), 645 (33.5), 307 (5960), and 246 (sh).

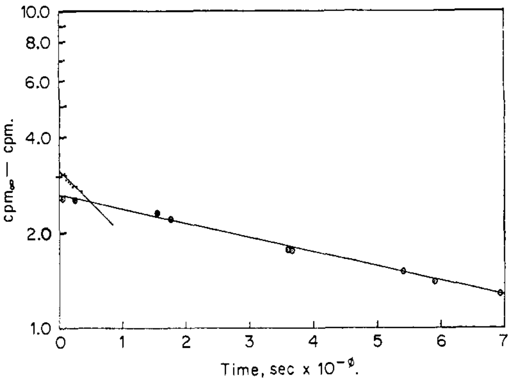

Figure 2. Chloride ion exchange of $[ReCl_5NO]^{2-}$. Scale factor: $\phi = 3$ for •; $\phi = 5$ for ⊙.

The infrared spectrum in the range 625–4000 cm^{-1} shows only one sharp absorption peak at 1720 cm^{-1} which is attributed to the NO stretch.

Both single crystal and powder X-ray data were obtained for $Cs_2[ReCl_5NO]$. The systematic extinctions in both cases showed no deviations from a cubic lattice belonging to the space group O_h^5-Fm3m. This is the potassium hexachloroplatinum(IV) structure having four molecules per unit cell, and confirms the fact that the negative ion is mononuclear. The inability to distinguish any difference in intensities for symmetry equivalent spots suggests that the –NO group is randomly oriented. For comparison, a single crystal of Cs_2ReCl_6 was mounted and photographed. The extinctions and relative intensities were identical within experimental error, but the cell constant was slightly different. A powder pattern was taken of $Cs_2[ReCl_5NO]$ and $Cs_2[ReCl_6]$ to determine the cell constants more accurately: $a = 10.285 \pm 0.005$ Å, $Cs_2[ReCl_5NO]$; $a = 10.260 \pm 0.005$ Å, $Cs_2[ReCl_6]$ (lit.[19] $a = 10.260 \pm 0.005$ Å). The density of $Cs_2[ReCl_5NO]$, determined experimentally, is 4.00 g/cm³; calcd from X-ray data, 4.024 g/cm³.

The $[ReCl_5NO]^{2-}$ complex ion was further characterized by ^{36}Cl exchange studies, $ReCl_5NO^{2-} + Cl^{*-} \rightarrow ReCl^*{}_5NO^{2-} + Cl^-$. Graphs of ln ($cpm_\infty - cpm_t$) of solid $Cs_2[ReCl_5NO]$ *vs.* time gave a curve which was easily separated into two straight lines corresponding to a faster exchange of one chloride followed by slower exchange of the other four. Extrapolation of values at long times gave an intercept of 262.0 ± 3.8; calcd for $4Cl^-$ exchanging, 263.25 cpm (see Figure 2). The overall rate of exchange for the *trans* chloride is $R_{tr} = 4.79 \pm 0.15 \times 10^{-7}$ M sec^{-1}, and the overall rate for the four equatorial chlorides is $R_{eq} = 3.14 \pm 0.05 \times 10^{-9}$ M sec^{-1} at 50°, with $[ReCl_5NO^{2-}] = 7.58 \times 10^{-4}$ M in 10 M HCl. The temperature dependence of the exchange was studied, and the data are presented in Table I. The activation energy for exchange of the *trans* chloride was found to be $E_a = 24.1 \pm 3.8$ kcal/mole, and for the equatorial chlorides, $E_a = 25.7 \pm 1.6$ kcal/mole. They are the same within experimental error.

The analytical data, infrared spectrum, X-ray analysis, and chloride exchange data confirm the identity of the new compound as $Cs_2[ReCl_5NO]$ with octahedrally coordinated Re in the +3 oxidation state assuming a formal charge of 0 for NO.

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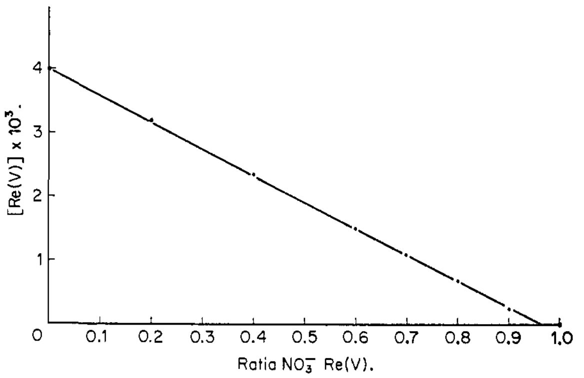

Figure 3. Stoichiometry of the $Re(V)-NO_3^-$ reaction in the presence of sulfamic acid.

