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Reactions of some transition metal complexes

Thomas Rodney Webb
Iowa State University

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Reactions of some transition metal complexes

by

Thomas Rodney Webb

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TABLE OF CONTENTS

PART I. THE REACTION OF DICHLORO-μ-TETRAPROPIONATODIRHENIUM(III) WITH BROMIDE ION

INTRODUCTION

Ligand substitution has been described as "the most pervasive reaction of metal ions in solution."[1] Substitution reactions of many metal complexes have been studied, and for some families of complexes impressive bodies of rate data, stereochemical results, solvent effects, and activation parameters have accumulated, from which inferences about the detailed mechanisms of ligand replacement have been drawn. Three basic mechanisms of ligand substitution have been described; these are the interchange mechanism and its two limiting forms, the associative and dissociative mechanisms.[2,3] The interchange mechanism (I) is sketched in its simplest form in reaction I, in which X and Y are the leaving and entering

$$MX + Y^- \rightleftarrows [M \genfrac{}{}{0pt}{}{X^-}{Y}]^\ddagger \rightleftarrows MY + X^- \qquad \text{(I)}$$

ligands and M denotes the metal center and the inner ligands. Ligand replacement is concerted; there is no discrete intermediate of increased or decreased coordination number in a reaction which occurs by an I mechanism. However, varying degrees of M-X bond breaking and M-Y bond making are allowed within the general scheme. If bond making is important in reaching the transition state, the reaction is called associative interchange (I_a or S_N2), whereas if bond breaking is important, the label dissociative interchange (I_d or S_N1) is applied. The two limiting cases occur when the M-Y bond is formed before the M-X bond has appreciably broken, with the resultant formation of an intermediate of increased coordination number relative to the reactant and product complexes, as in reactions II and III, or when the M-X bond has broken before the M-Y bond begins to form,

$$MX + Y^- \underset{2}{\overset{1}{\rightleftarrows}} MXY^- \qquad (II)$$

$$MXY^- \underset{4}{\overset{3}{\rightleftarrows}} MY + X^- \qquad (III)$$

giving an intermediate of reduced coordination number, as in reactions IV and V. These two mechanisms are the associative (A or S_N2(lim.)) and dissociative (D or S_N1(lim.)) mechanisms, respectively. If kinetic experiments are carried out at

$$MX \underset{2}{\overset{1}{\rightleftarrows}} M^+ + X^- \qquad (IV)$$

$$M^+ + Y^- \underset{4}{\overset{3}{\rightleftarrows}} MY \qquad (V)$$

sufficiently high concentrations of X^- and Y^- so that their concentrations are essentially constant, eq 1 is the valid integrated rate law for all three mechanisms.[4]

$$\ln \frac{[MX]_o - [MX]_\infty}{[MX]_t - [MX]_\infty} = k_{obs}t \qquad (1)$$

In this equation the subscripts o, t and ∞ refer to values at the initial time, at any time t, and at completion of reaction, respectively. k_{obs} is the pseudo-first-order rate constant for the approach to equilibrium and is equal to the sum of the forward and reverse rate constants.[4] For the interchange mechanism, this gives eq 2; for the associative mechanism, eq 3, if MXY^- is presumed to be a steady-state intermediate;

$$k_{obs} = k_1[Y^-] + k_2[X^-] \tag{2}$$

$$k_{obs} = \frac{k_1k_3[Y^-] + k_2k_4[X^-]}{k_3 + k_2} \tag{3}$$

and for the dissociative mechanism, eq 4, if M^+ is a steady-state intermediate.

$$k_{obs} = \frac{k_1k_3[Y^-] + k_2k_4[X^-]}{k_3[Y^-] + k_2[X^-]} \tag{4}$$

It is of some interest to note that the concentration dependences of eqs 2 and 3 are identical. This means that the I and A mechanisms cannot be distinguished from the rate data, although the chemistry that occurs is rather different. These mechanisms are usually differentiated on the basis of extrakinetic evidence. In particular, an increase in associative character should be marked by a more negative entropy of activation,[5] a more negative volume of activation,[6] and a larger variation in rates among a series of entering groups.[1,7]

In terms of real chemistry, each of these mechanisms describes substitutions observed for some transition metal complex. However, there are certain patterns within the area. To summarize all of the data in a short space inevitably oversimplifies the conclusions and neglects the exceptions. However, the following conclusions would appear to be generally valid. Square planar complexes react by associative mechanisms, as would be expected for such open systems.[8] Good confirmation comes from the strong entering group dependence and the large negative entropies of activation commonly observed. For octahedral complexes, bond breaking is more important than bond making. The I_d mechanism is most commonly found, as evidenced by rate expressions of the form of eq 2 coupled with small entering group effects. This mechanism explains the substitution data for most divalent and trivalent cations of the first series rather well.[9,10] There are some interesting exceptions, however. On the one hand, Baker, Sutin, and Welch[11] have argued that the reaction of the hydrated vanadium(III) ion with thiocyanate ion proceeds by an associative mechanism on the basis of a large negative entropy of activation. The large difference in rate for the corresponding reaction with hydrazoic acid[12] has been interpreted as agreeing with this conclusion. The rates of substitution on chromium(III) complexes are limited by the rate of loss of the leaving group, a feature very typical of an I_d or D mechanism. However, the rate constants for the reaction of the hydrated chromium(III) ion with several common monoanions vary by almost three orders of magnitude,[13] which would suggest that the entering ligand does exert some influence on the rate. For the corresponding reactions of aquopentaamminecobalt(III), for which the I_d mechanism appears certain, the spread is less than a factor of two.[14] Studies of the activation volumes for substitutions on chromium(III) indicate appreciable associative character; Carey, Jones and Swaddle[15] have postulated an I_a mechanism. On the other hand, the rate law for the anation of aquopentacyanocobaltate(III) has the form of eq 4, providing evidence for a D mechanism for these reactions.[16]

Some studies of reactions in non-aqueous solvents have been reported.[17-20] For the most part, the reactions are quite similar to those found in aqueous solution, although ion-pair formation is more important and solvolysis is often not noted. Thus in aqueous solution reaction VI proceeds through the aquo complex[21] whereas in methanol similar reactions proceed

$$Co(NH_3)_5Cl^{2+} + NCS^- = Co(NH_3)_5NCS^{2+} + Cl^- \qquad (VI)$$

directly through an ion pair.[22]

Substitution reactions of the second- and third-series elements have been less studied. Although there are extensive data for many complexes of the platinum metals, the same cannot be said about elements such as niobium, for which little or no data are available outside of organometallic systems. Part of this results from the fact that many of these complexes are rather difficult to handle, being air- and moisture-sensitive.[23]

Rhenium(III) compounds have been known for many years, but their chemistry has only recently been clarified. Sidgwick[24] noted the trichloride and tribromide and some complexes M^IReX_4. Kotel'nikov and Tronev[25,26] reported the preparation of several salts of "ReX_4^{2-}" by hydrogen reduction of perrhenate in the hydrohalic acid at 200° under 50 atm. These complexes and some derivatives, including some complexes of carboxylic acids, were not characterized structurally. Taha and Wilkinson[27] prepared some carboxylato complexes from $ReCl_3$. The orange solids, of stoichiometry $ReCl(RCO_2)_2$, were presumed to be dimeric because of the similarity of the infrared spectra to the spectra of complexes such as chromous acetate, which do have bridging carboxylates.

The basic structural relationships of Re(III) compounds were elucidated in 1964 and 1965. The trihalides were shown to be trimeric units Re_3Cl_9 with triangular Re_3 units held together by strong metal-metal bonding.[28,29] Cotton and his coworkers[30] demonstrated that the reported[25,26] rhenium(II) complexes were actually dimeric rhenium(III) complexes, $Re_2X_8^{2-}$ and its derivatives. The nature of the dirhenium complexes was established by the ready conversion to the carboxylato complexes of Taha and Wilkinson,[27] by the absence of other atoms, especially hydrogen, and by the x-ray diffraction investigation[31] of $K_2Re_2Cl_8 \cdot 2H_2O$. The rhenium complex was shown to consist of two $ReCl_4$ units in eclipsed conformation with the metal atoms displaced toward one another. These results, coupled with the short Re-Re distance (2.22 A), have been interpreted in terms of a quadruple metal-metal bond.[32]

The dinuclear rhenium(III) complexes have an extensive chemistry, much of it fairly tractable. The octachloro complex reacts with bromide ion[33] or thiocyanate ion[34] in methanol solution to give the corresponding octa-substitution product, with phosphines to give the hexachlorobisphosphine derivatives,[33] with thiourea to give monomeric rhenium(III) complexes (although some substituted thioureas give products analogous to the phosphine products),[35] and with dithiahexane to give rhenium(III) complexes,[35] presumably also dimeric, or reduced species. The octahalo complexes react with carboxylic acids and acid anhydrides under reflux to give the dihalo-μ-tetracarboxylato complexes.[36] The halo groups are subject to replacement by other groups. A pictoral representation of these reactions is given in Figure 1.

Structural studies of several of these complexes have been reported.[37,38] The basic features of the $Re_2Cl_8^{2-}$ structure are noted for the other rhenium(III) dimers as well--the eclipsed conformation of the ligands and the short Re-Re distance--implying that no major change in the metal-metal bonding has occurred. Some of these structures are illustrated in Figure 2. The octahalo complexes can be oxidized[39] and reduced,[40] and the relationship between these complexes and rhenium(IV) halides has also been studied.[41-43]

The tetracarboxylate complexes were chosen for investigation over the parent octahalo complexes for three reasons. First, the octahalo complexes undergo few simple reactions. Most of the reactions listed in Figure 1 involve at least two substitutions and are often complicated by precipitation

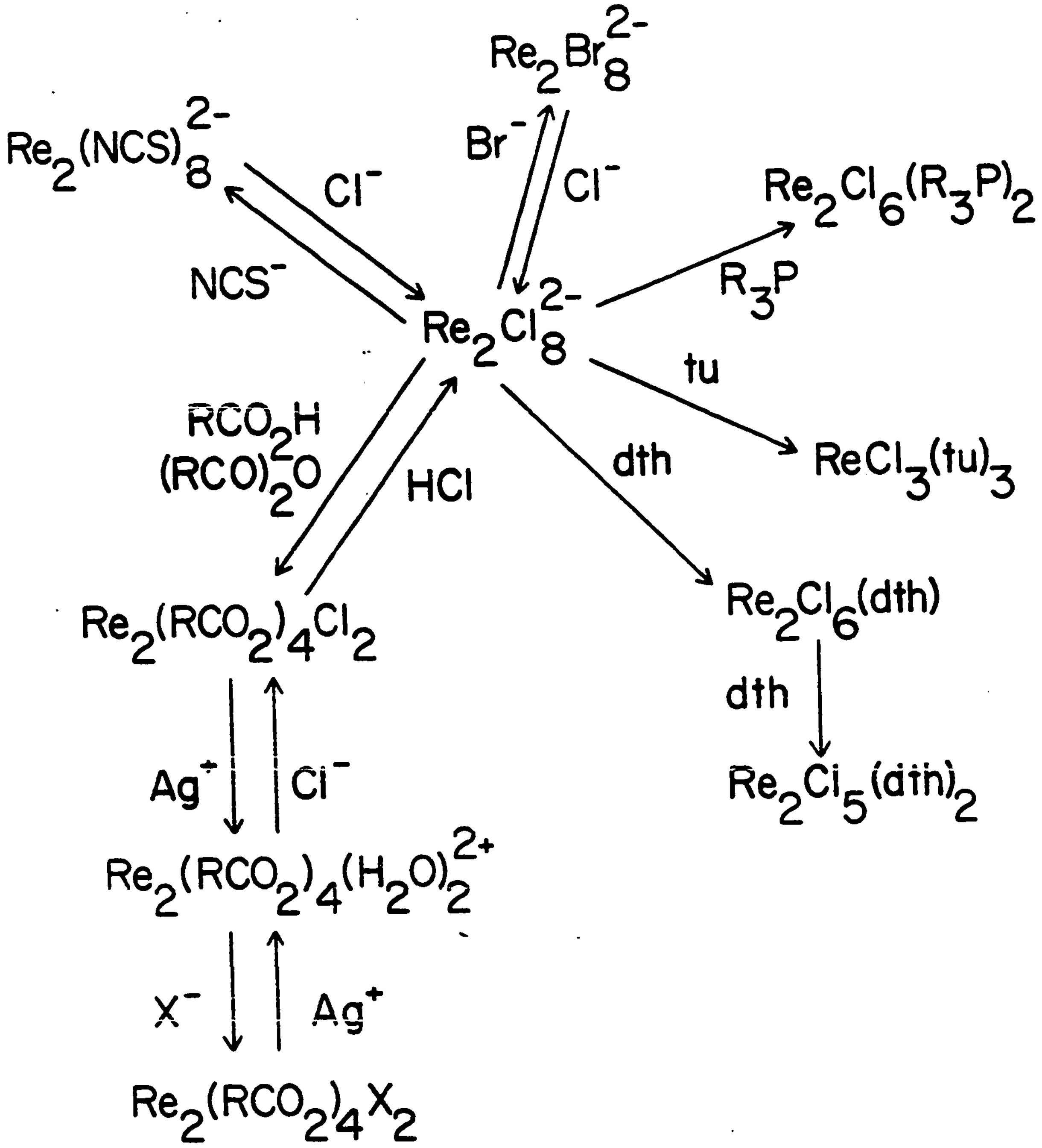


Figure 1. Some reactions of dirhenium(III) complexes

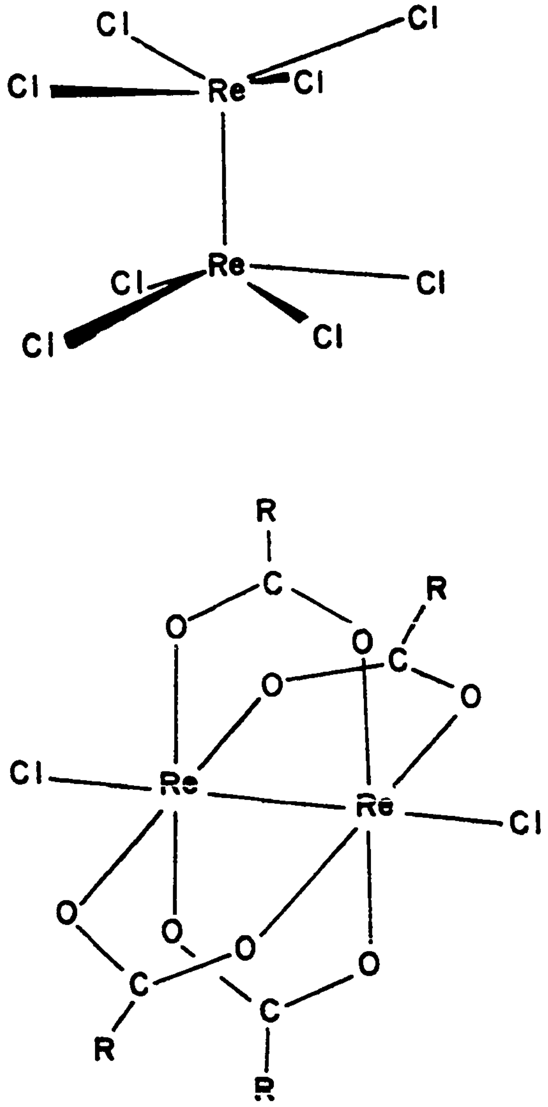


Figure 2. Structures of dirhenium(III) complexes; $Re_2Cl_8^{2-}$ and a tetracarboxylato complex $Re_2(RCO_2)_4Cl_2$

(phosphines),[33] monomerization (thioureas),[35] or reductions (dithiahexane).[35] Synthetic studies on the dihalotetracarboxylates[36] indicate that the two halo groups are much more labile than the carboxylate groups so that at most two substitutions must be considered. The second problem relates to the stability of these complexes. The octahalo complexes are stable in methanol in the presence of reasonably high concentrations of the corresponding HX compound (ca. 0.1 F HCl[30] for the chloro and 0.4 F HBr[44] for the bromo). Studies must therefore be restricted to acidic solutions with high concentrations of halide species. The carboxylate complexes are stable in neutral acetonitrile;[36] this situation allows more flexibility in experimental design. Finally, many reactions of charged complexes,[10,22] especially in non-aqueous solvents, involve ion pairs. A neutral complex would be preferred for studies, as it does not form ion pairs.

Hynes[44] has reported a study of some reactions of the octahalo complexes. His results confirm the worst expectations about the complexity of the system. Multiple reactions are the rule, and the identification of observed reactions with steps in a mechanism is not unambiguous. It was hoped that a study of a simpler system might provide more definitive information about the mechanisms by which these interesting complexes react, and a study of the dihalo-μ-tetracarboxylato complexes was begun. The propionate was chosen for its favorable solubility in acetonitrile. The study to be reported here concerns reaction VII.

$$Re_2(C_2H_5CO_2)_4Cl_2 + 2Br^- = Re_2(C_2H_5CO_2)_4Br_2 + 2Cl^- \qquad (VII)$$

In later equations and reactions, the complexes will be identified by their end groups; for instance, Re_2Cl_2 will identify the dichloro complex.

EXPERIMENTAL

Certain considerations had to be made regarding solvent and reagents for the study of reaction VII. The literature report of the electronic spectra[36] suggested that the ultraviolet was the region of choice for a spectral study. It appeared desirable to employ a solvent which would dissolve both the neutral complexes and an appropriate source of halide ion and which would be transparent in the uv to wavelengths of 250 nm or shorter. Acetonitrile seemed a reasonable choice on these counts. Its use as solvent dictates the use of halide salts of organic cations because of the fairly low solubility of alkali salts (especially chlorides).[45] Tetraethylammonium salts, which are readily available commercially, were chosen because of their good solubility in acetonitrile and because the tetraethylammonium ion does not add extra bands to the uv spectrum in the region of interest.

Acetonitrile. Acetonitrile was purified by distillation. 800 ml of commercial acetonitrile were treated with 12 g of sodium carbonate and 15 g of potassium permanganate and distilled; the middle 80% was collected, dried over phosphoric oxide, and redistilled.[46] The distillate (*ca.* the middle 80%) was used for stock solutions or was further dried and outgassed for use in vacuo. When Linde 4A molecular sieves were used as the drying agent, the solvent was outgassed and distilled in vacuo onto the sieves, which had been activated by heating to 280° under dynamic vacuum for 12-15 hours. When phosphoric oxide was used for further drying, the distillate was dried over phosphoric oxide and distilled in vacuo onto more oxide, over which it was stored. In some of the early experiments, the water content of the solutions was determined by the Karl Fischer method[47] by Mr. Gary Austin of the Ames Laboratory Analytical Services Group.

Rhenium Complexes. The dichloro-μ-tetrapropionato complex was prepared from the metal as follows. Rhenium metal was dissolved in dilute (*ca*. 8 F) nitric acid.[48] Lower oxides of nitrogen were removed with urea. Potassium perrhenate was precipitated by adding small amounts of potassium carbonate (vigorous evolution of CO_2!) until no further precipitation was noted. The white solid was filtered and washed with small amounts of cold water, alcohol, and ether. Tetrabutylammonium octachlorodirhenate(III) was prepared by Cotton's procedure.[33] 2 g potassium perrhenate, 2 g sodium chloride, and 40 ml commercial 50% hypophosphorous acid were heated at 90° for 12 hours. A solution of 4 g of tetrabutylammonium bromide in 75 ml 6 F hydrochloric acid was added, and the mixture was heated for another 10 hours. The solution was filtered and the blue solid washed with 6 F hydrochloric acid, ethanol, and ether. The octachloro complex was converted to the octabromo[33] by heating a solution of the octachloro in a mixture of 200 ml of methanol and 50 ml 6 F hydrobromic acid. The octabromo complex precipitates when the last of the methanol evaporates.

The dihalo-μ-tetraacetato complexes[36] were prepared by refluxing the corresponding octahalo complex in a mixture of 80 ml of acetic acid and 20 ml of acetic anhydride under nitrogen. The blue solution faded and an orange solid precipitated and was filtered. The tetraacetato complexes were converted to the tetrapropionate complexes by heating 0.5 g of the tetraacetato complex in a mixture of 100 ml of propionic acid and 50 ml of propionic anhydride under nitrogen in a distillation apparatus so as to distill about 50 ml of liquid from the reaction flask over a 3-6 hour period. The solution was cooled to ice-bath temperature, and the orange solid was filtered off under nitrogen and recrystallized from acetonitrile.

There are several alternative preparatory schemes. Taha and Wilkinson[27] prepared the carboxylato complexes in low yield directly from Re_3Cl_9. The conversion of Re_3Cl_9 to the octachloro complex by heating the trimer in molten diethylammonium chloride under nitrogen has been described;[49] this reaction would now appear to be the method of choice for preparing the octachloro complex.[50] In the synthetic scheme employed here, the preparation of the acetate was not necessary; the octachloro complex can be converted directly to the dichlorotetrapropionato complex.

Carbon and hydrogen analyses were performed by the Analytical Services Group of the Ames Laboratory. Calc for ReCl $(C_3H_6O_2)$: C 19.58%, H 2.72%. Found C 19.31%, H 2.72%. The visible spectrum was measured in acetonitrile. Maxima were found at 396 and 497 nm, $\varepsilon_{396}/\varepsilon_{497} = 1.03$. The peak positions agree with the reported values;[36] the reported intensity ratio is 1.06. The analogous preparation of the dibromo complex gave an orange solid whose visible spectrum had maxima at 410 and 500 nm of equal intensity (lit[36] maxima 419 and 509 nm, $\varepsilon_{509}/\varepsilon_{419} = 1.62$). Because of this discrepancy, it was presumed that the dibromo complex was contaminated with another material, perhaps a mixed acetato-propionato complex. For quantitative work, the dibromo complex was prepared in situ by adding a solution of a bromide salt to the dichloro complex.

Tetraethylammonium Salts. Commercial samples of tetraethylammonium salts are invariably contaminated with a yellow impurity which can be removed by any of several recrystallization techniques. Supin[51] has described an excellent procedure for purifying the bromide and iodide. 10 g of the salt is dissolved in chloroform (50 ml for the bromide, 100 ml with 5 ml methanol for the iodide) and reprecipitated with benzene (100 ml for the bromide and 50 ml for the iodide). The chloride was crystallized from 50 ml of acetonitrile by adding 50 ml of benzene or ether. The fluoride was crystallized from acetonitrile with benzene, using the same quantities as for the chloride. The commercial halides were obtained from Eastman.

Stock solutions of the halide salts were prepared in acetonitrile. Solutions of the iodide and bromide were analyzed by the Volhard method.[52] The chloride was standardized by passing aliquots of solution down an anion-exchange column loaded with Dowex 1-X8 resin in the bromide-ion form; the eluate was titrated by the Volhard method. This method was tested with a standard solution of potassium chloride of similar concentration in the presence of 50% acetonitrile. In all silver titrations, the acetonitrile content of solutions to be analyzed was reduced to *ca.* 25% before titration. A direct titration of chloride ion (Mohr method)[53] was not successful because the indicator precipitate does not form in the presence of large amounts of acetonitrile. The fluoride solution was analyzed by the gravimetric lead chlorofluoride method. Blank experiments indicated that an analogous ion-exchange method was not satisfactory for these solutions.

Tetraethylammonium perchlorate was prepared by mixing concentrated aqueous solutions of tetraethylammonium bromide and sodium perchlorate.[54] The product precipitated immediately as a white solid which was recrystallized twice from conductivity water. The solution from which the second crystallization was performed gave a negative test for bromide ion (silver nitrate). Calc for $C_8H_{20}NClO_4$: C 41.8%, H 8.7%, for the monohydrate $C_8H_2NClO_5$: C 38.8%, H 9.0%; found C 41.4%, H 9.0%. The compound was shown to be anhydrous by the absence of a water peak in the nmr spectrum (CD_3CN) and by thermogravimetric analysis; upon heating to 170° a weight loss of .04% was noted; for a monohydrate, a loss of 7.3% would be expected.

Other Reagents. Conductivity water was used in all experiments. Urea was recrystallized from acetone to mp 132-3° (lit[55] 132-3°). Commercial acetamide was recrystallized twice from methanol to give an odorless solid of mp 80.5-81.5° (lit 81-2°). Tetrahydrofuran (THF), propionitrile (prnt), and pyridine (py) were obtained from Drs. Ron Hoxmeier and Margaret Schafer King. THF had been dried over lithium aluminum hydride and stored in vacuo over the hydride; the other two reagents had been dried over barium oxide and stored over outgassed molecular sieves in vacuo. Dimethylformamide (DMF) was purified by refluxing for one hour, drying over phosphoric oxide, and distilling in vacuo from the oxide onto activated molecular sieves. It was stored in vacuo in the dark. Commercial tetramethylurea (TMU) was treated with phosphoric oxide to remove an amine impurity (detectable by odor) and was vacuum distilled onto molecular sieves. Triethylamine[56] was refluxed with acetic anhydride and distilled. The distillate was dried over $MgSO_4$ and vacuum distilled onto pretreated molecular sieves. Two attempts were made to prepare quinuclidine[57] from the commercial hydrochloride (Aldrich) by adding excess base followed by extraction with ether. The amine obtained from the ether fraction was not pure, as witnessed by its reluctance to crystallize.

Kinetic and Equilibrium Measurements. All spectra were measured on a Cary Model 14 uv-visible spectrophotometer. Equilibrium studies were made directly on the stock solutions.

Equilibrium studies and kinetic runs were carried out at 25°, maintained with a thermostated cell compartment.[58] A few runs were carried out on a Durrum-Gibson stopped-flow spectrophotometer[59] of path length 1.92 cm.[60] Most kinetic runs were carried out in a vacuum cell, shown in Figure 3. The cell is made of quartz tubing sealed to Vycor joints; the sidearm and upper fittings are of Pyrex. Although the optical surfaces are convex instead of flat, the cell is satisfactory for measurements in which the optical path is immersed in water to lessen the change in index of refraction.[61] The cell is usable at wavelengths longer than 240 nm; acetonitrile solutions of colored materials obeyed Beer's law to within 2%. The cell could not be used for quantitative absorbance measurements in which the cell had to be removed and replaced because the partial vitrification of the quartz made the measured absorbance a function of the orientation of the cell. The cell extended above the compartment by about 12 cm; to protect the phototube from stray light, the cell was covered with a metal can. The effective optical path length of the cell was ca. 2.5 cm.

To carry out a run, the following procedure was used. Known volumes of stock solutions of the rhenium complex and the halides were added to the cell as desired. The solvent was removed on a vacuum line. After the solid residue had been pumped on for approximately five minutes, the specially dried solvent was distilled in, also on the vacuum line. The cell was closed off, removed from the vacuum line, and thermo-

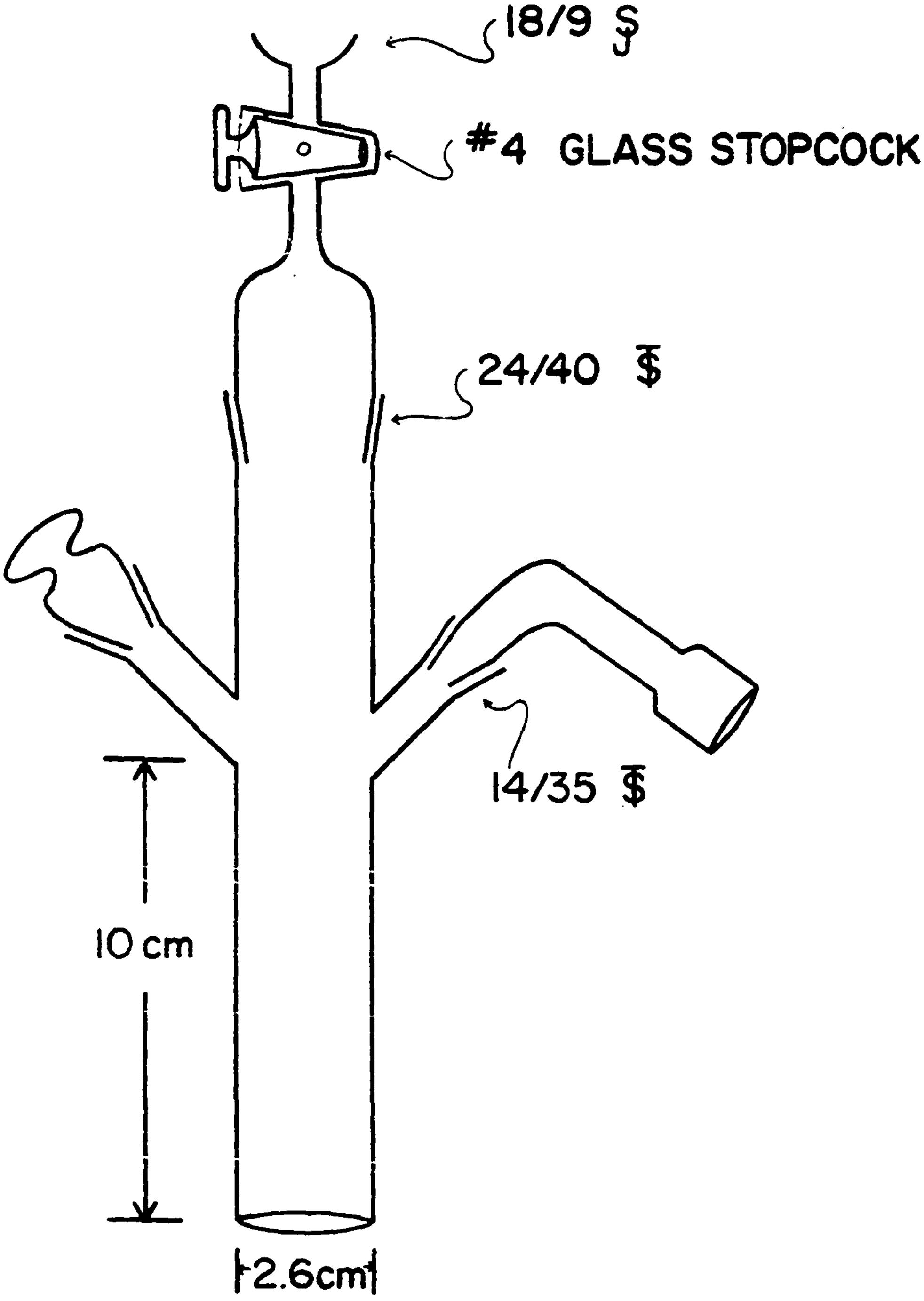


Figure 3. The vacuum cell

stated in the cell block or in the main Cary water bath. The solutions were mixed by tipping the side arm, followed by pouring the cell contents from the main chamber into the side arm and back out several times to insure complete mixing. The typical dead time was 20 seconds. The absorbance was recorded continuously as a function of time, with the cell fixed in the light beam of the spectrophotometer. After the reaction was completed, the cell was removed from the spectrophotometer and opened; the final volume was measured by pipet and graduated cylinder. A typical volume was 13 ml.

Urea and acetamide were added as solutions in acetonitrile in the same manner as the halides. Water was added from a 50 μl syringe into a melting-point capillary which was placed inside a larger capillary. The large capillary was attached to the vacuum line and outgassed. The water was distilled into the cell after the acetonitrile had been added. Other liquids were vacuum-distilled from storage flasks into calibrated capillaries, in which the volume could be measured, followed by distillation of the material into the cell. To assist in the transfer of the higher-boiling liquids, the line was heated to *ca*. 80° with heating tape.

The kinetic data were treated in pseudo-first-order fashion according to eq 5, which is of the same form as eq 1.

$$\ln \frac{[Re_2Cl_2]_0 - [Re_2Cl_2]_\infty}{[Re_2Cl_2]_t - [Re_2Cl_2]_\infty} = k_{obs}t \qquad (5)$$

The concentration ratio is the fractional extent of completion of the reaction, which can be expressed in terms of absorbance values[62] by eq 6. From plots of the left member of eq 6 vs

$$\ln|A_t - A_\infty| = \ln|A_o - A_\infty| - k_{obs}t \qquad (6)$$

time, k_{obs} could be evaluated. For many of the slower runs, the Guggenheim plotting method,[63] eq 7, was used instead.

$$\ln|A_t - A_{t+\tau}| = \ln[(A_o - A_\infty)(1 - e^{-k\tau})] - k_{obs}t \qquad (7)$$

τ values of 2-3 half lives were normally used. Necessary digital computer work was done using programs developed at Los Alamos.[64] Analog computer work was performed on a TR-48 analog computer.

RESULTS

Spectral and Equilibrium Studies. The uv spectrum of $Re_2(C_2H_5CO_2)_4Cl_2$ in acetonitrile is given in Figure 4. Molar absorptivities, based on the reported[36] ε_{max} 16,400 M^{-1} cm^{-1}, are given in Table I.

Table I

Molar Absorptivities of $Re_2(C_2H_5CO_2)_4Cl_2$[a]

λ, nm	$10^{-3}\varepsilon$, $M^{-1}cm^{-1}$	λ, nm	$10^{-3}\varepsilon$, $M^{-1}cm^{-1}$
320	0.3	280	11.2
315	0.4	275	15.5
310	0.4	272	16.4 (max)
305	0.6	270	16.1
300	0.8	265	13.2
295	1.2	260	9.6
290	2.7	255	7.7
285	5.9	250	6.5

[a] Measured at room temperature in acetonitrile.

Before meaningful kinetic data can be taken, certain questions about the chemistry must be answered. Reaction VII involves the substitution of two chloride ligands by two bromides. Most substitution reactions occur stepwise, so that the formation of the mixed bromochloro complex might also be expected. If there are two such reactions involved, it will be important to know whether one can be studied independently of the other. Likewise, the initial considerations of this reaction assumed that the carboxylato groups are inert to substitution. If they are not, this will also need to be

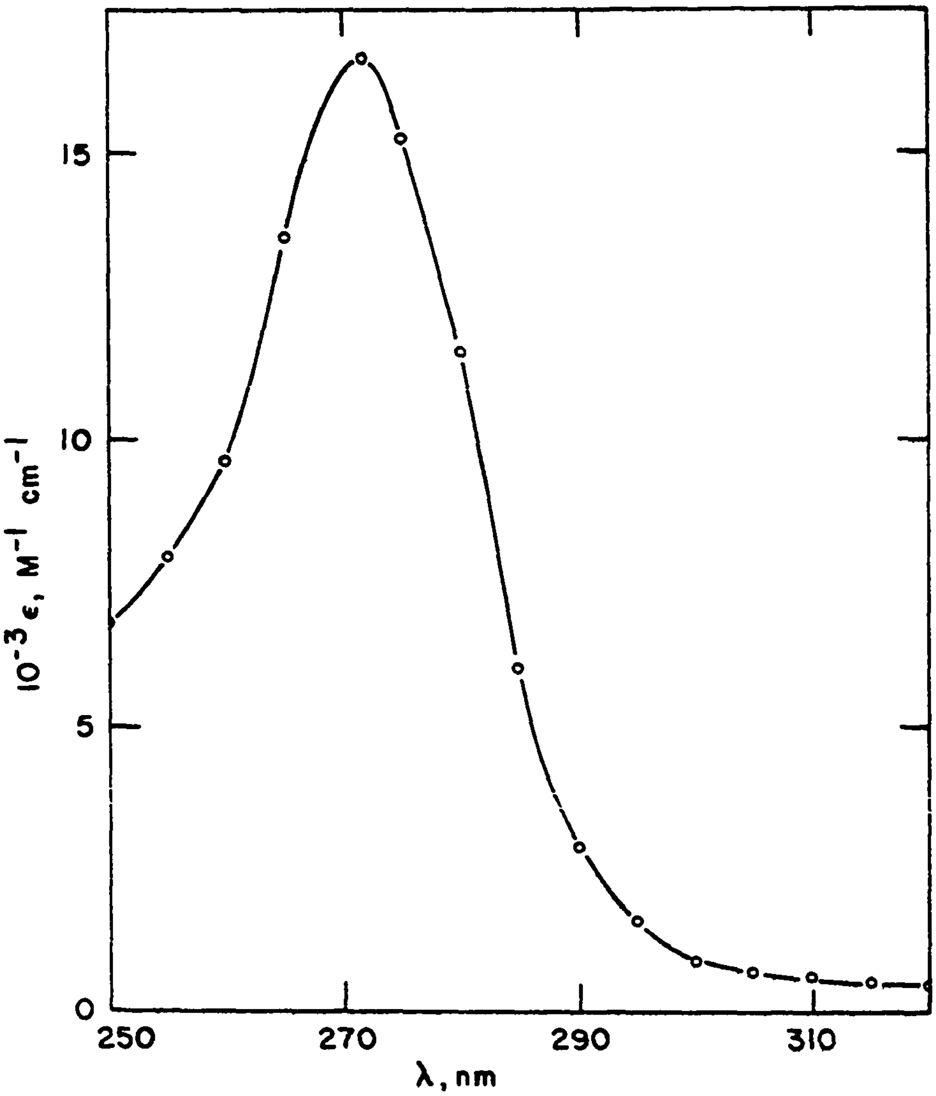


Figure 4. The uv spectrum of dichloro-μ-tetrapropionatodirhenium(III) in acetonitrile at room temperature

considered.

The spectral changes that result from increasing the bromide concentration in solutions of the dichloro complex are shown in Figure 5. Spectrum A is the spectrum of the dichloro complex, while spectrum E is the final spectrum, which is insensitive to additional bromide ion. On the basis of the similarity of spectrum E to the reported spectrum[36] of the dibromo-μ-tetrapropionato complex and to the spectrum of the impure dibromo complex prepared during the course of this study, the final product is identified as the dibromo complex. Under the conditions of this study, therefore, the propionate groups are inert to substitution, and reaction VII may be taken as a satsifactory description of the maximum chemical change possible in this system. However, the intermediate spectra do not correspond to simple mixtures of the dichloro and dibromo complexes; the failure to observe isosbestic points requires the presence of (at least) a third absorbing species, the most likely candidate being the unreported bromochloro complex. Reaction VII should be rewritten as two reactions, VIII and IX.

$$Re_2Cl_2 + Br^- = Re_2ClBr + Cl^- \qquad \text{(VIII)}$$

$$Re_2ClBr + Br^- = Re_2Br_2 + Cl^- \qquad \text{(IX)}$$

At this point it is convenient to define a new concentration variable R by eq 8. The absence of a large range of R for

$$R = [Br^-]/[Cl^-] \qquad (8)$$

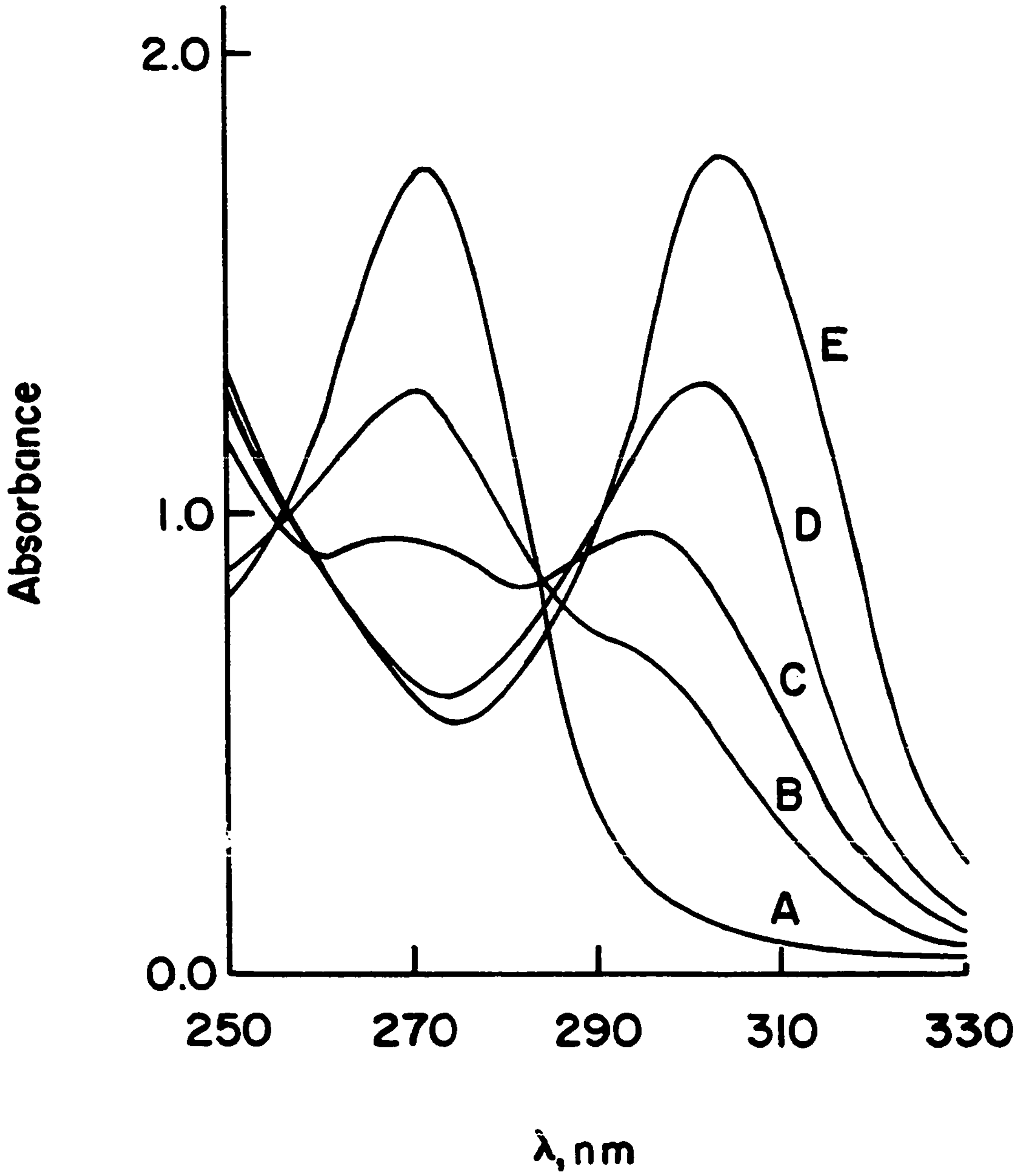


Figure 5. Absorption spectrum of dichloro-μ-tetrapropionato-dirhenium(III) in acetonitrile as a function of added bromide: A, no bromide; B, 0.0005 M Br^-; C, 0.002 M Br^-, D, 0.008 M Br^-; E, 0.05 M Br^-

which the intermediate spectra are constant suggests that the equilibrium constants, K_{VIII} and K_{IX}, are of the same order of magnitude. To check the separation of the equilibria a kinetic run was made at an R value of 60 in the vacuum cell and was monitored by scanning the uv spectrum as a function of time instead of measuring the absorbance at one wavelength. Isosbestic points at 257 and 284 nm were maintained throughout the reaction, suggesting that only two absorbing species were present. The maximum at 273 nm noted in the initial spectrum remained in the final spectrum, indicating that the dichloro complex was one species present and strongly implying that the bromochloro was the other. Under these conditions, reaction VIII appeared to be the only reaction occurring in solution, so that its kinetics could be measured without appreciable interference from reaction IX.

Further confirmation of two species is obtained when the absorbance data are tested according to the plotting method described by Coleman, Varga, and Mastin.[65] If absorbance data are expressed in terms of a matrix $||A_{ij}||$, where i indexes wavelength and j indexes solution number, usually as a function of concentration or time, the rank of $||A_{ij}||$ gives the number of absorbing species in solution. If there are N absorbing species in solution, any N+1-th order determinant constructed from $||A_{ij}||$ must be equal to zero. This fact can be used to construct determinental equations based on the absorbance matrix, which can be expanded to give equations suitable for plotting. If the reaction is run so that the total concentration of absorbing species is constant, as it would be for reactions VIII and IX during a kinetic run, the concentration of one species is dependent on the concentration of the others; the system has one less degree of freedom than it did without the restriction. This change is reflected in the absorbance matrix by choosing one solution j' as a reference. The absorbance matrix is now expressed as $||A_{ij}-A_{ij'}||$, whose rank is one lower than the rank of $||A_{ij}||$ without the restriction. Again, appropriate equations can be constructed for plotting, based on $A_{ij} - A_{ij'}$ instead of on A_{ij}.

To apply this method to the absorbance data, first-order kinetic plots were made at several wavelengths. From these plots values of A_{ij}, j indexing time, were interpolated and appropriate functions plotted for two and three species at constant stoichiometry. The data are given in Table II; the plots, in Figure 6. The two species plot gives the expected family of straight lines through the origin, but the three-species plot gives not a family of lines but one line, common to all wavelengths, for a given abscissa. This result also implies that two absorbing species are present in this solution.