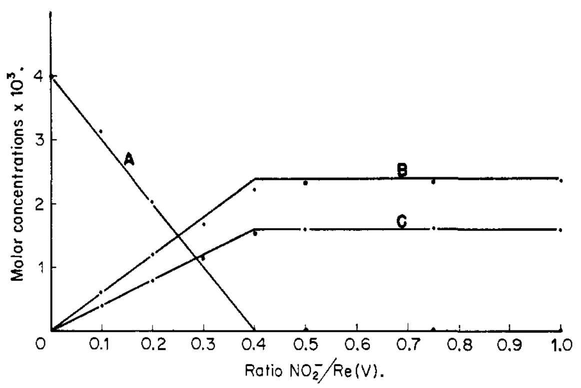

Figure 4. Stoichiometry of the $Re(V)-NO_2^-$ reaction: (A $[ReCl_4O(OH_2)]^-$, (B) (ReO_4), (C) $(ReCl_5NO)^{2-}$.

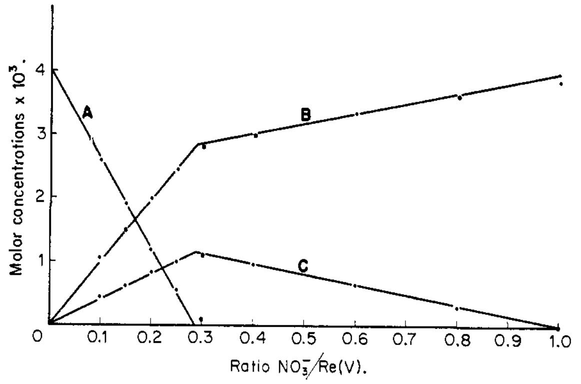

Figure 5. Stoichiometry of the $Re(V)-NO_3^-$ reaction: (A) $[ReCl_4O(OH_2)]^-$, (B) (ReO_4), (C) $([ReCl_5NO)]^{2-}$.

Stoichiometric Studies. Results of the study of the $Re(V)-NO_3^-$ reaction in the presence of high sulfamic acid concentration are presented in Figure 3. A 1:1 reaction is clearly indicated: $Re(V) + NO_3^- \rightarrow Re(VII) + NO_2^-$. The fact that the intercept comes at about 0.97 instead of 1.00 can probably be attributed to some inefficiency of the scavenger, since smaller concentrations of HSO_3NH_2 were shown to give lower stoichiometric ratios (0.64–0.92) and then some $[ReCl_5NO]^{2-}$ was detected.

Table I. Temperature Dependence of the $[ReCl_5NO]^{2-}-Cl^-$ Exchange[a]

Temp, °C	R, M sec^{-1} [b]
	trans-Chloride
40	$1.00 \pm 0.15 \times 10^{-7}$
50	$4.79 \pm 0.15 \times 10^{-7}$
60	$10.62 \pm 0.44 \times 10^{-7}$
	Equatorial Chlorides
40	$0.747 \pm 0.087 \times 10^{-9}$
50	$3.14 \pm 0.05 \times 10^{-9}$
60	$9.31 \pm 0.61 \times 10^{-9}$

[a] 7.584×10^{-4} M $[ReCl_5NO]^{2-}$, 10 M HCl. [b] Errors represent one standard deviation.

The results of the reaction between Re(V) and NO_2^- are shown in Figure 4. The break in the graph at $NO_2^-:Re(V) = 0.4$ suggests the following stoichiometry: $5Re(V) + 2NO_2^- \rightarrow 3ReO_4^- + 2[ReCl_5NO]^{2-}$. The points on the graph are experimental and the lines have been drawn for the above equation.