The equilibria were studied in the ultraviolet region. If the dichloro complex is mixed with chloride and bromide ions in solution, at equilibrium the system will be described by two equilibrium constants, K_{VIII} and K_{IX}. The absorbance of that solution, A, can be expressed in terms of an apparent

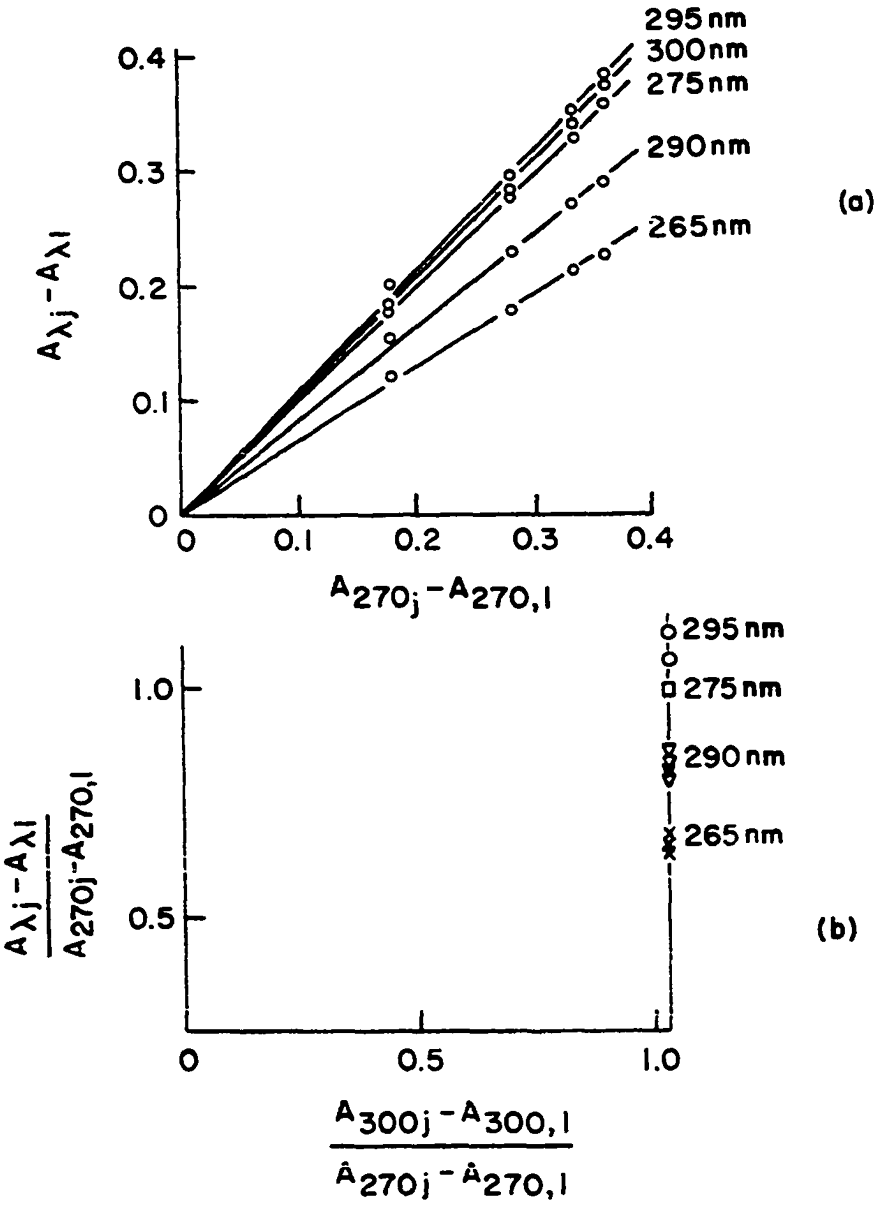


Figure 6. Species plot for a solution of the dichloro complex with Br^- and Cl^- at R=60: a, for two species at constant stoichiometry; b, for three species at constant stoichiometry

Table II

Absorbance Data for Species Plots[a]

	j=1 100 sec	j=2 300 sec	j=3 500 sec	j=4 700 sec	j=5 900 sec
300 nm	0.262	0.444	0.545	0.603	0.636
295 nm	0.368	0.568	0.665	0.721	0.752
290 nm	0.532	0.685	0.763	0.802	0.822
275 nm	1.747	1.569	1.470	1.419	1.388
270 nm	1.798	1.619	1.517	1.464	1.435
265 nm	1.546	1.427	1.367	1.336	1.321

[a] Measured in vacuo at 25° in acetonitrile.

molar absorptivity, $\bar{\varepsilon}$, by a modified form of Beer's law[66] expressed in terms of the total concentration of rhenium species C_T and the path length b

$$A = \bar{\varepsilon} b C_T \tag{9}$$

or in terms of the standard expression

$$A = \varepsilon_{Cl_2} b C_{Cl_2} + \varepsilon_{BrCl} b C_{BrCl} + \varepsilon_{Br_2} b C_{Br_2} \tag{10}$$

in which the subscripts denote the terminal ligands in the complex. If eq 9 and 10 are equated and the expressions for the equilibrium constants inserted, the resulting equation can be solved for $\bar{\varepsilon}$ to give eq 11.

$$\bar{\varepsilon} = \frac{\varepsilon_{Cl_2} + K_{VIII} R \varepsilon_{BrCl} + K_{VIII} K_{IX} R^2 \varepsilon_{Br_2}}{1 + K_{VIII} R + K_{VIII} K_{IX} R^2} \tag{11}$$

This equation is not amenable to plotting in any form. However, if reaction IX can be neglected at low R values, as is suggested by the spectral studies, the last term in the numerator and denominator can be dropped. The new equation can be rearranged to

$$\frac{\bar{\varepsilon}-\varepsilon_{Cl_2}}{R} = (\varepsilon_{BrCl}-\bar{\varepsilon})K_{VIII} \qquad (12)$$

A plot of the left member of eq 12 vs $\bar{\varepsilon}$ should be linear, with slope $-K_{VIII}$ and intercept $K_{VIII}\varepsilon_{BrCl}$. K_{VIII} and ε_{BrCl} can be derived from the plot. If this is done at several wavelengths, a spectrum of the bromochloro complex can be derived. Alternatively, if the difference in molar absorptivity $\varepsilon_{BrCl}-\varepsilon_{Cl_2}$ is known at one wavelength, it can be determined at any other wavelength from the absorbance changes measured in the kinetic run used to determine the number of species. The raw data for the determination of K_{VIII} are given in Table III. The plots

Table III

Equilibrium Data for K_{VIII}[a]

R	ε_{272} $M^{-1}cm^{-1}$	ε_{290} $M^{-1}cm^{-1}$	ε_{295} $M^{-1}cm^{-1}$	ε_{800} $M^{-1}cm^{-1}$	ε_{305} $M^{-1}cm^{-1}$
21.7	13,900	5400	4600	3800	2900
28.9	13,200	6000	5300	4500	3400
36.2	12,600	6600	6000	5200	4100
43.5	12,000	7100	6700	5900	4700
51.0	11,600	7600	7300	6400	5100
57.8	11,300	8000	7700	6900	5600
65.2	10,800		8100		
72.6	10,600				
79.5	10,400				

[a] Measured at 25° in acetonitrile; $Re_T \sim 1.3\times10^{-5}M$.

are given in Figure 7, and the spectrum of the bromochloro complex is tabulated in Table IV and sketched in Figure 8.

Table IV

Spectral data for bromochloro-μ-tetrapropionatodirhenium(III)

λ, nm	$10^{-3}\varepsilon, M^{-1}cm^{-1}$ (kinetic)	$10^{-3}\varepsilon, M^{-1}cm^{-1}$ (equilibrium)
310	7.7	
305	10.9	11.0
300	13.8	15.7
295	14.8	16.1
290	12.8	15.6
284	7.0	
280	4.6	
272	3.4	3.4
265	5.3	
257	8.5	

The value derived for K_{VIII} at 272 nm is 0.011 ± 0.001. The general agreement at other wavelengths is good, although the scatter is larger than normal. This reflects the larger error in reading values from a spectrum instead of carrying out experiments at a fixed wavelength, which is more accurate but less informative than a scan experiment, which allows direct comparison of data at several wavelengths. The accuracy problem is most severe on the side of a large peak; the value chosen for citation is the value obtained at the absorbance maximum. A second problem, although much less important, is that reaction IX does contribute slightly (a few per cent) to the measured absorbance changes even under these conditions, its effect is small around 290 nm.

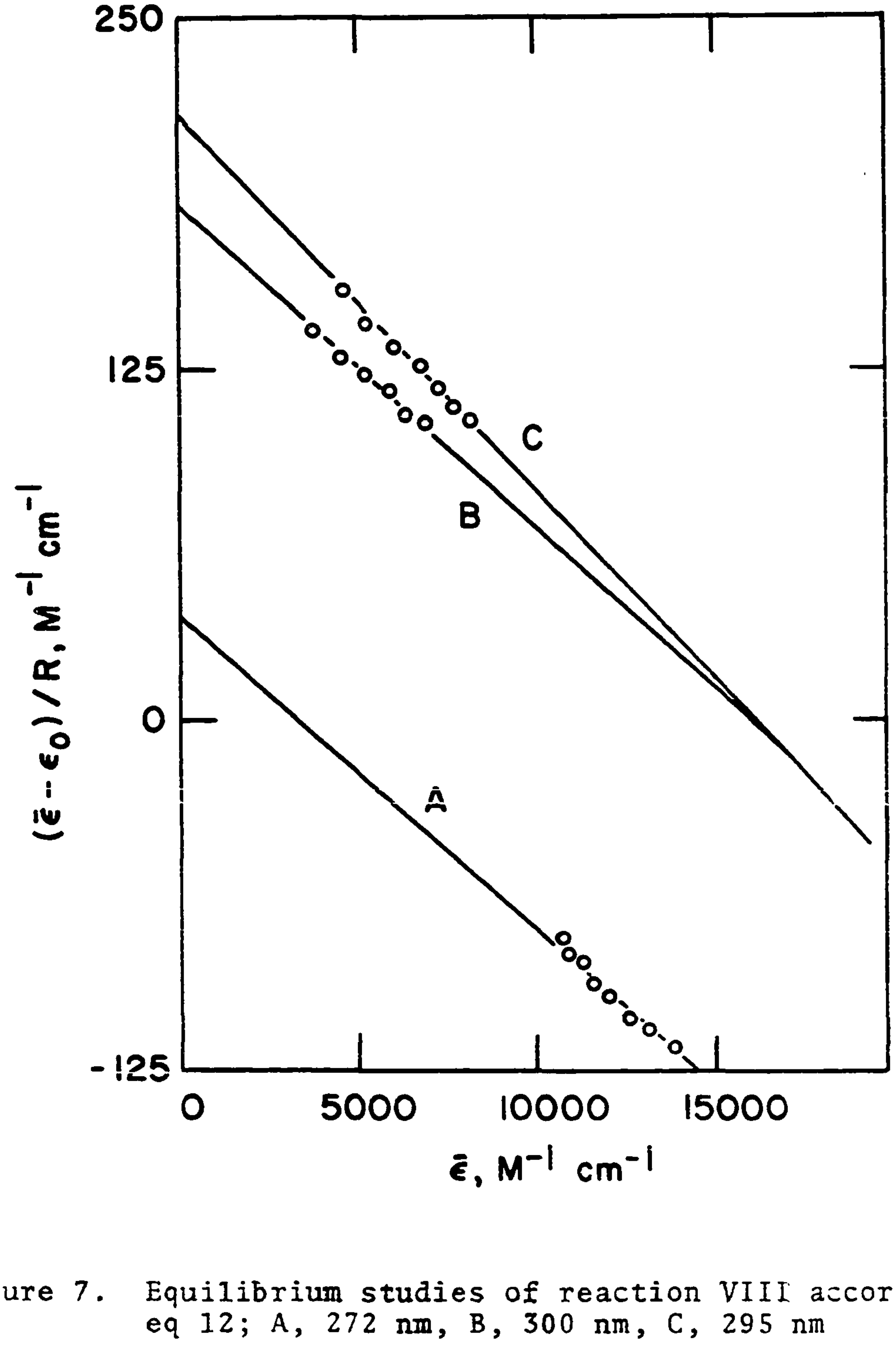


Figure 7. Equilibrium studies of reaction VIII according to eq 12; A, 272 nm, B, 300 nm, C, 295 nm

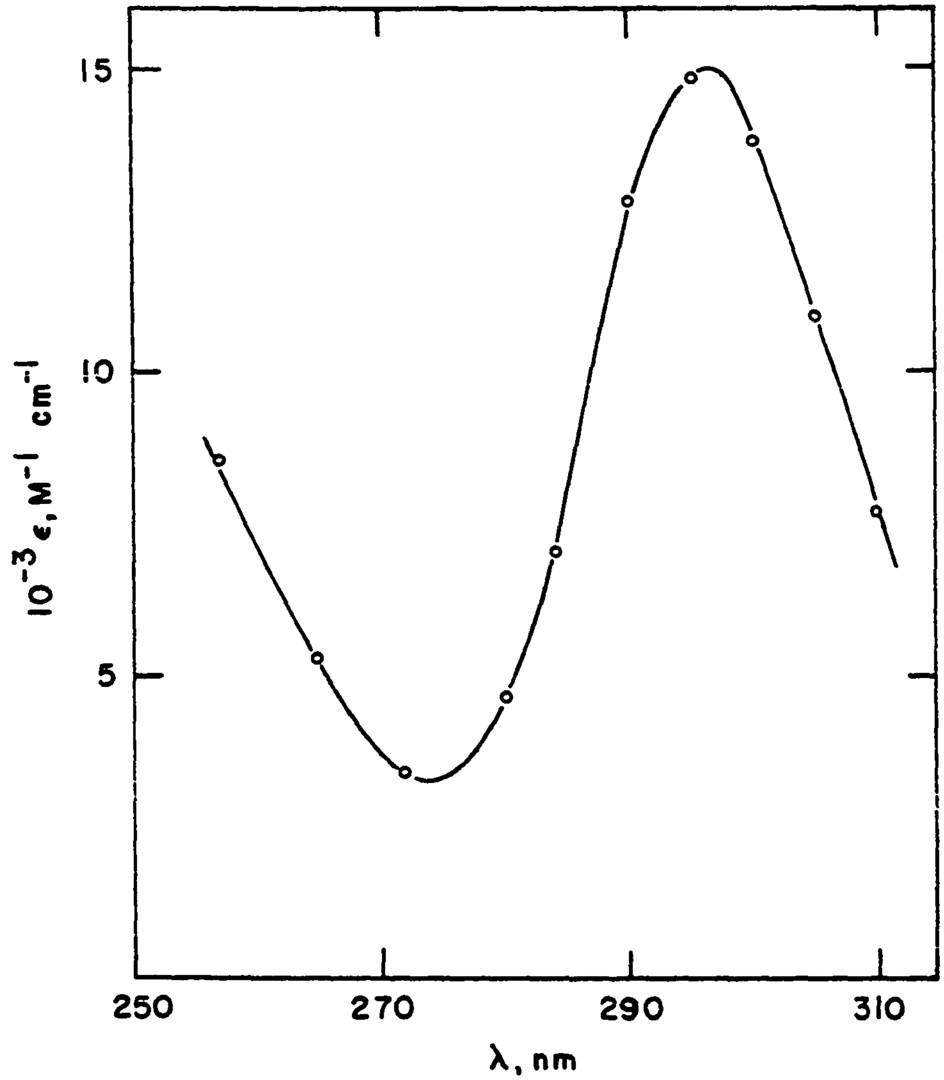


Figure 8. Derived spectrum of bromochloro-μ-tetrapropionato-dirhenium(III) in acetonitrile at 25°

Attempts to obtain K_{IX} from data measured over a more extensive range of R (to R = 180) were not particularly successful. These data are presented in Table V. Several computer fits were attempted at various wavelengths assuming ε_{Cl_2} and various combinations of K_{VIII} and one or both of the molar absorptivities, derived from the determination of K_{VIII} or from spectral studies such as those of Figure 5. Many of the fits refined to negative values of K_{IX}. In the cases where successful fits were obtained, values of K_{IX} ranged from 0.003 to 0.006, with standard deviations nearly equal to the parameters fitted. Some fits were made with a rearranged form of eq 11 in which K's were supplied and ε's calculated. The results suggest that a K_{IX} of approximately 0.004 'best' fits the data, although this value is very uncertain (at least by half its own magnitude. The data do not cover a sufficiently large range of R to give a good fit. Using these K

Table V

Absorbance data for determination of K_{IX}

R	$\bar{\varepsilon}_{292}$	$\bar{\varepsilon}_{305}$
23.6	5200	3200
47.2	6500	4700
70	8700	6200
92	9700	7500
115	10500	8400
137	11100	9300
159	11600	10100
181	12200	11000

values, at R of 180 the solution contains 20% unreacted dichloro, 45% chlorobromo, and 35% dibromo. This situation illustrates the problem of measuring equilibrium constants for successive processes which occur in the same concentration range.

Kinetic Results. Initial rate studies of reaction VIII were carried out in commercial acetonitrile or in acetonitrile which had been stored over molecular sieves. The pseudo-first-order kinetic plots according to eq 6 were linear for $\geq$80% completion, confirming the expected first-order approach to equilibrium. However, the data from supposedly duplicate experiments were not reproducible. For example, at R=30, k_{obs} values ranged from 0.0186 to 0.0562 s^{-1}. The problem was traced to the varying water content in the solvent, so that quantitative rate data could not be obtained under these conditions. It is possible to study a water-dependent reaction either at very high concentrations of water so that small variations in the concentration are swamped out by the large background or under conditions where water can be removed from the solutions until its concentration is reduced to a low and hopefully reproducible level.

Toward the first goal, kinetic data were taken in acetonitrile containing 5% water by volume (2.8 M). The raw absorbance data were treated in first-order fashion according to eq 6; values of k_{obs} are given in Table VI. These studies

Table VI

Rate Data for Reaction VIII in 5% Water-Acetonitrile[a,b]

$10^4[Cl^-]$,M	$10^3[Br^-]$,M	k_{obs},s^{-1}
5.00	1.00	23.6
5.00	1.60	28.1
5.00	3.00	21.8
5.00	3.00	22.4
5.00	3.00	23.8
5.00	3.00	24.8
5.00	5.00	22.3
5.00	5.00	22.4
5.00	6.40	18.5
5.00	8.00	19.5
8.00	1.00	27.2
8.00	3.00	26.0
8.00	3.00	27.2
8.00	5.00	19.1
8.00	7.50	17.8
8.00	7.50	18.3
10.00	5.00	21.2
10.00	5.00	27.6
16.00	5.00	27.2
16.00	5.00	27.8
50.00	5.00	38.9
80.00	5.00	23.2
80.00	5.00	23.1

[a] Measured at 25°.

[b] $Re_T \sim 1x10^{-5}M$.

were discontinued after it was found that solutions of the rhenium complexes are not uniformly stable at this water concentration. There is a discernible halide dependence; k_{obs} increases slightly with increasing concentration of chloride and decreases with increasing bromide concentration. This interesting dependence was also noted in other kinetics experiments and will be discussed later.

Vacuum experiments were then begun. Studies were carried out with acetonitrile which had been dried over molecular sieves or phosphoric oxide. The kinetic data also fit the first-order eq 6, although for most of the slower experiments the Guggenheim[63] form, eq 7, was used instead. The data from the sieve experiments are listed in Table VII; the oxide data are given in Table VIII and Figure 9. From duplicate experiments (in which R was the same but the final concentrations of the individual halides were not), k_{obs} was found to be independent of the total halide concentration, depending only on R. Both from duplicate kinetic experiments and from the scan experiment used to check isosbestic points and construct the species plots, k_{obs} was found to be independent of the wavelength used to study the reaction. k_{obs} was also found to be independent of ionic strength over the range 0.01-0.04 F. The same type of halide dependence noted in the experiments at high water concentrations is also seen in these; at higher R, k_{obs} seems to approach a limiting value, as is depicted in

Table VII

Rate Data for Reaction VIII in Sieve-dried Acetonitrile[a,b]

	$10^4[Cl^-]$,M	$10^3[Br^-]$,M	$10^2[ClO_4^-]$,M	R	10^3k_{obs},s^{-1}
Set 1	1.79	6.5		36	2.82
	1.69	7.7		45	2.80
	1.54	7.0		45	2.81
	1.82	8.2	2.67	45	2.93
	1.68	7.6	3.40	45	3.41
	2.12	10.0	3.08	47	3.23
	1.69	10.0	3.17	59	2.52
	1.81	10.7		59	2.68
	1.82	13.2	3.12	73	2.48
	1.75	12.7		73	2.44
	1.83	13.3		73	2.48
	1.72	15.6		91	2.43
	1.85	16.8	2.81	91	2.56
	1.91	17.3	2.61	91	2.58
	1.66	26.6	1.10	136	2.41
	1.65	37.4		227	1.90
Set 2	3.34	9.9		30	4.32
	1.71	6.2		36	3.99
	1.78	6.5		36	3.39
	2.81	11.1		39	3.88
	1.80	8.2		45	3.09
	1.85	8.4		45	3.19
	1.61	9.5		59	3.05
	1.68	9.9		59	2.97
	1.71	10.1		59	3.19
	1.72	10.2		59	3.25
	1.65	12.0		73	3.19
	1.66	15.1		91	3.03
	0.88	10.4		118	2.36

[a] Measured at 25°.

[b] $1x10^{-5}M<Re_T<4x10^{-5}M$.

Table VIII

Rate Data for Reaction VIII in P_2O_5-dried Acetonitrile[a,b]

$10^4[Cl^-]$,M	$10^3[Br^-]$,M	R	10^3k_{obs},s^{-1}	10^3k_{av}[c]	10^3k_{calc}[d]
6.83	4.03	5.9	2.39	2.39	2.60
3.44	6.24	18	2.34	2.34	2.08
1.48	3.42	23	2.01	2.01±0.24	1.96
1.56	3.55	23	1.71		
1.83	4.16	23	1.98		
2.80	6.8	24	1.95		
3.25	7.9	24	2.38		
2.51	8.5	35	2.00	1.69±0.23	1.70
1.49	5.3	36	1.74		
1.63	6.0	36	1.45		
1.71	6.2	36	1.81		
1.80	6.5	36	1.46		
1.46	7.0	48	1.54	1.69±0.18	1.55
1.56	7.6	48	1.59		
1.68	8.1	48	2.01		
1.79	8.7	48	1.69		
1.81	8.7	48	1.60		
1.47	7.7	53	1.47	1.44±0.04	1.51
1.62	8.5	53	1.40		
0.69	4.04	59	1.14	1.36±0.16	1.46

[a] Measured at 25°.

[b] $1\times10^{-5}M<R_{O_T}<4\times10^{-3}M$.

[c] Mean ± standard deviation.

[d] Calculated in the least-squares fit of the data to eq 18.

Table VIII (continued)

$10^4[Cl^-]$,M	$10^3[Br^-]$,M	R	10^3k_{obs},s^{-1}	10^3k_{av} [c]	10^3k_{calc} [d]
0.84	5.0	59	1.07		
1.37	8.1	59	1.52		
1.60	9.4	59	1.25		
1.67	9.9	59	1.41		
1.73	10.2	59	1.48		
1.74	10.2	59	1.19		
1.75	10.3	59	1.49		
1.79	10.6	59	1.24		
1.79	10.6	59	1.39		
1.86	11.0	59	1.59		
1.87	11.0	59	1.34		
2.80	16.5	59	1.40		
3.06	18.1	59	1.56		
1.21	7.8	65	1.51	1.51	1.41
1.49	10.6	71	1.61	1.61	1.37
1.72	15.8	91	1.14	1.23±0.07	1.27
1.78	16.1	91	1.29		
1.83	16.6	91	1.27		
0.77	7.4	97	1.21	1.39	1.25
1.62	15.8	97	1.58	1.39±0.18	

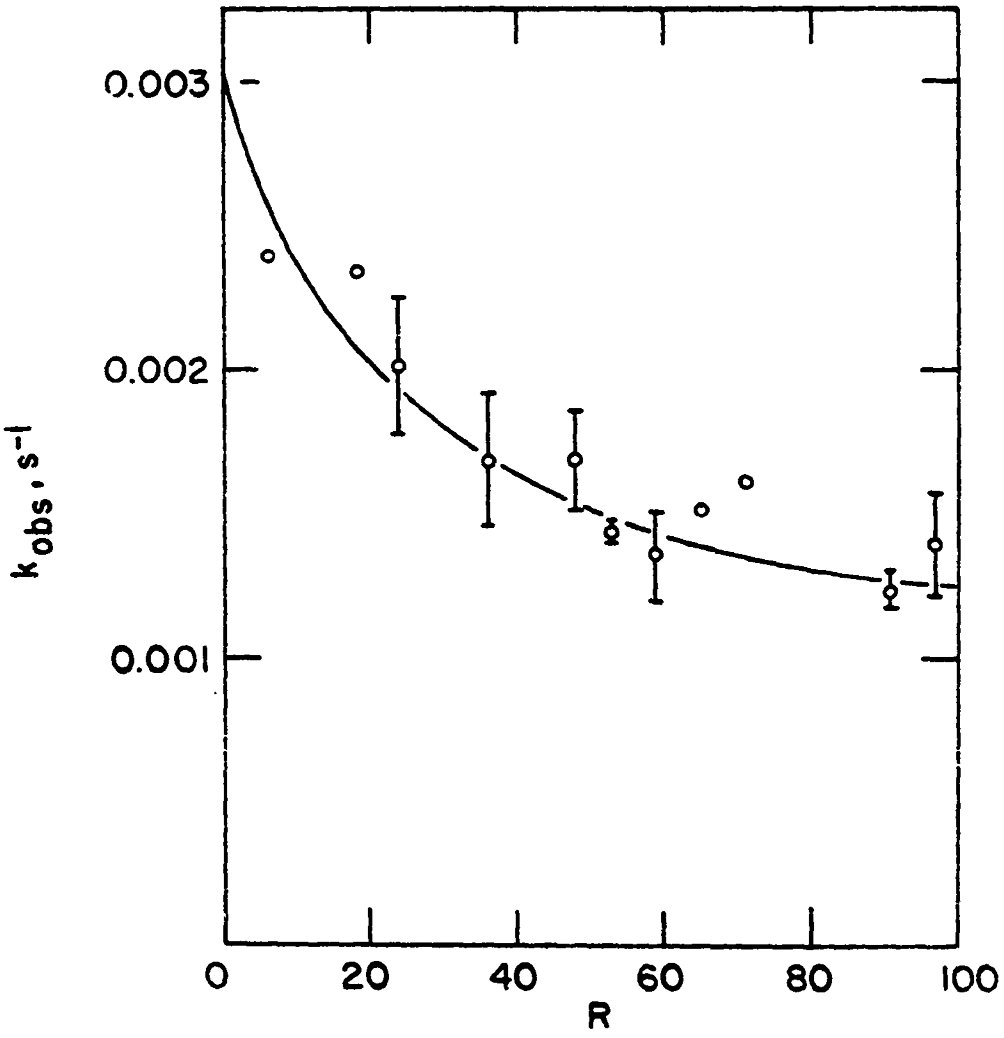


Figure 9. The variation of k_{obs} with R in phosphoric oxide-dried acetonitrile

Figure 9. The data are not so reproducible as would normally be expected of good kinetic data, and there are noted small trends in k_{obs} with the total concentration of halides in some of the data sets. These difficulties are believed to result from the water dependence for the following reasons:

1. k_{obs} depends quite strongly on the water concentration, as a comparison of data in Tables VI, VII, and VIII demonstrates. The comparison between Tables VII and VIII is particularly impressive, as solvent prepared by either method would normally be considered "dry".

2. Data from a number of reaction mixtures made up with a stock solution of tetraethylammonium bromide in undried solvent were not reproducible within the set or consistent with other data, the rates being somewhat larger than those noted when properly dried solvent was used.

3. All of the tetraethylammonium halides are hygroscopic, especially the chloride and fluoride, and the chloride at least can be obtained commercially as a monohydrate.[67] These observations suggest that the halides have some affinity for water and may prevent its complete removal during the pumping process.

4. At higher R values, when both reactions VIII and IX are important, k_{obs} depends on the pumping time and can be further reduced by distilling dry solvent onto the salts, dissolving them, distilling off the solvent, pumping on the salts

again, and distilling on more solvent. At high R, k_{obs} was dependent on the number of these "false starts" made before a run.

In order to explain the unusual halide dependence of reaction VIII and to obtain rate constants having more chemical significance, the data must be fit to a rate law and interpreted in terms of a mechanism. The data do impose certain restrictions on the choices: k_{obs} must be a function of R, not of individual concentrations, and k_{obs} must trend oppositely with the halide concentrations; in particular, retardation by a reactant must be explained. It is apparent from eq 2 and 3 that the associative and interchange mechanisms cannot be applied, but eq 4 suggests that a dissociative mechanism, or at least a mechanism in which chloride is lost before bromide reacts (and saying nothing about the role of water in the system for the moment), can be used to explain the data. The general form of the rate law, eq 4, becomes eq 13 for this system. This equation can be converted to a function of R by

$$k_{obs} = \frac{k_1k_3[Br^-] + k_2k_4[Cl^-]}{k_3[Br^-] + k_2[Cl^-]} \qquad (13)$$

dividing numerator and denominator by $[Cl^-]$. This gives eq 14.

$$k_{obs} = \frac{k_1k_3R + k_2k_4}{k_3R + k_2} \qquad (14)$$

That this form also explains the direction of the dependence of

k_{obs} on R is best demonstrated by differentiating eq 13 with respect to the concentrations, to give eq 15 and 16. Although

$$\left(\frac{\partial k_{obs}}{\partial[Br^-]}\right)_{[Cl^-]} = \frac{k_2k_3[Cl^-]}{\{k_3[Br^-]+k_2[Cl^-]\}^2}(k_1-k_4) \qquad (15)$$

$$\left(\frac{\partial k_{obs}}{\partial[Cl^-]}\right)_{[Br^-]} = \frac{k_2k_3[Br^-]}{\{k_3[Br^-]+k_2[Cl^-]\}^2}(k_4-k_1) \qquad (16)$$

the derivatives are both written in the positive sense, it is apparent that both derivatives cannot be positive because the signs of the difference terms are opposite in the two equations. The equilibrium constant of 0.011 indicates the greater stability of a rhenium-chlorine bond compared to a rhenium-bromine bond. Therefore the rhenium-bromine bond should break more readily than the rhenium-chlorine bond, making k_4 larger than k_1 and producing the rather novel concentration dependences observed.

More visual evidence that this model is basically correct was provided by simulation on an analog computer. This computer passes an electrical signal, used to represent a function or a variable, through circuitry which allows addition, integration, and other mathematical operations to be performed, and displays the output solution as a function of time in any of several ways. For use in chemical kinetics, the basic input corresponds to the differential equation for concentration with time, the output to the concentration itself. The application of analog computers to chemical kinetics has been recently reviewed by Crossley and Slifkin.[68]

To apply this computer to this reaction, the dissociative mechanism was recast under conditions of high halide concen-

$$Re_2Cl_2 \underset{k_2[Cl^-]}{\overset{k_1}{\rightleftarrows}} Re_2Cl^+ \underset{k_4}{\overset{k_3[Br^-]}{\rightleftarrows}} Re_2ClBr$$

trations to the system

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \underset{k_4}{\overset{k_3'}{\rightleftarrows}} C$$

The differential equations describing this system are

$$-\frac{d[A]}{dt} = k_1[A] - k_2'[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2'[B] - k_3'[B] + k_4[C]$$

$$\frac{d[C]}{dt} = k_3'[B] - k_4[C]$$

These were programmed as shown in Figure 10. The system was simulated by setting Cl^- at 1, holding k_2' constant at some arbitrary value, and varying k_3', corresponding to a variation in Br^-, and, correspondingly, in R. Since the problem is rather 'slow', i.e., the rate constants are rather small and the resulting real time solution slow, both k_1 and k_4 were increased by a factor of 10; to maintain k_2' and k_3' as reasonably large numbers relative to k_1 and k_4, amplifier gains of

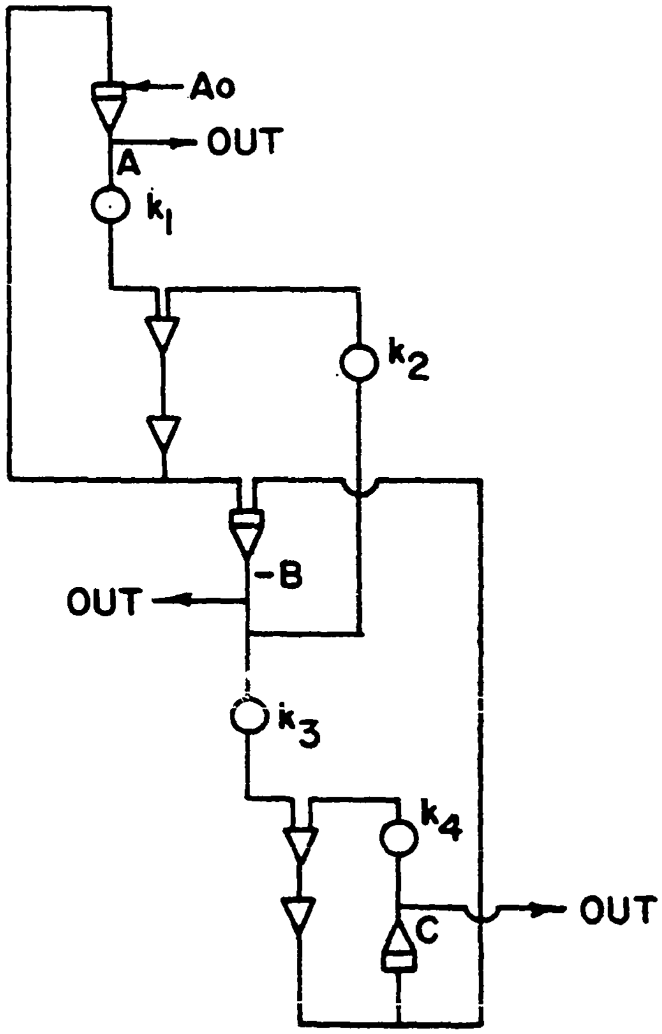


Figure 10. The analog program for the system $A \underset{2}{\overset{1}{\rightleftarrows}} B \underset{4}{\overset{3}{\rightleftarrows}} C$

10 instead of 1 were used for their inputs to the summers. The simulation was set up to learn if the system would reproduce values of k_{obs} under known steady state conditions and whether the concentration trends could be reproduced. The data and results are given in Table IX.

Table IX

Analog Simulation Results

R	k_1, s^{-1}[a]	k_2', s^{-1}	k_3', s^{-1}	k_4, s^{-1}[a]	k_{in}[b]	k_{out}[c]	k_{exp}[d]
10	0.0008	0.250	0.102	0.0030	0.00236	0.00271	0.00238
20	0.0008	0.250	0.205	0.0030	0.00201	0.00202	0.00205
40	0.0008	0.250	0.410	0.0030	0.00163	0.00170	0.00166
60	0.0008	0.250	0.615	0.0030	0.00143	0.00158	0.00145
80	0.0008	0.250	0.820	0.0030	0.00131	0.00140	0.00131

[a] In order to scale the problem for a reasonable time of solution and to allow k_1 to be set on the potentiometer, k_1 and k_4 were scaled up by a factor of 10 during the simulation.

[b] k_{in} is the first-order rate constant, calculated from eq 4 by assuming $[Cl^-]=1$, $[Br^-]=R$, $k_2=0.250\ M^{-1}s^{-1}$, and $k_3=.01025\ M^{-1}s^{-1}$.

[c] k_{out} is the first-order rate constant measured from a plot of $\ln|A-A_\infty|$ vs t.

[d] k_{exp} is the best value of k_{obs} for the R values as obtained from a fit of the data in Table VIII to eq 18. Small differences between these entries and k_{in} reflects roundoff error.

The data indicate that the concentration dependences can be reproduced quite well, and the values of k_{obs} calculated under known steady-state conditions do agree within reason with values measured experimentally, suggesting that the steady-state approximation is proper in this system. Some early trials with data from the sieve experiments indicated that reversing k_1 and k_4 values leads to a reversal of the concentration dependences. Simulation under those conditions gave slightly better fits with experimental data, partly because potentiometers could be set more precisely. (The k_1 potentiometer is only accurate to 1 part in 8!)

It is not possible to obtain all four rate constants from eq 13, as only three constants are independent. It is possible to get k_1, the rate constant for the loss of Cl^-, k_4, the rate constant for the loss of Br^-, and k_3/k_2, which measures the relative rates at which the halides react with the intermediate. These parameters were obtained by a digital computer fit. For these calculations, eq 13 can be cast into two useful forms. Eq 17 assumes that only raw rate data (Table VIII) are available, while eq 18 contains the equilibrium constant explicitly. The rate data were fit to both forms; the calculated

$$k_{obs} = \frac{aR + b}{cR + 1} \tag{17}$$

$$k_{obs} = \frac{K_{VIII}R + 1}{(K_{VIII}/k_1)R + (1/k_4)} \tag{18}$$

rate constants are given in Table X, with uncertainties of one standard deviation. The similarity of the values suggests that the given description of the system is basically correct. However, the uncertainty in the fits is very large, especially in the fit to eq 17 where three variables are important. This difficulty is thought to arise from the combination of a

Table X

Fitted Rate Parameters[a]

Parameter	Eq 17 Fit	Eq 18 Fit
k_4	$2.85 \pm 0.34 \times 10^{-3} s^{-1}$	$3.03 \pm 0.25 \times 10^{-3} s^{-1}$
k_3/k_2	$2.8 \pm 1.7 \times 10^{-2}$	$4.1 \pm 0.6 \times 10^{-2}$
k_1	$0.6 \pm 0.8 \times 10^{-3} s^{-1}$	$0.81 \pm 0.07 \times 10^{-3} s^{-1}$

[a] Data of Table VIII.

relatively small change in k_{obs} (a factor of <3 when R varies by a factor of 15) and the large experimental uncertainty resulting from the water dependence. Considering these problems the results are in satisfactory agreement.

Some alternative mechanisms were considered. Ion-pair formation between tetraethylammonium ion and halide ions, reaction X, is known to occur in acetonitrile solution. For

$$Et_4N^+ + X^- = Et_4N^+ \cdot X^- \qquad (X)$$

the bromide, a value of the ion-pair formation constant of 14.5 M^{-1} has been reported.[69] Reliable numbers do not seem to be available for the chloride, but a number of *ca.* 100 would not be too unreasonable.[70] Under typical concentrations in this study, approximately 10% of the bromide salt and possibly half of the chloride salt would exist as ion pairs. If the ion pairs are not reactive, a correction should be applied for their concentration. For an interchange mechanism, the rate law would become

$$k_{obs} = \frac{k_1[Br^-]_T}{1 + K_{IP_{Br}}[Et_4N^+]} + \frac{k_2[Cl^-]_T}{1 + K_{IP_{Cl}}[Et_4N^+]} \qquad (19)$$

The apparent retardation by bromide would result from an increase in the tetraethylammonium ion concentration. This mechanism is disfavored because the ionic tetraethylammonium perchlorate does not retard the reaction at high concentration. The ion pairs are probably sufficiently reactive so that their formation does not retard the reaction appreciably.

The reaction was measured as a function of added water concentration. The data are listed in Table XI and plotted as k_{obs} vs. $[H_2O]$ in Figure 11. The plot shows why small changes in the water content of the solutions have such large rate effects. The data at 5% water fall somewhat above the linear relationship between k_{obs} and H_2O. This may be a definite chemical effect or a medium effect; in view of the stability problem, it was not pursued further.

The catalytic effect of a number of neutral molecules was studied. The molecules chosen included acetamide and urea, which are oxygen donors[71] and hydrogen bonders like water, DMF and TMU, which have lost their hydrogen bonding ability because of alkyl substitution, THF, which is also an oxygen donor but a somewhat weaker base than most of the other molecules, pyridine, a much stronger base than the other molecules, and propionitrile, which is a model for the solvent acetonitrile. Rate data for these molecules are also given in Table XI and

Table XI

Rate Data in the Presence of Neutral Catalysts

Catalyst	10^2[Catalyst],M	10^3k_{obs},s^{-1}[a]
H_2O	0.65	4.79
	0.87	14.0
	1.1	9.7
	1.4	14.2
	1.9	16.7
	2.2	19.2
	2.4	23.7
py	0.54	8.1
	0.85	11.8
	0.87	7.2
	1.46	12.2
	1.51	18.0
	1.56	13.8
	1.82	13.5
	2.20	17.6
	2.30	27.1
	2.50	19.4
Urea	0.256	4.50
	0.377	3.78
	0.511	4.47
	0.795	5.21
	0.842	4.79[b]
	0.853	7.62[c]
	0.866	5.36
	1.28	7.0
	1.43	7.9
	1.47	7.2
	2.10	11.2
	2.90	13.5
DMF	1.72	3.17
	1.96	3.42
	3.64	5.88
	5.78	7.4

[a] Measured at 25° in P_2O_5-dried acetonitrile: R = 48 except where noted.

[b] R = 96.

[c] R = 25.

Table XI (continued)

Catalyst	10^2[Catalyst],M	10^3k_{obs},S^{-1}[a]
Acetamide	0.92	2.25
	1.61	2.42
	2.22	3.42
	2.82	3.38
	4.49	4.53
	6.47	5.90
TMU	3.05	2.91
	4.41	3.06
	8.26	5.02
THF	29.2	2.15
	57.5	2.55
	95.2	2.93
prnt	11.5	1.45
	26.0	1.66
	33.2	1.73

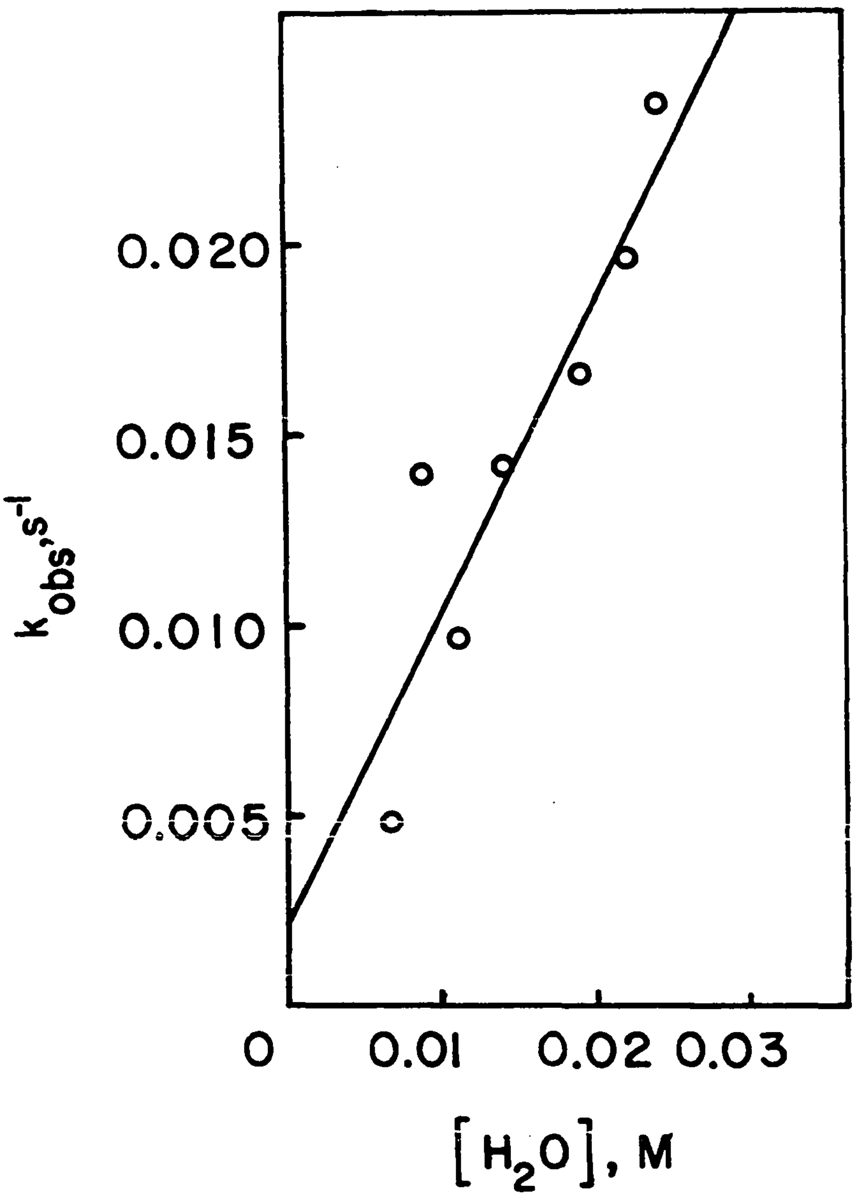


Figure 11. The dependence of k_{obs} on $[H_2O]$, measured at 25° in phosphoric oxide-dried acetonitrile with R=48

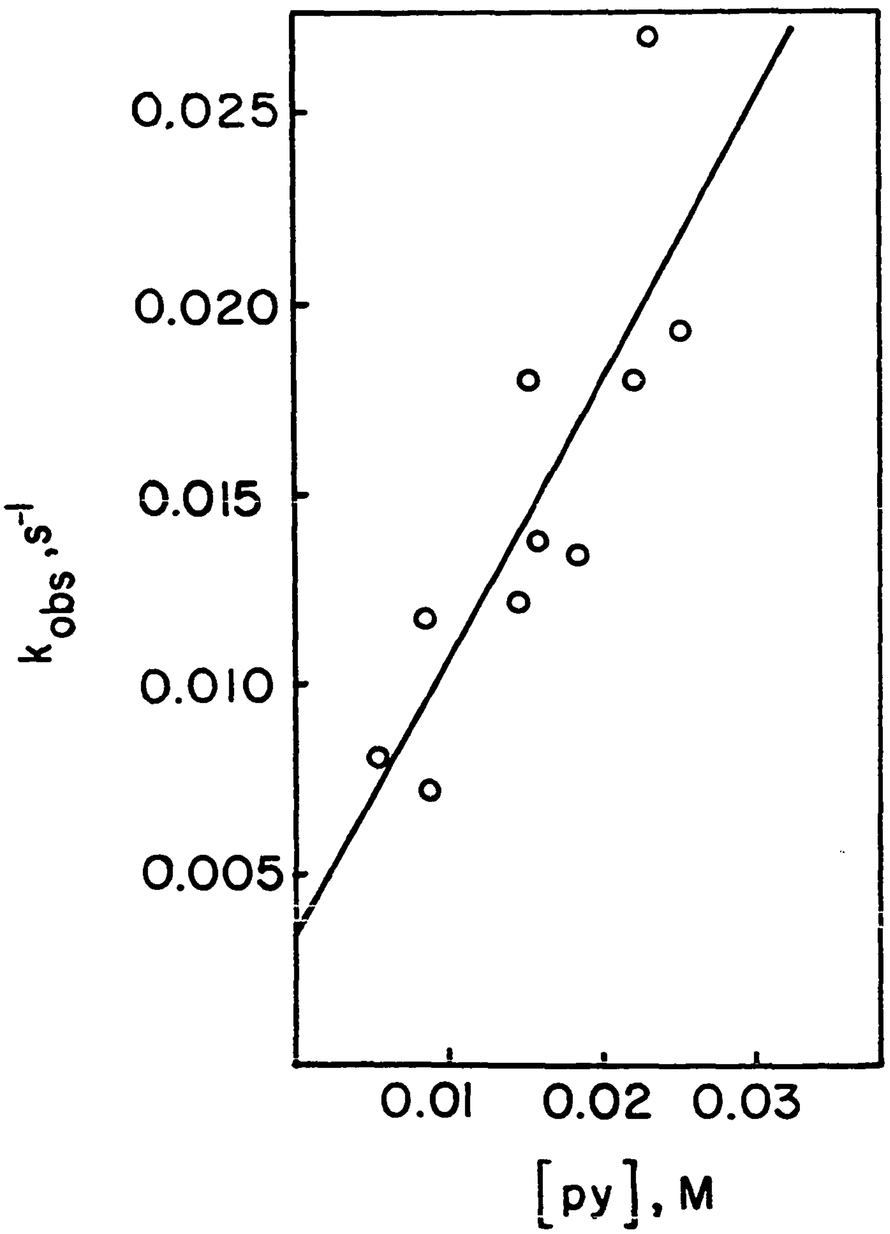


Figure 12. The dependence of k_{obs} on [py], measured at 25° in phosphoric oxide-dried acetonitrile with R=48