To confirm its stepwise nature, the reaction between Re(V) and NO_3^- was studied in the absence of nitrite ion scavenger. These results are presented in Figure 5. The break in the lines at $NO_3^-:Re(V) = 0.29$ indicates the stoichiometric ratio of $NO_3^-:Re(V) = 2:7$ and suggests the overall reaction $7Re(V) + 2NO_3^- \rightarrow 5ReO_4^- + 2[ReCl_5NO]^{2-}$. The fact that the amounts of products do not remain constant once the stoichiometric amount of NO_3^- has been added is easily understood if the overall reaction is written as a composite of its stepwise parts (eq 1). The reaction ratio of NO_3^-:

$$\begin{aligned}
&2[ReCl_4O(OH_2)]^- + 2NO_3^- \xrightarrow{\text{fast}} 2ReO_4^- + 2NO_2^- \\
&5[ReCl_4O(OH_2)]^- + 2NO_2^- \xrightarrow{\text{slower}} \\
&\qquad\qquad 3ReO_4^- + 2[ReCl_5NO]^{2-} \\
\hline
&2H_2O + 7[ReCl_4O(OH_2)]^- + 2NO_3^- \longrightarrow \\
&\qquad 5ReO_4^- + 2[ReCl_5NO]^{2-} + 8Cl^- + 8H^+ \quad (1)
\end{aligned}$$

Re(V) = 2:7 will be observed up to the point at which the stoichiometric amount of NO_3^- has been added. When additional NO_3^- is present, however, and if the first reaction is fast compared to the second, NO_3^- will consume Re(V) quickly in a 1:1 ratio, leaving only excess Re(V) for the slower nitrite ion reaction. Thus, as a limiting case, at a ratio of $NO_3^-:Re(V) = 1.0$, all of the Re(V) will react with NO_3^-, producing ReO_4^-, and leave no Re(V) for the NO_2^- reaction. Then no $[ReCl_5NO]^{2-}$ is produced. That this conforms to the facts is indicated in Figure 5. The lines in the figure are theoretical for the above-described reactions and the points are experimental.

Kinetics of the $Re(V)-NO_2^-$ Reaction. Preliminary studies indicated a first-order dependence on each reactant. Table II contains a summary of kinetic data for reaction between Re(V) and NO_2^-. The tabulated second-order rate constant, k, is defined by the rate law $-d[Re(V)]/dt = k[Re(V)][NO_2^-]$. The integrated equation

$$\frac{1}{[NO_2^-]_0 - 0.4[Re(V)]_0} \ln \frac{[Re(V)]_0[NO_2^-]_t}{[Re(V)]_t[NO_2^-]_0} = kt$$

can be converted to usable form by substitution of absorbance values for concentration, giving, when excess Re(V) is present

$$\ln \frac{a}{2.5b + (a - 2.5b)(A_0 - A_\infty)/(A - A_\infty)} = (b - 0.4a)kt$$

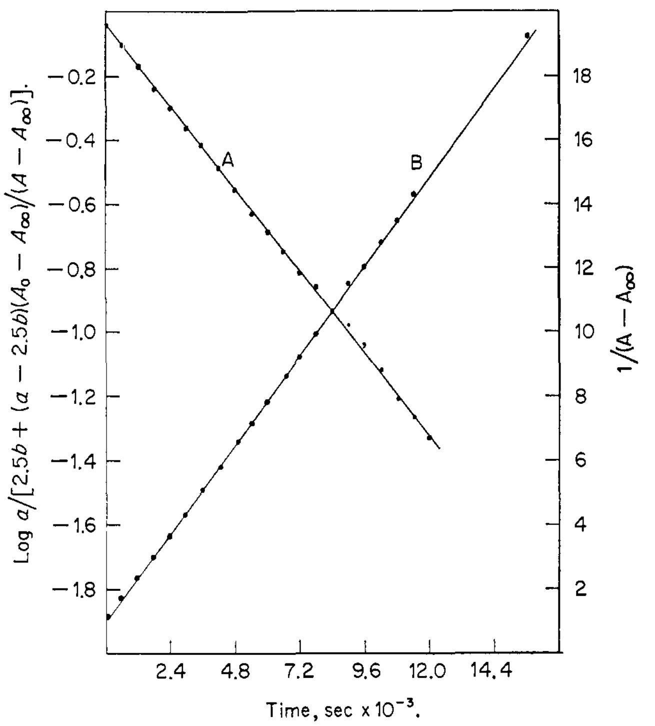

Figure 6. Kinetics of the Re(V)–NO_2^- reaction, representative graphs. (A) Left axis, excess Re(V): 0.00254 M Re(V), 0.000642 M NO_2^-. (B) Right axis, stoichiometric concentrations: 0.00646 M Re(V), 0.00258 M NO_3^-, 10 M HCl, 25°.

or when excess NO_2^- is present

$$\ln \frac{0.4a + (b - 0.4a)(A_0 - A_\infty)/(A - A_\infty)}{b} = (b - 0.4a)kt$$

and for stoichiometric amounts

$$\frac{1}{(A - A_\infty)} - \frac{1}{(A_0 - A_\infty)} = \frac{10\epsilon ab}{(A_0 - A_\infty)}2kt$$

In the above equations, a represents the initial Re(V) concentration and b is initial NO_2^- concentration; A, A_0, and A_∞ are absorbance values at time t, time zero, and infinite time, respectively; and the numerical values of 2.5 and 0.4 reflect the stoichiometry. In the last equation, 10 is the cell path length and $\epsilon = 21.9$, the extinction coefficient of Re(V) at 800 mμ. Absorbance, as a function of time, data were analyzed according to a linear least-squares program on the IBM 7040 computer. Figure 6 shows representative graphs from which values of k were obtained. A value of $k = 0.644 \pm 0.010$ M^{-1} sec^{-1} at 25° is defined for conditions of stoichiometric concentrations or an excess of Re(V). The indicated error is the standard deviation of the mean; its rather large value may be partially due to decomposition of nitrite ion in the highly acid solutions.

Attempts to carry out runs in which an excess of NO_2^- was present resulted in nonlinear second-order graphs. The initial rate approximated that predicted by the second-order rate law, but the reaction rate was slower than anticipated at longer times. A larger excess of NO_2^- produced a greater deviation. This effect will be discussed later.

Table II. Kinetics of the Re(V)–NO_2^- Reaction[a]

Run	[Re(V)]	[NO_2^-]	k, M^{-1} sec^{-1} [b]
1	0.006463	0.002585	0.6180 ± 0.0003
2	0.006463	0.002585	0.6305 ± 0.0003
3	0.004000	0.001600	0.5948 ± 0.0017
4	0.004000	0.001600	0.6468 ± 0.0015
5	0.003210	0.000642	0.6200 ± 0.0008
6	0.002859	0.000642	0.6543 ± 0.0010
7	0.002541	0.000642	0.6523 ± 0.0010
8	0.002541[c]	0.000642	0.6512 ± 0.0007
9	0.002220	0.000642	0.6680 ± 0.0005
10	0.001906	0.000642	0.7037 ± 0.0003

[a] Conditions: 10.0 M HCl and 25°. Runs 1–4 represent stoichiometric concentrations of reactants; runs 5–10 have an excess of Re(V). [b] k is defined by the rate law $-d[\mathrm{Re(V)}]/dt = k[\mathrm{Re(V)}] \cdot [NO_2^-]$. Errors listed are one standard deviation. [c] 0.00473 M ethylenediamine in addition to what is normally present, which is 2[Re(V)].

The effect of adding large amounts of ReO_4^- to the Re(V) solution before reaction was initiated by addition of NO_2^- was investigated. The ReO_4^- had a retarding effect which was greater at longer times. This is significant since ReO_4^- is produced in the reaction between Re(V) and NO_2^-. However, the amount of ReO_4^- present at the end of a run in which the effect was detected was greater, by a factor of 2.67, than that present at completion of a similar run with no excess ReO_4^-. Thus the amount of ReO_4^- produced during the reaction will probably not have a great effect but may well be the cause of a slight curvature, noted at long times, where reaction is greater than 90% complete, resulting again in a large excess of ReO_4^- over Re(V). This effect of ReO_4^- is probably another factor contributing to the large deviation in the final value for k. The data presented in Table II (runs 7 and 8) show that there is no major effect of enH_2^{2+}, which is always present in the system due to the method of preparation of Re(V) solutions.