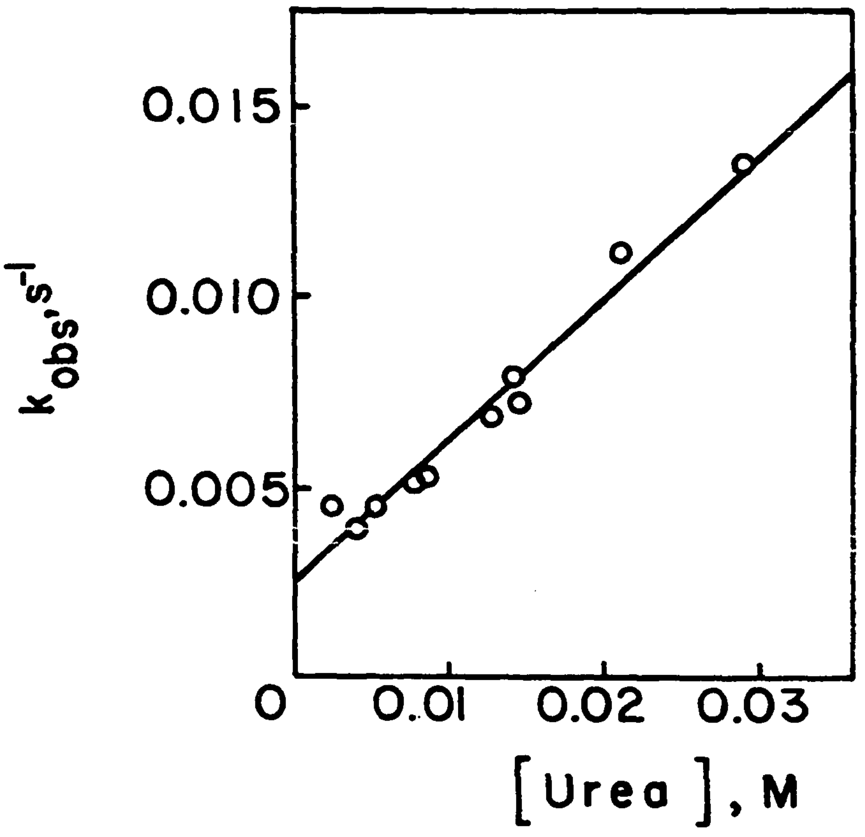


Figure 13. The dependence of k_{obs} on [urea], measured at 25° in phosphoric oxide-driec acetonitrile with R=48

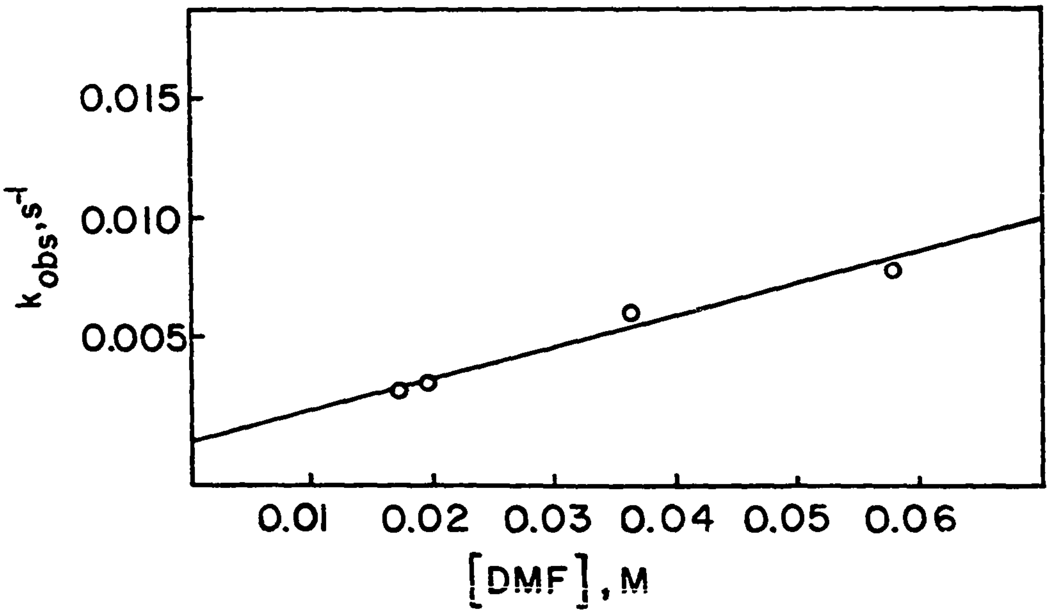


Figure 14. The dependence of k_{obs} on [DMF], measured at 25° in phosphoric oxide-dried acetonitrile with R=48

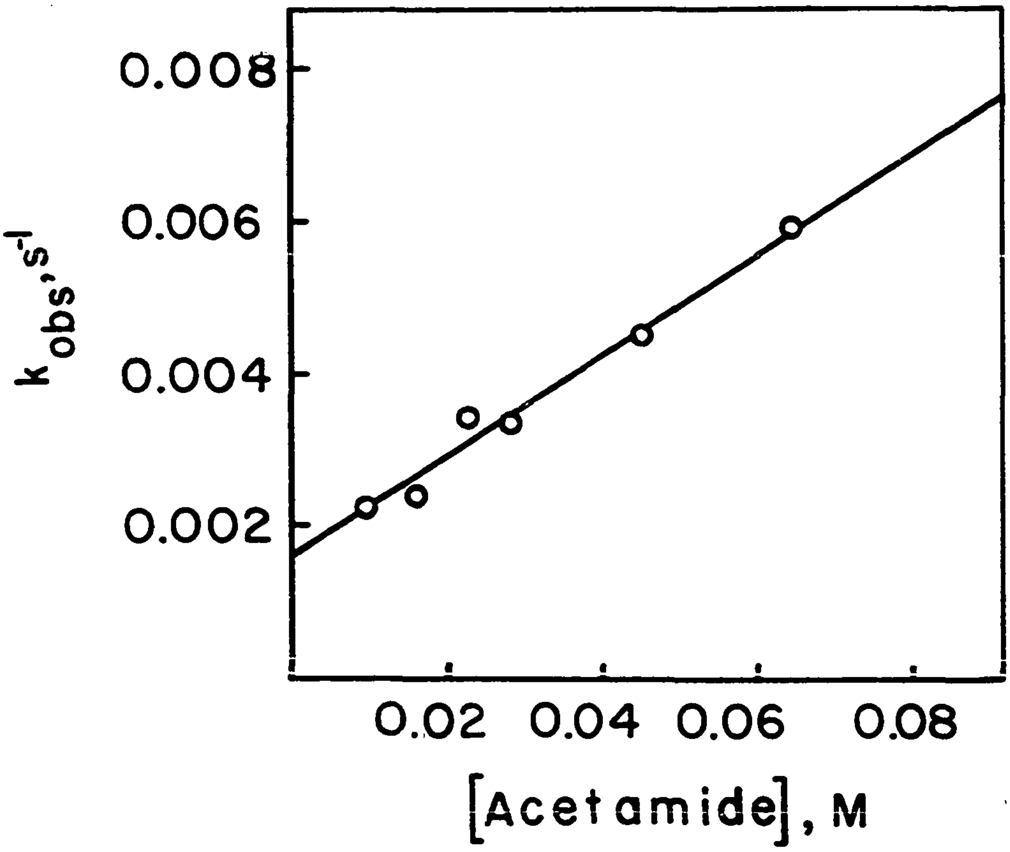


Figure 15. The dependence of k_{obs} on [acetamide], measured at 25° in phosphoric oxide-dried acetonitrile with R=48

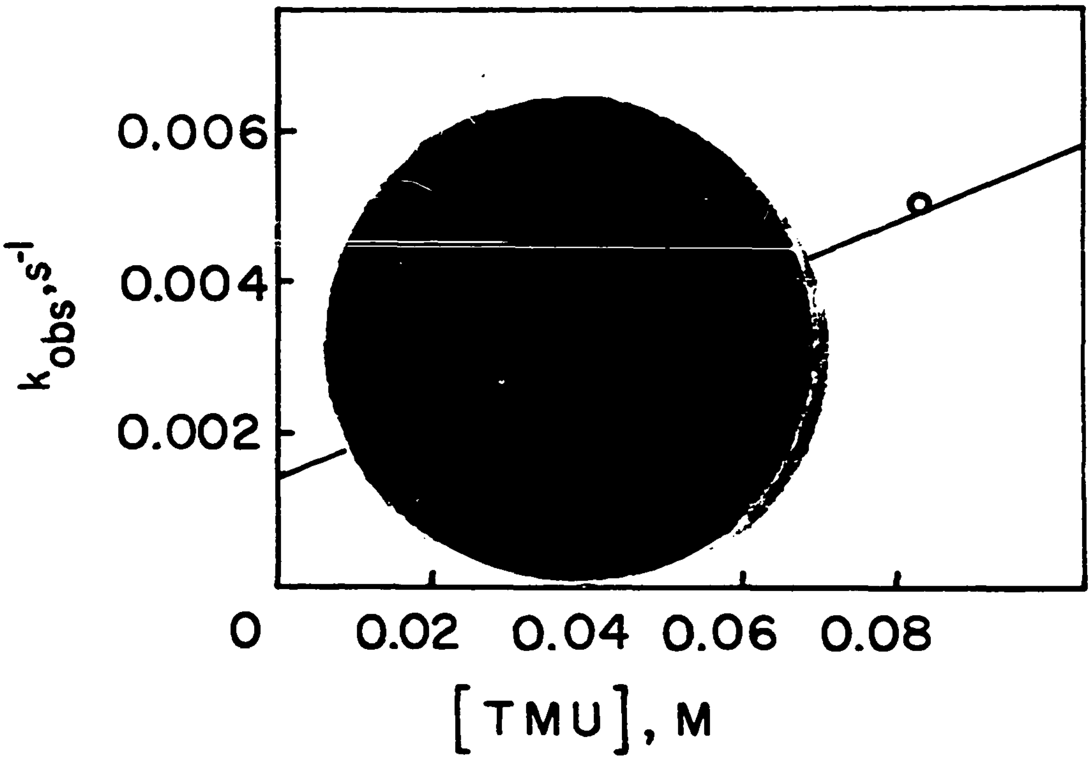


Figure 16. The dependence of k_{obs} on [TMU], measured at 25° in phosphoric oxide-dried acetonitrile with R=48

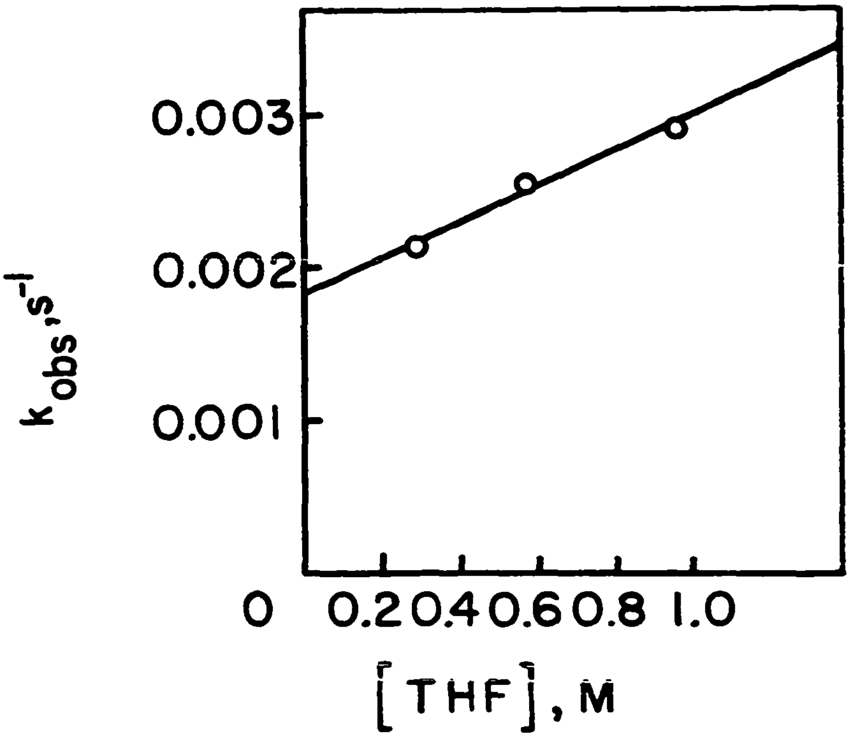


Figure 17. The dependence of k_{obs} on [THF], measured at 25° in phosphoric oxide-dried acetonitrile with $R=48$

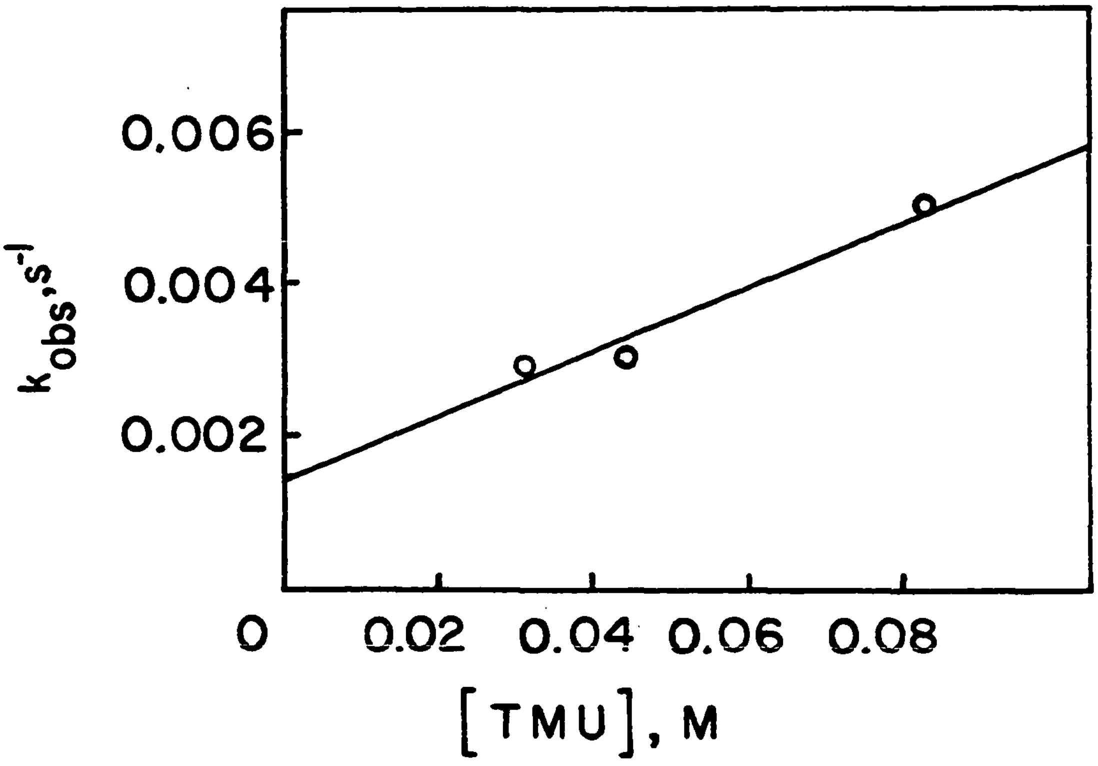


Figure 16. The dependence of k_{obs} on [TMU], measured at 25° in phosphoric oxide-dried acetonitrile with R=48

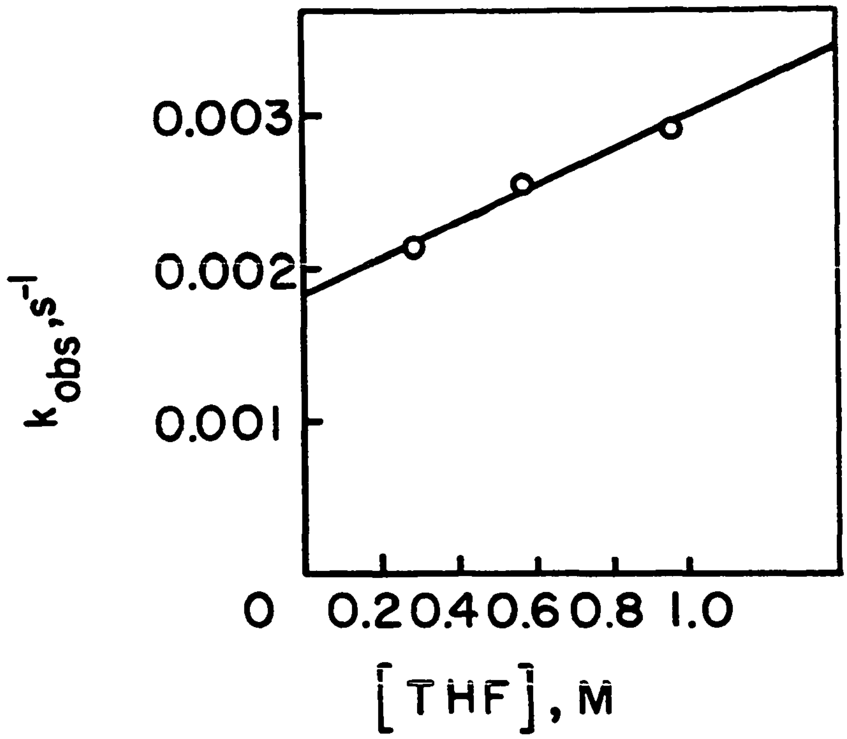


Figure 17. The dependence of k_{obs} on [THF], measured at 25° in phosphoric oxide-dried acetonitrile with R=48

and are plotted in Figures 12 to 17. The data were fit to eq 20, where S and I are the slope and intercept, respectively,

$$k_{obs} = S[L] + I \qquad (20)$$

of the plot of k_{obs} vs L, the concentration of added neutral molecules. Values of S and I are given in Table XII.

Table XII

Summary of Catalytic Data for Neutral Species

Catalyst	$S, M^{-1}s^{-1}$	$10^3 I, s^{-1}$
H_2O	0.83 ± 0.16	2.06 ± 2.68
py	0.74 ± 0.17	3.28 ± 2.92
Urea	0.40 ± 0.02	2.11 ± 0.30
DMF	0.105 ± 0.014	1.40 ± 0.50
Acetamide	0.066 ± 0.005	1.60 ± 0.17
TMU	0.043 ± 0.008	1.42 ± 0.47
THF	0.0012 ± 0.0001	1.83 ± 0.07
prnt	$\leq$0.0005	

The intercepts are common within experimental error. The slopes measure the catalytic strength of each molecule and fall off in the order $H_2O \sim$ py > urea > DMF > acetamide > TMU > THF > prnt, An. Although k_{obs} increases systematically with increasing concentration of propionitrile, the data are not outside the experimental scatter observed at this R value. The two urea experiments in which R was varied confirm that the halide dependence holds here also. It would be possible to make sufficient rate measurements to repeat the fitting procedure of eq 17 and 18, although this was not done. Dimethylsulfoxide was not studied because of its extremely sluggish rate of transfer on a vacuum line. Triethylamine was not employed because it reacted with the dichloro complex; the orange material turned green. This reaction is the only evidence of reaction of any of the neutral species tested with the rhenium complex. A diaquo complex[27,36] and a bis-pyridine[72] complex are known but their formation requires more forcing conditions than were used in these studies. The green complex could be a di-amine complex, analogous to the other two. In all other cases, the product of reaction was the chlorobromo complex.

Kinetics with Iodide and Fluoride Ions. As a further check on the model, it should be possible to predict and verify the behavior of iodide and fluoride ions in a similar reaction. The iodide complex would be expected to be much less stable than the bromo and the fluoro complexes more stable than the chloro species. Some predictions about the rate can also be made. First, k_1 and k_2 should be the same, as they do not depend on the entering group. Second, k_3 should be smaller and k_4 larger for the iodide reaction than for the bromide reaction, based on the stability arguments. The reverse should be true for the fluoride reaction. The maximum rate constant for the iodide reaction would also be k_4 and the minimum k_1, so that the iodide reaction should be faster than the bromide. The maximum rate constant in a fluoro reaction should be k_1, so that the fluoride reaction should be slower than the bromide reaction and should show normal kinetic behavior, as opposed to the inverted behavior noted in the bromide reaction.

These expectations are not borne out particularly well. The iodide is quite unfavored by equilibrium as expected. The spectrum of the diiodotetrabutyrato has an intense maximum at 386 nm.[36] At an R of 300, a small peak formed at 350 nm, possibly indicating a chloroiodo complex. Estimating a molar absorptivity for this peak of _ca_. 15,000 M^{-1} cm^{-1}, it appeared that less than 10% of the dichloro complex had reacted. The measured rates were very slow, with very small absorbance changes. The rates were not reproducible and not particularly regular in all cases. It is fair to note that because of the non-uniform absorbance of the cell and the long mixing time, a small and rapid absorbance change (_ca_. 0.02 units in the initial 20 seconds) would have been missed.

Addition of traces of fluoride ion to the dichloro complex leads to its disappearance as manifested by the total loss of the 273 nm peak. The resulting spectrum has no discrete uv peak; only end absorption is noted. Spectrophotometric titrations of the system were ambiguous, in that it could not be determined whether there were two breaks or three. Reproducible kinetic data also could not be obtained, although it was noted that on increasing the fluoride concentration from 0.0002 to 0.002 M or decreasing the chloride concentration from 0.02 to 0.002 the reaction became too fast to measure in the vacuum cell.

The kinetic behavior is quite reminiscent of the problems noted in the preliminary experiments on the bromide reaction. The fluoride solutions do contain large amounts of water (about 50% more water than fluoride, by nmr) although this amount of water would probably be less than what is already present. It was noted during the course of experiments that the fluoride samples did not pump down so well on the vacuum line as did the other halides. The cause of this observation was not ascertained.

In order to learn more about the reaction apparently occurring with fluoride, an attempt was made to prepare authentic samples of the fluoro complexes. Tetrabutylammonium octachlorodirhenate was heated on a steam bath in a solution of KF in 50% HF under nitrogen (using polyethylene vessels) for ca. two hours. A solid was precipitated as a paste when trimethylamine in methanol was added; the colors of the solids obtained in several tries varied from blue to purple. The spectrum of one sample in methanolic HF solution had a maximum at 580 nm (compared to 690 for $Re_2Cl_8^{2-}$ and above 700 for $Re_2Br_8^{2-}$), but the spectra were not uniform from product to product. There was no discrete uv peak; the spectrum of $Re_2Cl_8^{2-}$ has two, at 250 and 300 nm. The crude solids could be converted to orange products by refluxing in acetic acid-acetic anhydride under nitrogen. The spectra of these materials in acetonitrile were devoid of uv peaks, only end absorbance being noted. It appears that these materials may be legitimate rhenium(III) complexes although their identity is still not settled. Until such time as the real octafluorodirhenate and the carboxylato fluorides are characterized, the nature of this system must be considered in doubt.