Kinetics of the Re(V)–NO_3^- Reaction. Although preliminary investigations showed the reaction between Re(V) and NO_3^- to be quite fast, it seemed desirable to try to obtain kinetic data to define the rate expression and rate constant. Initial attempts to treat the data suggested a second-order reaction, first order in Re(V) and in NO_3^-, and also suggested competition by the subsequent reaction between Re(V) and NO_2^- at relatively short times.

$$\mathrm{Re(V)} + NO_3^- \xrightarrow{k_1} ReO_4^- + NO_2^-$$

$$2.5\mathrm{Re(V)} + NO_2^- \xrightarrow{k_2} 1.5ReO_4^- + [ReCl_5NO]^{2-}$$

The data were therefore treated following the method of Widequist[20] for competitive, consecutive second-order reactions, with appropriate modifications for stoichiometry. The final equation used to evaluate k_1 was

$$k_1 = \frac{z}{3.5bv - A - (2.5b/k_2)(1 - e^{-k_2 v})}$$

where $z = [\mathrm{Re(V)}]_0 - [\mathrm{Re(V)}]_t$, $b = [NO_3^-]_0$, $v = \int_0^t [\mathrm{Re(V)}]dt$, and $A = \int_0^v z\,dv$; v and A are evaluated by graphical integration. The results of this study are presented in Table III. A value of $k_1 = 2.19 \pm 0.13$ M^{-1} sec^{-1} is defined. The indicated error is the stan-

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(20) S. Widequist, *Acta Chem. Scand.*, **4**, 1216 (1950).

Table III. Kinetics of the Re(V)–NO_3^- Reaction[a]

Re(V)	NO_3^-	k_1, M^{-1} sec^{-1} [b]
0.0200	0.0200	2.06 ± 0.16
0.0200	0.0240	1.83 ± 0.04
0.0200	0.0280	1.59 ± 0.02
0.0200	0.0320	1.69 ± 0.01
0.0200	0.0360	2.61 ± 0.09
0.0200	0.0400	1.89 ± 0.05
0.0175	0.0200	2.51 ± 0.09
0.0150	0.0200	2.54 ± 0.04
0.0125	0.0200	2.54 ± 0.04
0.0100	0.0200	2.69 ± 0.04

[a] 10.0 *M* HCl, 25°C. [b] k_1 is defined by the rate law $-d[Re(V)]/dt = k_1[Re(V)][NO_3^-]$. Errors listed are the average deviation from the mean of 12–20 experimental points.

dard deviation of the mean. Its rather large value is attributable mainly to reactions of the product, NO_2^-. Preliminary experiments did not indicate the importance of these reactions, and so precautions were not taken to exclude oxygen. Also, as described above, the value of k_2 is not constant when NO_2^- is in excess as it is in this system when the Re(V)–NO_2^- reaction is important. In spite of the difficulties, there is little doubt that the rate law is $-d[Re(V)]/dt = k_1[Re(V)][NO_3^-]$.

Discussion

Kinetics of the Re(V)–NO_2^- Reaction. The overall stoichiometry of the reaction, the second-order rate expression, and the deviations from the rate law in the presence of an excess of either ReO_4^- or NO_2^- lead to postulation of the mechanism shown in eq 2. On the

$$
\begin{aligned}
&2([ReCl_4O(OH_2)]^- + NO^+ \xrightleftharpoons[k_{-1}]{k_1} [ReCl_4O(NO)] + H_2O)\\
&2([ReCl_4O(NO)] \xrightleftharpoons[k_{-2}]{k_2} Re(VII) + HNO)\\
&2([ReCl_4O(OH_2)]^- + HNO \xrightarrow{\text{fast}} [ReCl_4O(NO)]^{2-} + H_2O + H^+) \qquad (2)\\
&2[ReCl_4O(NO)]^{2-} + [ReCl_4O(OH_2)]^- \xrightarrow{\text{fast}} 2[Re(III)\text{–}NO] + Re(VII)\\
\hline
&5[ReCl_4O(OH_2)]^- + 2NO^+ \longrightarrow 3Re(VII) + 2[Re(III)\text{–}NO]
\end{aligned}
$$

basis of known chemistry of the $[ReCl_4O(OH_2)]^-$ complex ion, an initial equilibrium reaction is postulated in which the NO^+ ion occupies the position *trans* to coordinated oxygen. Formation of the rhenium(V), $[ReCl_4O(NO)]$, complex is thought to be followed by a second reversible step involving two-electron transfer from rhenium(V) to NO^+ resulting in formation of Re(VII) and HNO. (The data are also consistent with a one-electron transfer followed by another fast one-electron transfer.) The very reactive HNO must be quickly consumed by a third step, most likely reaction with rhenium(V). Subsequent steps must be fast and result in the observed stoichiometry; no further information is available about them, so formulation is only speculative. The observed second-order rate law would be accommodated by either of two possibilities for the relative magnitudes of rate constants controlling the first two steps. Either the electron transfer can be rate controlling and be preceded by a rapid equilibrium, or the association of N(III) can be rate controlling and be followed by a rapid electron transfer. The lack of discrimination of Re(V) toward the group occupying the *trans*-O position and the probability of considerable rearrangement required before electron transfer make it seem more likely that the electron transfer is the rate-determining step.

The deviations from linearity in second-order graphs, observed when a large excess of perrhenate ion is present in the system, can be explained in terms of the fate of the reactive intermediate HNO. If the HNO did not react quickly with some other species, it would dimerize with formation of N_2O; this was not observed. It is likely that there is a competition for HNO between $[(ReCl_4O(OH_2)]^-$ and Re(VII). The reaction of HNO with Re(V) is usually dominant; however, the presence of an excess of ReO_4^- makes Re(VII) much more competitive. The result of this would be slower overall removal of Re(V) as observed. Addition of excess nitrite ion to the reaction solution would cause an initial faster reaction, as predicted by the rate law. However, under these conditions, the Re(V) source would become depleted so that again competition by Re(VII) for the HNO would become effective. The observed decrease in rate would result.

Thus, the proposed reaction scheme is in agreement with the stoichiometry, the rate expression, and the deviations from the rate expression under specified conditions.

Kinetics of the Re(V)–NO_3^- Reaction. The stoichiometry of the reaction and the second-order rate expression must be accommodated by a mechanism proposed for the Re(V)–NO_3^- reaction. With the knowledge that in the $[ReCl_4O(OH_2)]^-$ complex ion the position *trans* to the multiply bonded oxygen atom can be occupied by a very labile water molecule or chloride ion, it is not unreasonable to propose, as a first step, an equilibrium in which NO_2^+ occupies that position. Following association of NO_2^+, a two-electron transfer from Re(V) to N(V) could occur, causing reaction to go to completion and resulting in Re(VII) and N(III). (In this case also, the data are consistent with a one-electron transfer followed by another fast one-electron transfer.) The general mechanism can be written as follows.

$$
\begin{gathered}
[ReCl_4O(OH_2)]^- + NO_2^+ \xrightarrow[k_{-1}]{k_1} [ReCl_4O(ONO)] + H_2O\\
[ReCl_4O(ONO)] \xrightarrow{k_2} [Re(VII)\text{–}N(III)]\\
[Re(VII)\text{–}N(III)] \longrightarrow ReO_4^- + NO_2^-
\end{gathered}
$$

In order for the reaction to show the observed rate equation, two limiting possibilities arise for the relationship between k_1, k_{-1}, and k_2. The first is that the initial equilibrium for association of NO_2^+ is very rapid and electron transfer is the rate-controlling step, or $k_{-1} > k_1 > k_2$. With these conditions, the steady-state approximation can be applied, $d[Re(V)\text{–}ONO^+]/dt = 0$, and the rate equation thus derived has the form

$$-d[Re(V)]/dt = [k_1k_2/(k_{-1} + k_2)][Re(V)][NO_3^-]$$

Thus, the observed rate constant would be equal to the term $k_1 k_2/(k_{-1} + k_2)$. The other possibility is that the initial association of NO_2^+ is rate determining and this is followed by rapid electron transfer, or $k_2 > k_{-1} > k_1$. Again the steady-state approximation can be applied, resulting in the rate equation just described. A limiting

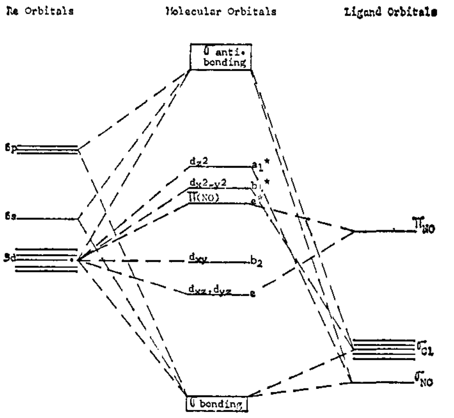

Figure 7. Molecular orbital diagram for $[ReCl_5NO]^{2-}$.

case would be if $k_2 \gg k_{-1}$ (or $k_{-1} = 0$), and this would result in the simplified expression $-d[Re(V)]/dt = k_1 \cdot [Re(V)][NO_3^-]$, where the measured rate constant would be k_1.