Reaction IX. A serious study of reaction IX was not attempted when the strong rate dependence on the sample treatment was noted, since these experiments would need to be carried out at fairly high R (several hundred) to maintain pseudo-first-order conditions and ensure that reaction IX was the only reaction of importance in the system. A few runs were made, however. The rates are similar to those expected for reaction VIII under similar concentration conditions. However, they are not considered too significant in view of the water dependence.

DISCUSSION

Equilibrium Constant. The measured value of K_{VIII} is

$$Re_2Cl_2 + Br^- = Re_2ClBr + Cl^- \qquad (VIII)$$

0.011 ± 0.001 at 25° in acetonitrile. The equilibrium constant for any transanation reaction, of which VIII is an example, will depend on the bonding preferences of the reacting site and on the solvation energies of the various species involved in the reaction. The solvation energies of the rhenium complexes should be fairly similar, but the solvation energy of bromide ion will be greater than that of chloride ion; because of the large ion-acetonitrile interaction resulting from the mutual polarizability, a larger more polarizable anion is better solvated than a smaller, harder one.[70] In this respect acetonitrile differs from such hydrogen-bonding solvents as water and methanol, for which the order of solvation would be opposed to that seen here.[70] Since the direction of the equilibrium is that expected on a solvation argument alone, it is reasonable to ask whether this result is only a solvent effect. Although a direct answer cannot be given, since K_{VIII} was not determined in other solvents, the observations of the stabilities of the parent octachloro and octabromodirhenates relative to decomposition in acidified methanol[44] offers indirect support to the view that the dirhenium complexes bind chloride ion preferentially to bromide ion, so that solvation energies and binding energies do work in the same direction. However, it has been noted before that binding trends can be influenced by the other ligands in the complex;[73] in the presence of thio-carboxylates or cyanide ligands, the binding trends could well reverse. In this case, the observed stability order is influenced in the same direction by the metal core, the coligands, and the solvent in this system.

The Mechanism of Reaction VIII. The form of eq 13, the rate law for reaction VIII, has the form of an equation describing a purely dissociative mechanism. However, the observation of strong catalysis by the neutral molecules requires that such a conclusion be postponed for the moment. The form of the rate expression does require that chloride ion be lost before bromide enters. The linearity of the plots of k_{obs} vs the concentration of added catalyst requires that k_{obs} be first order in that catalyst. This is best explained by assuming that k_1 and k_4 are each first order in the catalyst concentration.

There are several possible explanations for this behavior. One possibility is that the catalysts interact with the anions to assist in their removal from the complex. This kind of electrophilic catalysis has parallels in aqueous chemistry of halo complexes, where silver or mercuric ions are effective in promoting reaction.[74] The most reasonable explanation for electrophilic catalysis in this system would be hydrogen bonding.[70] However, a glance at the data indicates that this explanation cannot be general, since pyridine and DMF, which cannot hydrogen bond to anions, are still effective catalysts. A second possibility is a general solvent effect, such as a change in bulk dielectric constant or solvent polarity, and a third is coordination to the metal site which has lost a halide. These possibilities must be considered in more detail.

Table XIII lists the observed slopes from Table XII and the dipole moments[75] and dielectric constants[76-80] of the neutral catalysts and pK_a values for their conjugate acids.[81-85] Except for the THF and propionitrile data, the rate effects seem rather large to be just medium effects, the more so when the low concentrations employed are considered. Particularly noticeable is the comparison between DMF and acetonitrile. The dipole moments and dielectric constants of the two molecules are very similar but their rate effects are rather different. The best correlation appears to be with ligand basicity. The correlation is not exact, but a comparison between the dirhenium core and the proton can hardly be exact. The basicity data, which were measured in aqueous sulfuric acid, almost certainly will not be identical to that found in acetonitrile. The most reasonable explanation for these results is that the neutral molecule occupies the vacated coordination site to form a "solvent" complex, as in reactions XII and XIII.

Table XIII

Comparison of Catalytic Constants with Solvent Properties

Catalyst	S,$M^{-1}s^{-1}$	Dipole Moment, D^a	Dielectric Constant	$pK_a{}^b$
H_2O	0.83	1.91	78^c	-1.7^d
py	0.74	2.22	12.3^e	$+4.7^f$
Urea	0.40	4.56		$+0.50^f$
DMF	0.105	3.86	36.7^g	$-0.70^{f,h}$
Acetamide	0.066	3.90		-1.4^h
TMU	0.043	3.49	23.1^g	$+0.40^f$
THF	0.0012	1.84	8.2^i	-2.08^j
Acetonitrile		3.56	37.5^k	-9.5^l

[a] All dipole moment data were taken from reference 75. All moments were reported in dioxane solution at 25° except for DMF, which was measured in benzene.

[b] Defined in terms of the reaction BH^+ $B+H^+$

[c] Reference 76.

[d] Reference 81.

[e] Reference 77.

[f] Reference 82.

[g] Reference 78.

[h] Reference 83.

[i] Reference 79.

[j] Reference 84.

[k] Reference 80.

[l] Reference 85.

$$\mathrm{ClRe{\equiv}ReCl + L \xrightleftharpoons[2]{1} ClRe{\equiv}ReL^{+} + Cl^{-}} \qquad \text{(XII)}$$

$$\mathrm{ClRe{\equiv}ReL^{+} + Br^{-} \xrightleftharpoons[4]{3} ClRe{\equiv}ReBr + L} \qquad \text{(XIII)}$$

The intermediacy of a solvent complex is quite common in the chemistry of transition metal complexes; reaction VI in aqueous solution is one famous example. Tobe and Watts[86] have summarized reactions of *cis-* and *trans*-$\mathrm{Co(en)_2Cl_2{}^+}$ in various solvents, considering solvolysis, exchange, and isomerization. In good coordinating solvents, solvolysis dominates, whereas in more weakly coordinating solvents, solvolysis is unimportant. Reaction VIII seems to proceed by a solvolytic pathway, although such solvents as DMF, which do not effectively solvolyze cobalt(III) complexes, are effective here. The change from a cationic cobalt complex to a neutral complex here may be partly responsible.

In view of the water dependence, it is interesting to ask whether the intercept noted in the catalytic data corresponds to the reaction in the absence of all water or in the presence of persisting traces of water, and what would happen were such presumed residual water quantitatively removed. No experimental proof can be offered, of course, but an examination of Figure 11 is interesting. The intercept on the concentration axis is *ca*. -0.003 M. If the reaction did not proceed at all in the absence of water, this concentration, 0.003 M, would be background concentration of water present in all runs in the vacuum cell. The total concentration of halide salts was typically 0.01-0.02 M. That these hygroscopic materials could retain 10-30 mole per cent water does not seem too unreasonable. The data allow neither outright rejection nor total acceptance of the interesting proposal that the reaction would not proceed at all in the absence of a donor catalyst. The observations on the water dependence made earlier indicate that the reaction which was measured does not correspond to the reaction in the absence of all water.

To this point the discussion of reaction VIII has dealt with the gross features of the mechanism--which molecules and ions are involved at which stage of reaction. The more interesting question of how reaction occurs in any given step has not been treated yet, but it is worth some consideration. The observation that each step obeys second-order kinetics is not particularly informative, because both A and I mechanisms would follow these kinetics. Any arguments must be based on extrakinetic evidence.

A good starting point is a comparison of the molecular and electronic structures of the dichloro complex with a square-planar platinum(II) complex and a trans-disubstituted "octahedral" complex. Simplified molecular orbital diagrams[87] are given in Figure 18. For the purposes of this thesis, π bonding has been ignored; its inclusion where appropriate would not affect the qualitative arguments to be advanced.

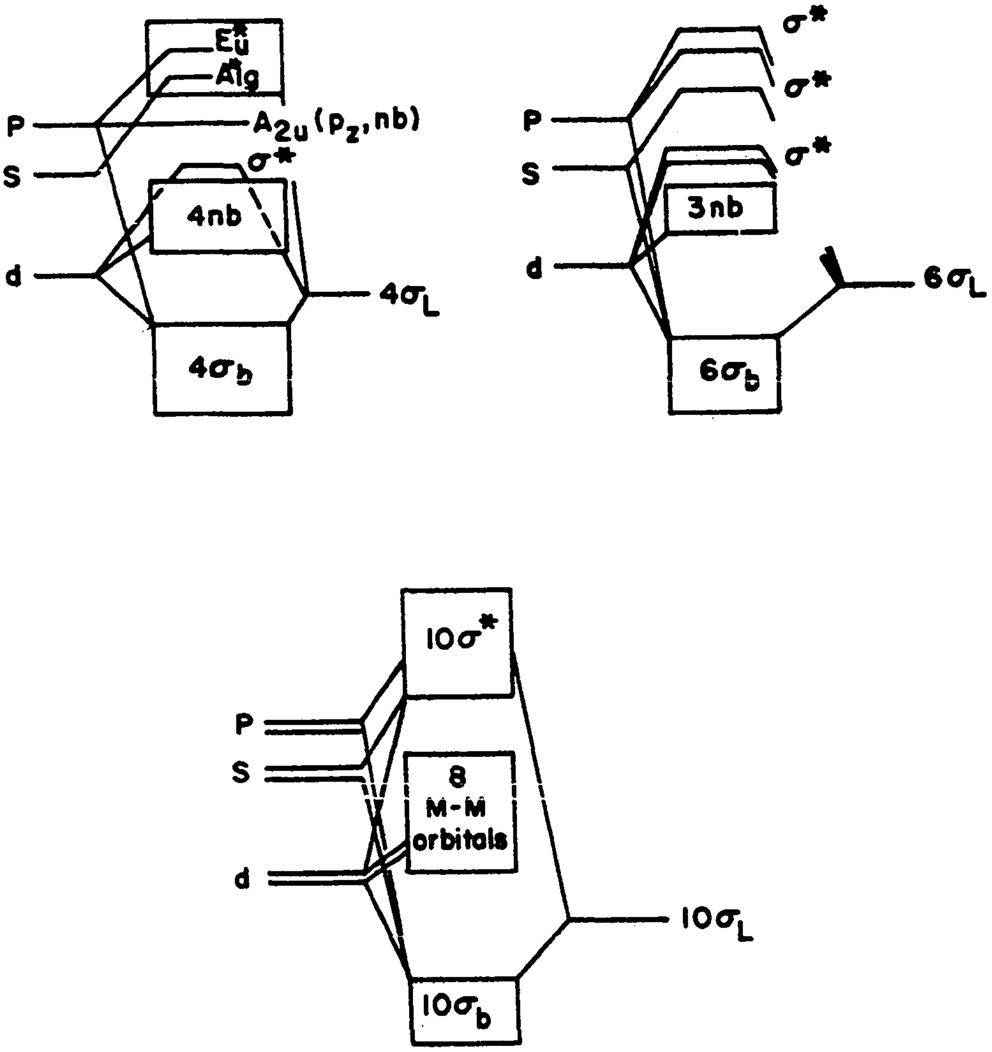


Figure 18. Simplified molecular orbital diagrams for tetragonal complexes: upper left, $Pt(NH_3)_4^{2+}$; upper right, trans-$Co(NH_3)_4Cl_2$; lower, $Re_2(C_2H_5CO_2)_4Cl_2$

The p_z orbital in the platinum complex is not used in σ bonding with the ligands; this orbital can help to bond with an entering group attacking from above or below the plane of ligands in the square complex. The combination of favorable stereochemistry and an available orbital should favor an associative mechanism. The p_z orbital in the six-coordinate complex is used in bonding, and there are no open coordination sites, unlike the situation in the square system. A dissociative mechanism of some sort should therefore be favored. The expectations based on these simple arguments are well documented experimentally. The bonding and stereochemistry of the rhenium complex resemble the six-coordinate complex and not the four-coordinate complex in that the p_z orbitals of the rhenium complex are used in metal-ligand binding and there is no open site for ligand attack. Therefore bond breaking should be favored over bond making.

Some information can be gleaned from the rate law and from a comparison of the catalysis data. Of importance is the fact that neutral donors accelerate (and may be required for) the reaction, although chloride and bromide are the most reactive nucleophiles in the system.[70] If bond making were of major importance, it would seem more reasonable that direct attack by bromide occur. The catalysis by neutral species may occur because the departing chloride repels anions in the vicinity of the reacting site more strongly than it repels neutral molecules. The relatively small spread in catalytic ability from water to TMU (less than a factor of 30) is more suggestive of bond breaking than bond making. This may explain why pyridine is only about as reactive as water despite its much greater basicity. The THF data were taken at much higher concentrations (up to 10% THF) than the other neutrals; at these levels some of the rate effect may be a measure of a change in the medium. From these considerations an I_d mechanism for the reaction would seem most reasonable.

It would be useful to confirm this model with other experiments. The failure of the fluoride and iodide systems to give useful data must be considered disappointing, although some of the problems noted were anticipated from the chloride-bromide results. Other potential anions for study would have been thiocyanate, azide, and nitrite. These ligands were not employed in the study because it did not appear possible to prepare solids or solutions of their quaternary ammonium salts sufficiently free of water, ammonia, or other presumably reactive impurities to allow the collection of meaningful data from the system. Similarly, although activation parameters can provide information about the mechanism, they are of less use when the gross temperature dependence must be apportioned among four rate constants, and are of still less use in cases where trace catalysis increases the uncertainty in rate data. One potentially interesting study would be a tracer experiment to measure the rate of halide exchange. If the model is correct, it should be possible to confirm that k_1 and k_4 are indeed first order in catalyst concentration. The experiment would appear to be thwarted for the moment because of the problem with sampling. A direct precipitation method in the cell (silver ion to remove chloride, for instance) would also remove halide from the complex,[36] and any effort to remove aliquots from the cell would allow the introduction of water vapor, leading to the probable failure of the experiment.

PART II. SOME ELECTRON TRANSFER REACTIONS OF NITROSYLPENTAAQUOCHROMIUM(III)

INTRODUCTION

Numerous studies of the oxidation and reduction of metal ions in such complexes as azidopentaamminecobalt(III) by other metal complexes have been reported since Taube and Myers'[88] studies in the early 1950's. Less attention has been paid to the reactions of the ligands in such complexes, but some studies of the oxidation of coordinated ligands have been made, and the reduction of ligands has been noted in a few instances.

A typical set of results is seen from a comparison of the reactions of cerium(IV) with free and coordinated oxalate. The oxidation of free oxalate[89] is described stoichiometrically by reaction XIV. Complex formation between cerium and oxalate

$$2\ \mathrm{Ce}^{IV} + \mathrm{C_2O_4^{2-}} \rightarrow 2\ \mathrm{Ce}^{III} + 2\ \mathrm{CO_2} \qquad \text{(XIV)}$$

was noted; the kinetic data support the scheme

$$\mathrm{Ce}^{IV} + 4\ \mathrm{C_2O_4^{2-}} = \mathrm{Ce(C_2O_4)_4^{4-}} \qquad \text{(XV)}$$

$$\mathrm{Ce(C_2O_4)_4^{4-}} \rightarrow \mathrm{Ce(C_2O_4)_2^{-}} + \mathrm{C_2O_4^{2-}} + \mathrm{C_2O_4^{-}} \qquad \text{(XVI)}$$

$$\mathrm{Ce(C_2O_4)_4^{4-}} + \mathrm{C_2O_4^{-}} \rightarrow \mathrm{Ce(C_2O_4)_2^{-}} + 2\ \mathrm{C_2O_4^{2-}} + 2\ \mathrm{CO_2} \qquad \text{(XVII)}$$

The important feature of this mechanism is the intermediacy of the oxalate radical anion. The reaction is quite rapid; under the conditions of the study, the reaction is complete in a few minutes.

The oxidation of some oxalatochromium(III) complexes by cerium(IV) has been described.[90] The reactions follow the general stoichiometry of reaction XVIII, which illustrates the

$$2\ \mathrm{Ce}^{IV} + \mathrm{Cr(C_2O_4)}^{+} \rightarrow 2\ \mathrm{Ce}^{III} + \mathrm{Cr}^{3+} + 2\ \mathrm{CO_2} \qquad \text{(XVIII)}$$

oxidation of the monooxalato complex. The kinetics support a mechanism similar to that found for the oxidation of free oxalate; the radical anion may remain as a ligand. The reaction is somewhat slower than the oxidation of free oxalate.

Something new is noted in the oxidation of oxalatopentaamminecobalt(III) with cerium(IV).[91] The stoichiometry is given by reaction XIX. The noteworthy feature is that only

$$\mathrm{Ce}^{IV} + \mathrm{Co(NH_3)_5(C_2O_4)}^{+} + 5\mathrm{H}^{+} \rightarrow \mathrm{Co}^{2+} + \mathrm{Ce}^{III} + 5\mathrm{NH_4^{+}} + 2\ \mathrm{CO_2} \qquad \text{(XIX)}$$

one equivalent of cerium is consumed in the reaction; the cobalt(III) center is also reduced in the reaction. The reaction requires many hours for completion but no kinetics were measured.

A comparison of the results from these three studies indicates general results common to many similar reactions. In particular, the oxidation of free and coordinated ligands with a particular oxidizing agent occur by similar mechanisms, with the oxidation of the coordinated ligand being somewhat slower than that of the free ligand. The stoichiometry of the reaction is sensitive to the metal core in the complex; if the metal is reducible, there is a possibility for reduction of the core. The difference noted between the cobalt and chromium complexes can readily be explained on the basis of the reduction potentials of cobalt(III) and chromium(III) complexes, for which typical data[92] are given below. In general, cobalt(III) is much more susceptible to reduction than is chromium(III).

$$Co(NH_3)_6^{3+} + e^- \rightarrow Co(NH_3)_6^{2+} \qquad E^o = 0.1 \text{ v}$$

$$Cr^{3+} + e^- \rightarrow Cr^{2+} \qquad E^o = -0.43 \text{ v}$$

Haim and Taube have studied the oxidation of iodopentaamminecobalt(III) by several oxidants, both one-electron reagents[93] such as cerium(IV) and two-electron reagents[94] such as chlorine. The two-electron reagents produce cobalt(III) complexes. However, cerium oxidation produces equal amounts of cobalt(III) and cobalt(II) products. These results were interpreted[93] in terms of a mechanism in which iodine atoms

$$Co\text{-}I^{2+} + Ce^{IV} \rightarrow Co\text{-}OH_2^{3+} + Ce^{III} + I\cdot \qquad \text{(XX)}$$

$$I\cdot + Co\text{-}I^{2+} \rightarrow I_2 + Co^{2+} \qquad \text{(XXI)}$$

are produced. If radical species are generated externally, for instance on addition of ferrous ion to hydrogen peroxide, yields of cobaltous in the oxidation reaction approach 100%. Ozone and persulfate, which normally react with the iodo complex to give cobalt(III) complexes, can also be diverted to the radical reaction by adding Fe(II).

In some systems, mixed products are observed, characteristic of competition for an intermediate. The oxidation of formatopentaamminecobalt(III)[95] with permanganate obeys simple second-order kinetics. Two products are noted - cobaltous and the aquo complex - in a ratio $Co^{III}/Co^{II} = 300(MnO_4^-)$. The intermediate in this system is more stable than that noted in the cerium oxidation of the oxalato complex, which produces only cobaltous. Similar results have been noted in the oxidation of the corresponding isothiocyanato complex with hydrogen peroxide,[96] in which internal electron transfer competes with acid hydrolysis.

Somewhat fewer reactions of chromium(III) complexes have been studied. The iodopentaaquo complex reacts with hydrogen peroxide and iron(III) at rates sufficiently close to the aquation rate of the complex that it cannot be said definitely that either oxidant does in fact react with bound iodide at all.[97] Other studies are lacking, probably because of the lack of the interesting redox behavior noted for the cobalt complexes.

Reduction of bound ligands has been noted in a few systems. Gould[98] has reported that in the reaction of pentaamminecobalt(III) complexes of easily reduced organic ligands with chromium(II), there are instances in which preferential reduction of the ligand occurs. Ligands containing nitro or azo groups sometimes react in such a manner.

A potentially interesting ligand for oxidation and reduction reactions is nitric oxide, which can be converted to a number of products. Several "inert" cobalt and chromium nitrosyls have been reported, including a nitrosyl pentaaquo complex of chromium,[99] pentaammine[100,101] and pentacyano complexes[102,103] of both metals, and chlorobis-ethylenediamine and bis-o-phenylenebis(dimethylarsine) complexes of cobalt,[104] as well as a few β-diketone[105] and related[106] cobalt complexes. There have been a few studies of ligand exchange in the chromium series; several reactions of the sort illustrated in reaction XXII have been noted.[100,107] However, most studies of

$$Cr(X)_5NO + 5\ Y \rightarrow Cr(Y)_5NO + 5\ X \qquad \text{(XXII)}$$

these complexes have been investigations into the molecular and electronic structures of the complexes, in order to understand the nitrosyl-metal bond. The major interest in nitrosyl complexes is whether a given complex, such as $Cr(H_2O)_5NO^{2+}$, should be regarded as a complex Cr^{I}-NO^{+}, Cr^{II}-NO^{o}, or Cr^{III}-NO^{-}, or whether the question of electron distribution has any meaning at all. Early discussions were based on the crystal structures and ir data. Complexes of NO^{+} were expected to have linear M-NO units and high (1660-1940 cm^{-1}) N-O stretching frequencies, while complexes of NO^{-} were expected to have bent M-NO units with low (1000-1200 cm^{-1}) N-O stretching frequencies.[108,109] The original infrared criteria have since been shown to be wrong,[110] and recent arguments by Pierpont and Eisenberg[108] suggest that the structure observed for a given complex is a function of the number of electrons present in the complex and not of their distribution. Feltham and Nyholm[104] have argued that the cobalt nitrosyl ammine and arsine complexes should be considered as Co^{III} complexes. The chromium complexes have been quite thoroughly discussed, with fewer conclusions drawn. Structural work[111] indicates that the Cr-NO unit is linear in the pentacyano complex (and presumably in the related ammine and aquo complexes as well), and epr[112,113] and magnetic[100] data indicate that one unpaired electron is present in these complexes. These facts have been interpreted in terms of Cr^{I}. Four of the "d" electrons reside in a set of bonding orbitals made up of the $d_{xz,yz}$ pair on chromium and the π^* orbitals on NO,[114] but any degree of interaction equal to or greater than that needed to pair spins is consistent with the data. The x-ray photoelectron spectrum of the Cr 3p level in the pentacyano complex[115] suggests that the charge at chromium is similar to that in the bona fide Cr(III) complex $Cr(CN)_6^{3-}$. The chemistry of the aquo complex favors its designation as Cr(III). The complex can be made by the reaction of chromous ion with nitric acid, as in reaction XXIII. There is a further reaction of chromous with the nitrosylpentaaquo complex which gives chromium(III) products and reduced nitrogen species.[99] The chromium(III) label will be used for $CrNO^{2+}$ in further discussion, with the note that it is a label and not necessarily a statement of complete chemical

$$4\ Cr^{2+} + HNO_3 + 3\ H^+ \rightarrow 3\ Cr^{3+} + CrNO^{2+} + 2\ H_2O \qquad \text{(XXIII)}$$

truth.

Of the possible complexes, the nitrosylpentaaquochromium(III) ion appeared to be the most interesting complex for several reasons. First, it is stable in the acidic solutions required by several of the oxidizing agents used in the study. Several of the cobalt nitrosyls are decomposed by acid,[101,105,106] and the stabilities of the others could therefore be questioned. Second, in perchloric acid there will be no side reactions of the type illustrated by reaction XXII. Third, chromium will probably not participate in the oxidations in the manner noted in many cobalt systems.

There are some added interests. If a chromium(II) intermediate is involved in the oxidation process, it should be detected in the products of the reaction. Several oxidants, including molecular oxygen, oxidize chromous to the green hydrolytic dimer of chromium(III),[116] $Cr(OH)_2Cr^{4+}$. The absence of the dimer would suggest that chromium(II) was not involved in a particular reaction. This may allow more to be said about the apparent oxidation states in the complexes. A second interesting prospect is the possibility of a linkage isomerization. The pair of complexes $CrNCS^{2+}$ and its less stable isomer $CrSCN^{2+}$ have been well studied.[117] Linkage isomerization of CN^- has been noted in reactions of chromium[118] and cobalt[119] complexes. Coordinated nitrite can be found as both the N-bonded (nitro) and O-bonded (nitrito) forms. Although both isomers are known in many cobalt complexes, only a few chromium complexes are known, these being almost exclusively nitrito complexes, which decompose in acid.[120] It would be interesting to make the nitrochromium(III) complex, which might be expected to form if $CrNO^{2+}$ were treated with an oxidant which donates an oxygen atom, as in reaction XXIV.

$$CrNO^{2+} + [O] \rightarrow CrNO_2^{2+} \qquad \text{(XXIV)}$$

The chemistry and spectroscopy of a nitro complex would be an interesting addition to the body of knowledge of chromium(III) chemistry.

A survey of the oxidation and reduction of $Cr(H_2O)_5NO^{2+}$ in perchloric acid was begun to learn what reactions occur and to study kinetically any that appeared interesting.

EXPERIMENTAL

Materials. Hexaaquochromium(III) perchlorate was prepared by reducing chromium(VI) with hydrogen peroxide in perchloric acid. 130 g chromium trioxide were dissolved in 70 ml of water and 400 ml of concentrated perchloric acid were added. The mixture was cooled in an ice bath. Hydrogen peroxide was added dropwise until the reddish color of chromium (VI) was no longer apparent and no effervescence was noted upon the addition of more peroxide. The solution was boiled to remove excess peroxide and to reduce the volume of the solution. Heating was continued until samples withdrawn from the solution crystallized on scratching the sides of the vessel and cooling to room temperature. The solution was then allowed to cool slowly to room temperature. The solution was seeded with crystals of chromic perchlorate until such time as crystallization was induced. The product supersaturates quite badly; if the product precipitated as a mushy solid because of too rapid cooling, water was added to dissolve it and the crystallization procedure was repeated. The product was recrystallized once from conductivity water.

No effort was made to analyze the solid because the crystals, although often large and very well formed, are not pure hexaaquochromium(III) perchlorate; they also contain water and perchloric acid. A solution of these crystals which is 0.1 M in chromic ion is also typically 0.1 M in acid.

Solutions of the oxygen-sensitive chromium(II) perchlorate were prepared by reducing acidic chromium(III) perchlorate solutions electrolytically at a mercury pool cathode. Oxygen was produced at the platinum anode, which was contained inside a glass tube terminating in a sintered glass disk. The tube was filled with 1 M perchloric acid and set partially in the solution. This effectively separates the incompatible oxidation product, oxygen, from the desired reduction product, chromium(II). The electrolysis was carried out under nitrogen in a three-necked flask or a separatory funnel. The electrolysis vessel was cooled with an ice bath or cold towels; if the solution becomes too warm, some reduction of perchlorate will occur. For use in quick, bench-top experiments, chromium(II) was prepared by reducing chromium(III) perchlorate solutions with amalgamated zinc under nitrogen.

Nitric oxide was generated as needed by the reaction of ferrous ion with nitrous acid. A saturated solution of sodium nitrite in water was dripped into a mixture of a ferrous salt (usually the sulfate) and 6 M sulfuric acid, with quantities chosen to prepare _ca._ 5 moles of nitric oxide per mole of chromous. Some solid ferrous sulfate was present at the start of all preparations; its presence is not harmful, and during the course of the synthesis it dissolves. The mixture was stirred with a magnetic stirring bar. The product NO reacts with oxygen to form brown NO_2; the vessel and NO line were flushed with nitrogen before gas generation began.

Nitrosylpentaaquochromium(III) was prepared in several ways. The simplest experimentally was the nitric acid reaction,[99] described by reaction XXIII, in which a volume of

$$4\ Cr^{2+} + HNO_3 + 3\ H^+ \rightarrow CrNO^{2+} + 3\ Cr^{3+} + 2\ H_2O \qquad (XXIII)$$

chromium(II) solution was added under nitrogen slowly to a well-stirred solution of nitric acid of similar volume and concentration to the chromium(II) solution. The most used method was the reaction with nitric oxide, reaction XXV. A gas delivery system was set up consisting of a three-necked flask

$$Cr^{2+} + NO \rightarrow CrNO^{2+} \qquad (XXV)$$

for the generation of nitric oxide, a base trap containing 2 M sodium hydroxide solution to remove NO_2, and the reaction vessel, a three-necked flask fitted with a gas bubbler, an addition funnel or stopper, and a gas outlet tube connected to a safety trap and a mineral oil bubbler. The contents of the flask were stirred magnetically. If the chromium(II) solution was not prepared in the reaction flask, the flask was charged with 200 ml of 0.5 M perchloric acid. The system was flushed with nitrogen for 15 minutes; that gas was then shut off. The nitrite solution was slowly dripped into the acidic iron(II) solution; the gas was bubbled through the base trap into the reaction flask. The gas was allowed to run for 5-7 minutes before chromous addition was begun. The solution was added at a rate of about 2 ml per minute while the NO bubbling was continued. Drops of the blue chromium(II) solution turned red as they fell through the gas in the flask. When the chromium(II) solution was prepared in the reaction flask, the electrodes were replaced with the necessary fittings, after which the NO was bubbled in. After any of these reactions, the solution was bubbled with nitrogen for 15 minutes to remove nitrogen oxides, after which the solution was removed from the flask and stored until it was further purified.

Although the various preparations each give the desired complex, they differ in one important respect. The reaction of chromium(II) with nitric acid is carried out under oxidizing conditions. The side products are more highly oxidized species than NO^- which result from the incomplete reduction of nitric acid. The reaction of chromium(II) with nitric oxide occurs under reducing conditions, and the side products result from the further reduction of nitrosylchromium(III) to produce such nitrogen species as hydroxylamine. Several of the side products are quite reactive toward oxidizing or reducing agents, and the ion exchange purification procedure described below does not necessarily remove such impurities effectively. Their presence in several of the studies had a marked effect on the observed reactions, as will be noted later. A criterion of purity adequate for the purposes of this study has not been developed; for studies in which the absence of these side products is critical to success, it would appear best to add chromium(II) slowly to a well-stirred solution of nitric acid. In no case should this complex be prepared in the presence of a large excess of chromium(II); not only are impurities produced in larger amounts under these conditions but yields are reduced, because of the further reaction of $CrNO^{2+}$ with chromous.

By any of these schemes, three chromium(III) products are obtained--the desired complex $CrNO^{2+}$, Cr^{3+}, and the dimer $Cr(OH)_2Cr^{4+}$. The products have different charges, and good separation is possible by cation-exchange chromatography. Dowex 50W-X8 resin, 50-100 mesh, was used for the separation. A column 0.8 cm in diameter and 25 cm long was loaded with the resin. The crude product mixture was diluted with water to reduce the acidity to <u>ca</u>. 0.2 M and was poured on the column. The column was loaded until the leading edge of the red-brown band had passed 50-75% of the way down the column. The column was washed with 100 ml of 0.2 M perchloric acid and the desired complex eluted with 1 M perchloric acid. Some samples were treated with hydrogen peroxide before chromatography; others were treated with cerium(IV) or nitrous acid and rechromatographed. Individual samples were analyzed for total chromium, and visible spectra were measured.

Dowex 50W-X8 resin was cleaned by washing with water to remove small amounts of a reddish material, then with 4 M hydrochloric acid until no iron(III) could be detected in the eluate by spot-testing with thiocyanate ion. The resin was bleached overnight with hydrogen peroxide in dilute sodium hydroxide and reconverted to the acid form by washing with 4 M hydrochloric acid in a column, followed by water. Before use, the resin was washed with 4 M hydrochloric acid followed by conductivity water.

Chloropentaaquochromium(III) was prepared by adding a trace of chromium(II)[88] to a solution of hydrated chromic chloride (trans-$Cr(H_2O)_4Cl_2^+$) followed by cation-exchange separation similar to that described for the nitrosyl complex.

Lithium perchlorate was prepared by the reaction of the carbonate with perchloric acid. The solid was crystallized by evaporation of water, similar to the chromic salt, except that the precautions against supersaturation were not taken. The salt was recrystallized twice from conductivity water.

The syntheses of several of the oxidizing and reducing agents used in this study warrant some comment. Cerium(IV) solutions were prepared from the hydrous oxide or primary standard ceric ammonium nitrate and perchloric acid, since the commercial ceric perchlorate solutions usually contain appreciable cerium(III). The hydrous oxide was precipitated with ammonia or with urea homogeneously[121] from a solution of the ignited oxide or a commercial ceric sulfate in sulfuric acid. The gelatinous oxide was allowed to digest and the bulk of the supernatent poured off. The precipitate was washed with water and either centrifuged or allowed to settle. Washing was discontinued after the supernatant gave no spot test for sulfate with barium ion; this point was also marked by partial peptization of the precipitate. The oxide was dissolved in concentrated perchloric acid, diluted with cold water, and filtered; solutions 0.03 M in cerium(IV) can be prepared in this way without heating the solution or adding other chemicals.

Ozone was prepared by electric discharge in an Ozonator.[122] In this apparatus, a stream of oxygen is passed through a discharge cell, converting some of the oxygen to ozone. Aqueous solutions of ozone were prepared by bubbling water with ozone; however, for most of the ozone studies solutions of nitrosylchromium(III) were bubbled directly with the ozone-oxygen mixture.

Vanadium(II) perchlorate solutions were prepared as needed by reducing acidic solutions of vanadium(IV) perchlorate with amalgamated zinc under nitrogen. The vanadium(IV) perchlorate solution had been prepared by the electrolytic reduction of solutions of vanadium pentoxide in perchloric acid.

Europium(II) perchlorate solutions were prepared by reduction of acidified europium(III) perchlorate solutions with amalgamated zinc under nitrogen. The europium(III) solutions had been prepared previously from the oxide and perchloric acid by Mr. R. J. Christensen of these laboratories.

Spectral and Kinetic Measurements. Spectral measurements were made using a Cary 14 recording spectrophotometer. Since most of the reactions studied are rather slow, kinetic data were most frequently measured by scanning the visible spectrum from 600 to 310 nm as a function of time instead of continuously monitoring absorbance at one wavelength, although a few such studies were carried out. From the spectra, absorbance-time data were read off at any desired wavelength and the appropriate rate plots constructed. Fast reactions were monitored on a Durrum-Gibson stopped-flow spectrophotometer equipped with a D-131 logarithmic amplifier, which allowed the output to be read directly as absorbance. Absorbance data were read from the oscillograms and the appropriate rate plots made.

Analyses and Product Determinations. Solutions of chromium complexes were analyzed for chromium by oxidizing the chromium to chromate[123] with hydrogen peroxide in basic solution; the chromate was measured spectrophotometrically at 372 nm (ε 4830 M^{-1} cm^{-1}). The acid in solutions of nitrosylchromium contributed appreciably to the total acidity in solutions used in kinetic runs. The free acid was determined by titrating the solutions with sodium hydroxide, using methyl orange as indicator. Methyl orange turns in the pH range 3-4, whereas the pK_a's of most of the $Cr(H_2O)_5X^{2+}$ complexes are approximately 6;[124] therefore it should be possible to titrate perchloric acid to its endpoint without appreciably affecting the chromium complex. In agreement with this expectation, sharp endpoints were observed. In solutions more concentrated than 0.01 M in nitrosylchromium, the endpoint was harder to detect; this problem was solved by diluting the sample with water. Lithium perchlorate was analyzed by passing aliquots down a column of cation exchange resin in the acid form and titrating the eluted acid with base. Ceric perchlorate and sulfate solutions which were not prepared from ceric ammonium nitrate were standardized against ferrous ammonium sulfate, using ferroin as the indicator.

Products of these reactions were characterized by their electronic spectra and their elution behavior on a cation-exchange column. Since the elution behavior of ions depends largely on their charge, similar-appearing ions of different charge can readily be distinguished. This is especially useful for distinguishing between hexaaquochromium(III) and the nitrate complex, which have very similar visible spectra. For reactions in which chromium(VI) was apparently produced, the spectrum was recorded in both acidic and basic solution; the spectral change is particularly distinctive.

In some cases, yields of chromium products were determined. These were measured by passing the reaction mixture (diluted where necessary to keep the desired ions from self-eluting) down a cation-exchange column and eluting the various fractions, +1 cations with 0.2 M perchloric acid, +2 ions with 1 M acid, and +3 (when desired) with 3 M acid. The chromium in the fraction of interest was determined spectrophotometrically as alkaline chromate, as before.

RESULTS

Properties of Nitrosylchromium Ion. The visible spectrum of nitrosylchromium(III) is given in Figure 19. The molar absorptivity of this complex is tabulated as a function of wavelength in Table XIV. The absorption maxima of this complex[99] and of other chromium complexes,[116,123,125-129] of interest in this section are given in Table XV.

Table XIV

Molar Absorptivities of Nitrosylchromium[a]

λ, nm	ε, M^{-1} cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}
600	14	450	120
590	18	440	118
580	24	430	111
570	27	420	99
560	28	410	93
550	27	400	89
540	25	390	86
530	24	380	80
520	25	370	72
510	38	360	66
500	56	350	70
490	78	340	80
480	94	330	88
470	108	320	89
460	117	310	85

[a] At room temperature in 1 M perchloric acid.

The stability of nitrosylchromium(III) has not been extensively discussed in the literature. Ardon and Herman[99] noted that aquation occurred over a period of days. During this work it was noted that solutions which had been "substantially" freed of reducing impurities were less stable than

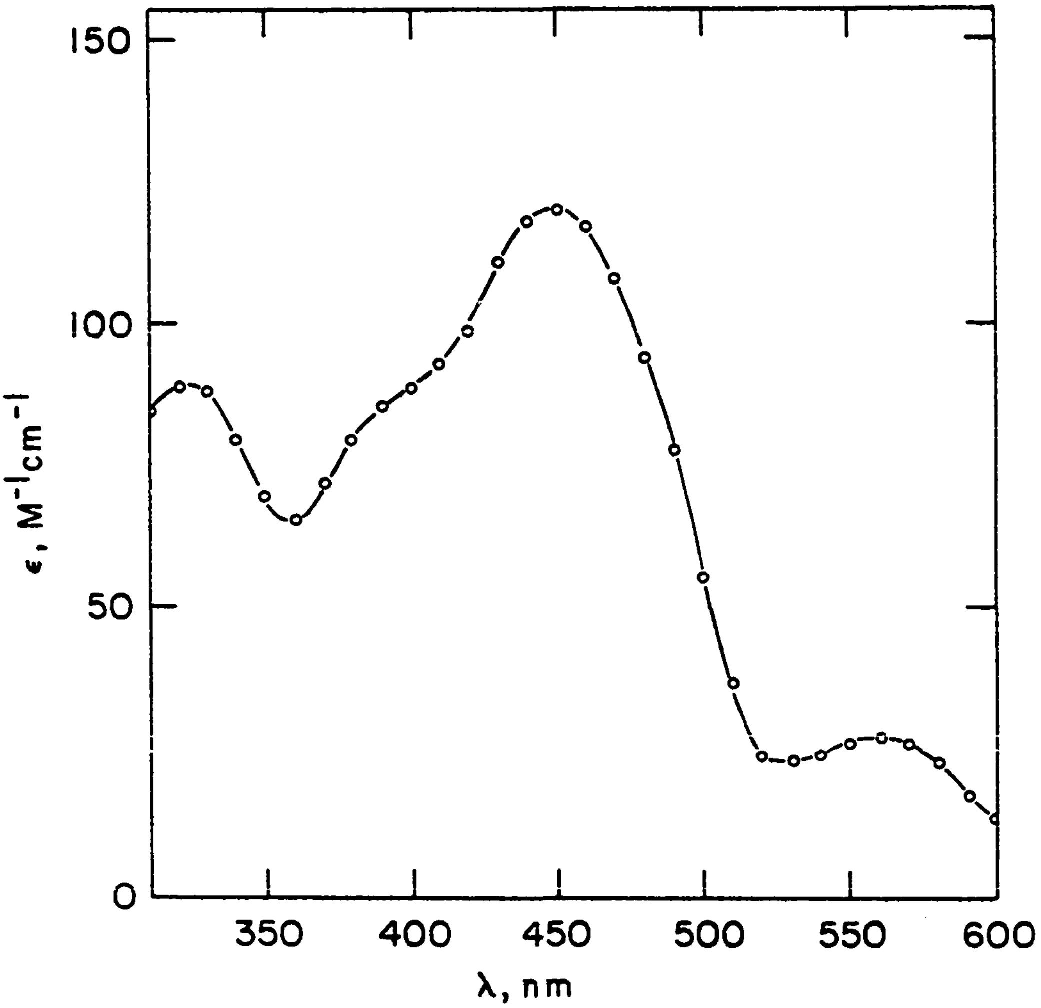


Figure 19. Absorption spectrum of $Cr(H_2O)_5NO^{2+}$ in 1 M perchloric acid at room temperature

Table XV

Absorption Maxima of Chromium Complexes

Complex	λ_{max}, nm	ε, M^{-1} cm^{-1}
$CrNO^{2+}$[a]	559 449 323	28 120 92
$CrNO^{2+}$[b]	562 449 323	28 120 90
$Cr(OH)_2Cr^{4+}$[c]	580 418	19 22
Cr^{3+}[d]	574 408	13.8 15.6
$CrOHO_2^{2+}$[e]	581 412	16.1 18.9
$CrCl^{2+}$[f]	609 428	16.4 20.8
$CrOSO_3^{+}$[g]	587 417	19.0 18.8
$HCrO_4^{-}$[h]	350	1560
CrO_4^{2-}[i]	372	4830

[a] Reference 99.

[b] This work.

[c] Reference 116.

[d] Reference 125.

[e] Reference 126.

[f] Reference 127.

[g] Reference 128.

[h] Reference 129.

[i] Reference 123.

unpurified solutions, although all solutions kept well at -10° for up to three weeks. The complex is less stable in strongly acidic solutions (for instance, $\geq$15 M sulfuric acid) although stability is increased markedly in the absence of air. It would therefore seem that some of the slow aquation noted[99] could be slow air oxidation.

Reductions of Nitrosylchromium(III). Reductions of nitrosylchromium(III) with chromous, vanadous, and europous ions were briefly examined. The chromous reaction was examined spectrally, the others in bench-top experiments. All reductions were studied under nitrogen.

A series of spectra was run on a solution of chromium(II) and nitrosylchromium(III). Some of these spectra are displayed in Figure 20. The absence of isosbestic points in these crossing spectra indicates the presence of more than two absorbing species and possibly of several reactions. Absorbance-time traces were constructed from the spectra and are displayed in Figure 21. The presence of extrema in some of the curves indicates that at least two reactions are occurring in these solutions. Armor[130] has recently reported that the reaction proceeds with the consumption of more than one chromous ion per nitrosylchromium, giving $Cr(OH)_2Cr^{4+}$ as a product. Spectral and chromatographic examinations of the solution after all reactions were complete suggested that a small amount of a tripositive chromium product, tentatively identified as

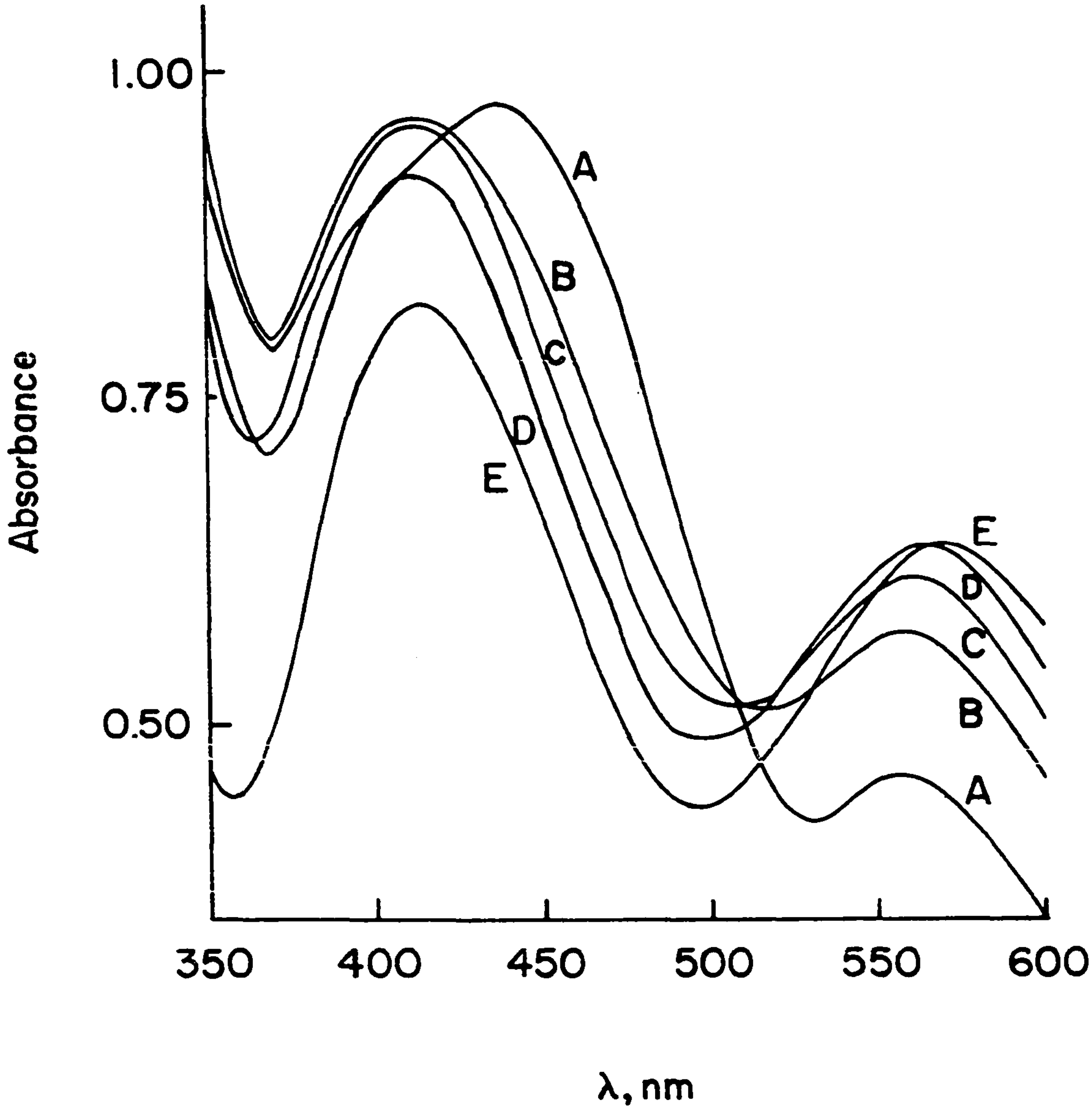


Figure 20. Visible spectra of a solution of nitrosylchromium (0.003 M) and chromium(II) (0.02 M) in acidic solution with time: A, 18 seconds after mixing; B, 400 seconds; C, 800 seconds; D, 2690 seconds; E, 3890 seconds. No baseline correction was made