It is not possible from the experiments conducted to choose unequivocally between the two modes of reaction. However, the ease and lack of discrimination with which groups are accepted into the *trans*-O position of the rhenium(V) ion suggest that this is probably not the slow step. In addition, it is likely that a considerable amount of rearrangement must occur prior to the electron transfer, thus causing electron transfer to be the slow step. The fact that the rate constants for the NO_2^+ and NO^+ reactions with rhenium(V) differ by only about a factor of 3 suggests that the same type of rate-controlling step is operative.

Thus, the mechanism may be described as a rapid equilibrium involving association of NO_3^- with the rhenium(V), followed by a rate-determining electron transfer. The resultant rhenium(VII) then must undergo successive substitutions of oxide ion for chloride ion to arrive at the ReO_4^- product.

Molecular Orbital Description. On the basis of data presented here and previous calculations for other nitrosyl complexes,[21–24] a reasonable molecular orbital description of the $ReCl_5NO^{2-}$ complex ion can be derived. With the knowledge of the extreme stability of the Re–NO bond (heating a solution of complex in 10 *M* HCl for 1 week at 90° causes no measureable decomposition), and the differing rates of exchange of the two types of chloride, the picture of bonding is dominated by a strong Re–NO interaction, any π bonding to chlorides is ignored, and bonding to the fifth (*trans*) chloride is weak. The resulting molecular orbital diagram is presented in Figure 7. The 17 electrons are placed in the molecular orbitals giving a $e^4b_2^1$ ground state, in agreement with magnetic susceptibility measurements[14] which indicate one unpaired electron (1.47 BM).

The spectrum of $ReCl_5NO^{2-}$ is accounted for as follows. Bands at 14,700 cm^{-1} (31.7) and 15,500 cm^{-1} (33.5) are assigned to the split transition $(e^4b_2^1) \rightarrow (e^3b_2^2)$, absorption at 32,600 cm^{-1} (5960) is attributed to the transition $(e^4b_2^1) \rightarrow (e^4e^{*1})$, and the band at 47,600 cm^{-1} (5130)[12] is assigned to $(e^4b_2^1) \rightarrow (e^3b_2^1e^{*1})$. Both of the latter transitions are to a level which is essentially localized on the NO; they may therefore be termed charge-transfer bands, thus accounting for their rather high extinctions. We may further note that the difference in energies of these two bands (15,000 cm^{-1}) should be approximately the energy of transition between the e^b and b_2 levels; and this is, in fact, the case (14,700 and 15,500 cm^{-1}). Finally, the weaker shoulder at 40,600 cm^{-1} is assigned to the transition $(e^4b_2^1) \rightarrow (e^4b_1^*)$.

Since one can picture the $ReCl_5NO^{2-}$ complex ion as being formed from $ReCl_6^{2-}$ by replacement of a Cl by an NO group, it is interesting to compare the rates of chloride ion exchange of the two complexes. Putting observed rates on the basis of rate of exchange of one chloride ion of each type, for $ReCl_5NO^{2-}$, $R_{trans} = 5 \times 10^{-7}$ *M* sec^{-1}, $R_{\text{equatorial}} = 8 \times 10^{-10}$ *M* sec^{-1}, and for $ReCl_6^{2-}$[25] corrected to the same conditions, $R = 1.4 \times 10^{-10}$ *M* sec^{-1}. As expected, the chloride *trans* to the NO group is much more labile than those in the hexachloro complex, while the equatorial chlorides exchange at a rate of the same order of magnitude as the $ReCl_6^{2-}$ chloride exchange, indicating a comparatively small effect of the NO group on these ligands. The somewhat faster rate may be attributed to the lower effective oxidation state of Re in the nitrosyl complex, causing increased repulsion of the chlorides.

Acknowledgment. We wish to thank Dr. E. O. Schlemper for assistance with the X-ray work. J. C. is grateful for financial aid of an NDEA Graduate Fellowship. The support of the National Science Foundation. Grant No. GP-2664 is also gratefully acknowledged.

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