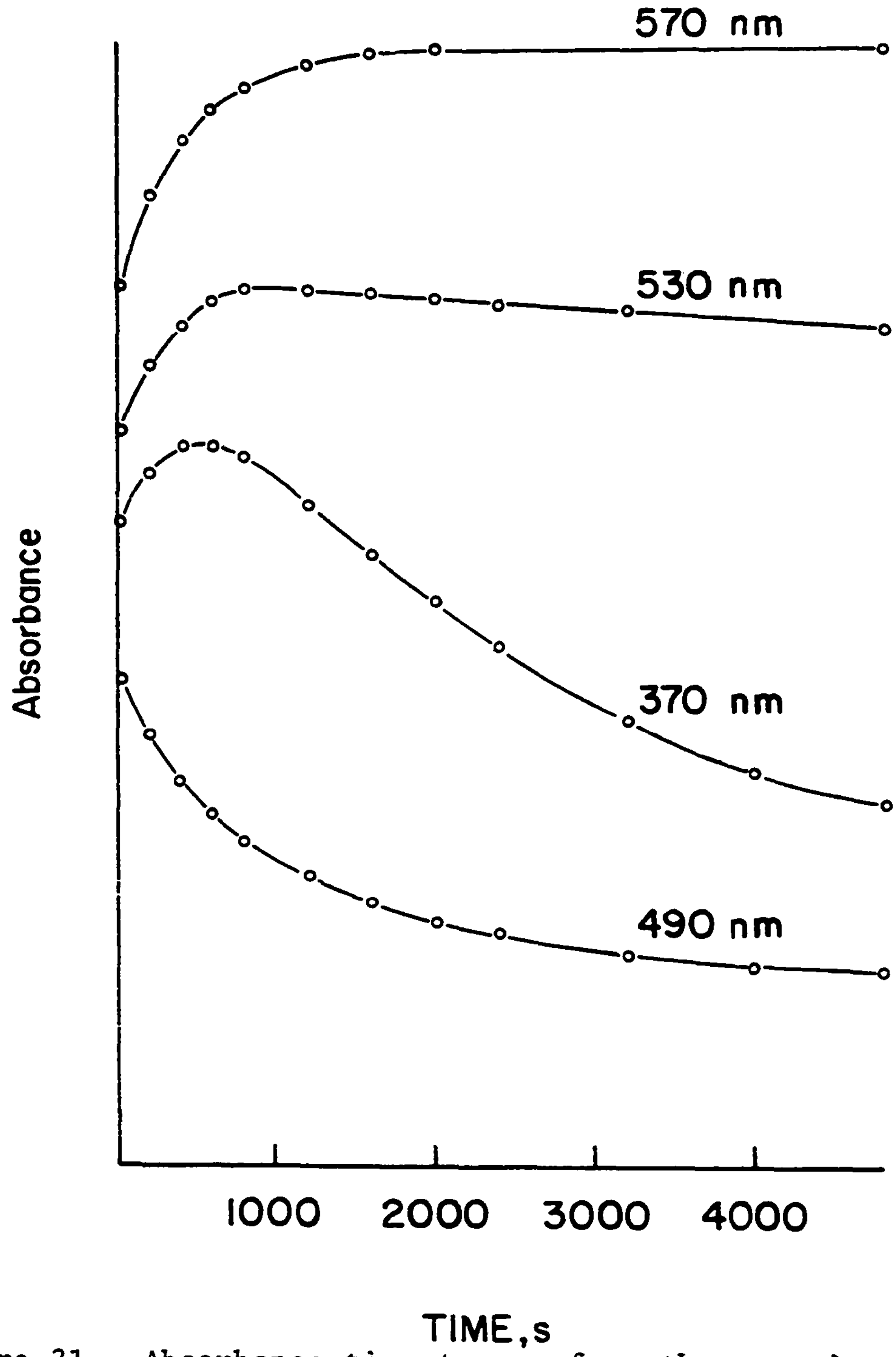


Figure 21. Absorbance-time traces from the reaction of nitrosylchromium and chromium(II), plotted from the scan spectra. The curves have been displaced to allow direct comparison of their shapes; on the ordinate 0.1 absorbance unit is represented by 1.8 cm

hexaaquochromium(III), is also produced, although possibly not in the main reaction. Bench-top experiments suggested that the reaction is somewhat more rapid at lower acidity. This is similar to the chromous-catalyzed aquation of chromium(III) complexes,[131] reaction XXVI, which proceeds through a transition state $[CrOHCrX^{3+}]^{\ddagger}$.

$$Cr^{2+} + CrX^{2+} \rightarrow Cr^{2+} + Cr^{3+} + X^{-} \qquad \text{(XXVI)}$$

Vanadium(II) also reacts in a few minutes. The products appear to be V^{3+} and Cr^{3+} on the basis of ion-exchange and spectral results. Rough experiments suggested that several vanadous ions are oxidized for each nitrosylchromium reduced. Europous ion appeared to be rather unreactive toward the complex; after 45 minutes a solution ca. 0.01 M in europous and 0.002 M in nitrosylchromium had not changed appreciably in color. A spot test with ferric-thiocyanate solution[132] indicated that loss of europous by possible air leakage was not a problem in the experiment.

Oxidations of Nitrosylchromium(III). A number of oxidizing agents, both one- and two-electron reagents, were employed in the survey. The results of these reactions will be treated now.

The reaction of nitrosylchromium(III) with hydrogen peroxide is rather slow, occurring over two to three hours in 3 to 6 M (10-20%) hydrogen peroxide. In acidic solution the chromium product was characterized as hexaaquochromium(III),

Cr^{3+}, by its visible spectrum and its ion-exchange properties. The nitrogen product was not determined but is presumed to be nitrate ion. These products would give the stoichiometry

$$2\ H_2O_2 + CrNO^{2+} \rightarrow Cr^{3+} + NO_3^- + 2\ H_2O \qquad \text{(XXVII)}$$

Visible spectra were measured as a function of time during the reaction of a solution 0.5 M in perchloric acid and 0.004 M in nitrosylchromium in 4.5 M hydrogen peroxide; some of these are shown in Figure 22. The spectra change smoothly from the spectrum of the reactant to that of the product without forming any new bands. Since the spectra of the reactant and product do not cross, the absence of isosbestic points does not necessarily indicate the presence of more than two absorbing species. The data for a species plot[65] are given in Table XVI, using data from Figure 22. The observation of a

Table XVI

Absorbance Data for Species Plot[a]

	j=1 400s	j=2 1200s	j=3 2000s	j=4 2800s	j=5 4000s	j=6 4800s
530 nm	0.180	0.141	0.112	0.095	0.081	0.079
450 nm	0.873	0.575	0.338	0.210	0.119	0.091
400 nm	0.670	0.471	0.326	0.240	0.176	0.159
370 nm	0.578	0.403	0.274	0.198	0.143	0.127

[a] Measured at room temperature in 0.5 M perchloric acid and 4.5 M hydrogen peroxide.

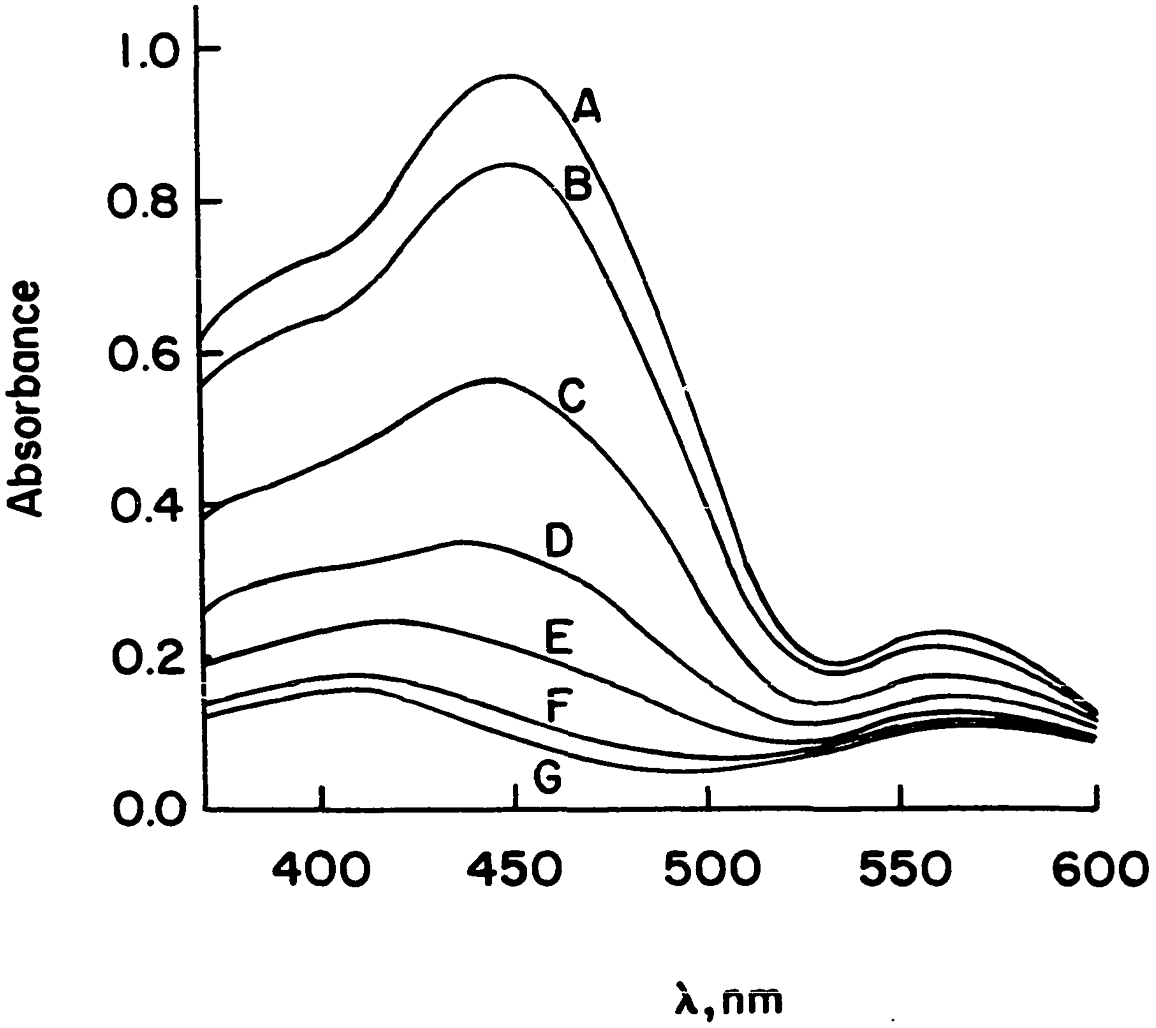


Figure 22. Visible spectra of a solution of nitrosylchromium in acidic hydrogen peroxide during the reaction: A, 40 seconds after mixing; B, 400 seconds; C, 1200 seconds; D, 2000 seconds; E, 2800 seconds; F, 4000 seconds; G, 4800 seconds

family of straight lines passing through the origin in the plot of Figure 23 is a strong indication of the presence of two species--reactant and product--the sum of whose concentrations is constant.

Small-scale (within a factor of two) concentration variations indicated that the reaction is accelerated by both increasing acidity and increasing concentrations of peroxide. Cerium(III), iron(II), silver(I), and chromium(VI) were found to be ineffective as catalysts. Some studies were made in the presence of chloride ion to learn whether chlorochromium complexes could be formed. Under conditions identical to those described above but with 0.15 M hydrochloric acid also present, the reaction was slightly slower than in the absence of chloride, but the spectra were similar in the two experiments; the final spectra were identical, implying that chlorochromium products are not formed in appreciable amounts under these conditions. An ion-exchange experiment was carried out in which a sample of nitrosylchromium was oxidized in 2.5 M hydrochloric acid and 4.5 M hydrogen peroxide. Blank experiments established that chlorochromium(III) is stable (<2% decomposition) over the five-hour period allowed for the reaction and that nitrosylchromium does not react with chloride (<1%) in that time. The final solution was purple, and only a purple band (hexaaquo) was seen. Five per cent of the total chromium was recovered as mono- or di-positive chromium complexes, presum-

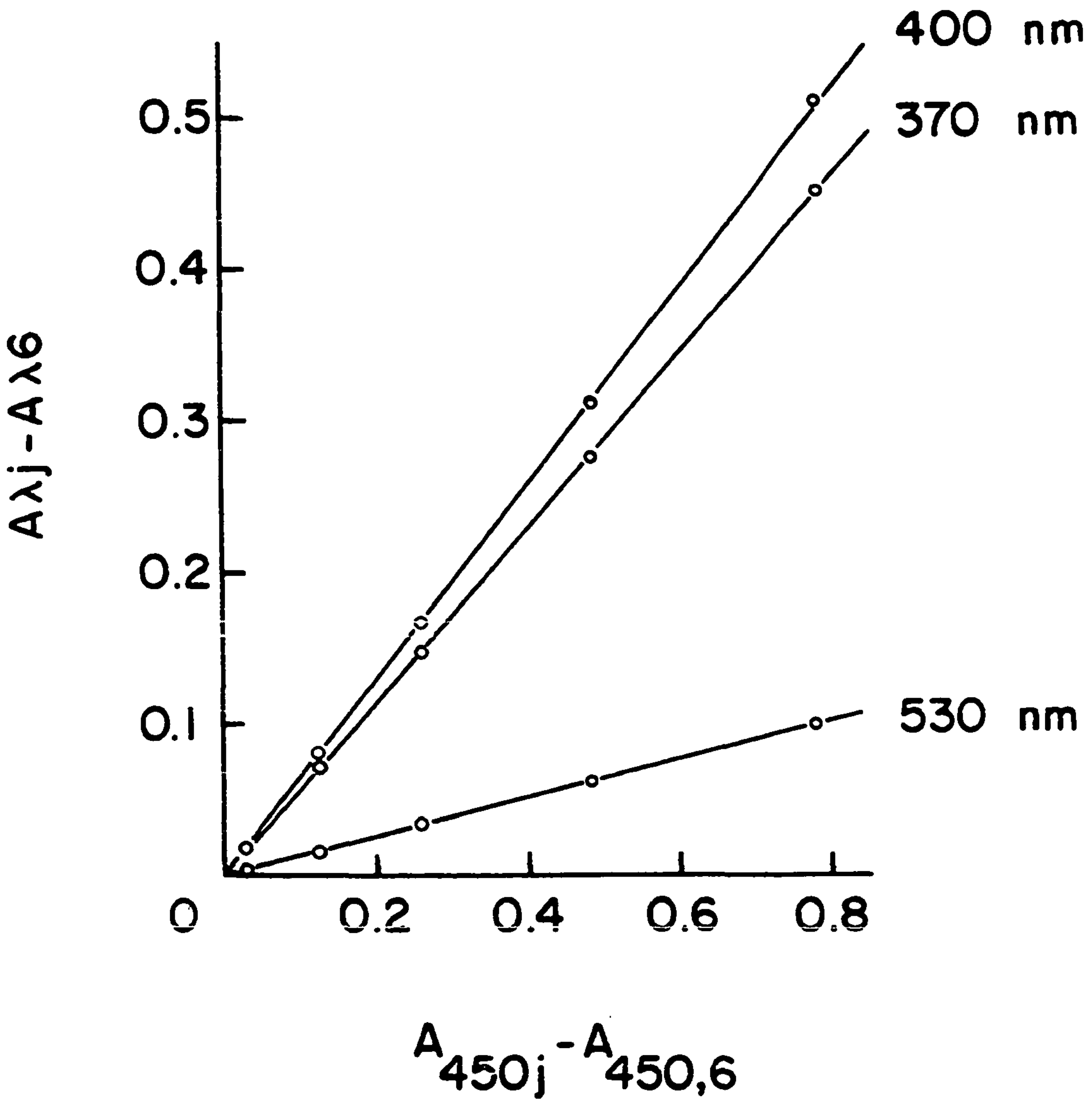


Figure 23. Species plot for nitrosylchromium with hydrogen peroxide: for two species at constant stoichiometry

ably chloro species. This result agrees qualitatively with the findings of Thompson and Kaufmann,[133] who noted a 2% yield of $CrCl^{2+}$ when nitrous acid reacted with azidochromium(III) in 0.5 M Cl^-.

$$CrN_3^{2+} + HNO_2 + H^+ \rightarrow Cr^{3+} + H_2O + N_2O + N_2 \qquad \text{(XXVIII)}$$

The oxidation of nitrosylchromium(III) with ozone was examined as a possible reaction for the formation of nitrochromium(III). Solutions of $CrNO^{2+}$ reacted only slightly with

$$CrNO^{2+} + O_3 \overset{?}{\rightarrow} CrNO^{2+} + O_2 \qquad \text{(XXIX)}$$

saturated aqueous solutions of ozone. However, after bubbling an acidic solution (0.5 M perchloric acid) of the complex with ozone for 20 minutes, the nitrosyl complex was oxidized to a purple product, identified as hexaaquochromium(III) by its visible spectrum and its elution characteristics. The reaction was run several times at lower acidity (pH 4 to 7), and the chromium complexes were separated after various times of reaction. In some experiments sodium-form resin and sodium perchlorate eluting solution were used instead of the usual acid-form resin and perchloric acid eluting solution, in case the nitro complexes were acid-sensitive. Chromium(VI), hexaaquochromium(III), and unreacted nitrosyl were found in these solutions; no spectral or ion-exchange evidence points to formation of the nitro complex.

The reaction of nitrosylchromium with peroxodisulfate was studied initially at millimolar concentrations of oxidant; no reaction was detected, although in the presence of silver(I), $HCrO_4^-$ was produced overnight. At 0.1 M peroxodisulfate, 2% reaction was noted in an hour. Silver again was a strong catalyst, ultimately producing acid chromate. A set of spectra was measured as a function of time; some of these spectra are shown in Figure 24. They indicate that acid chromate is not the first chromium product of the oxidation. The absorbance at 350 nm decreases until about half of the nitrosyl complex has been oxidized, after which it increases markedly to indicate the formation of acid chromate. Some turbidity (silver sulfate) was noted as the reaction progressed; this may account for the isosbestic at 593 nm, which was not found in the peroxide oxidation. Initially it was thought that the isosbestic might reflect the formation of sulfatochromium(III). However, in a reaction solution examined at 60% completion, only 8% of the total chromium was found as sulfatochromium or acid chromate, but a large band of the hexaaquo complex was found on the column. This result suggests the scheme

$$2\ H_2O + CrNO^{2+} + 2\ S_2O_8^{2-} \xrightarrow{Ag^+} Cr^{3+} + NO_3^- + 4\ HSO_4^- \qquad (XXX)$$

$$2\ Cr^{3+} + 3\ S_2O_8^{2-} + 8\ H_2O \xrightarrow{Ag^+} 2\ HCrO_4^- + 6\ HSO_4^- + 8\ H^+ \qquad (XXXI)$$

in which the role of oxidized silver ions is unknown.

To learn more about the reactive species in this system, other possible catalysts were studied. Nitrate (which had been

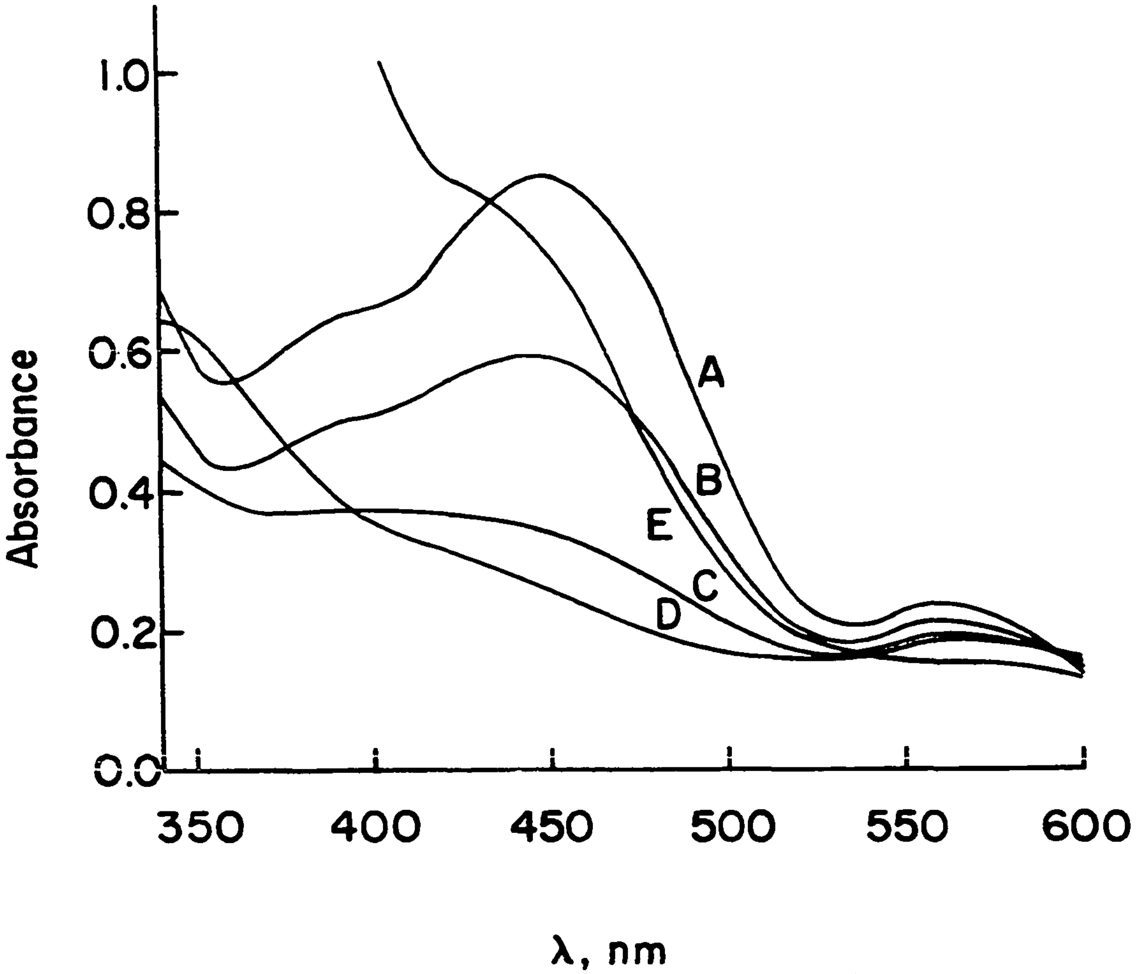


Figure 24. Visible spectra of a solution of nitrosylchromium (0.004 M) and ammonium peroxodisulfate (0.1 M) in 0.5 M perchloric acid and 0.008 M Ag^+: A, 38 seconds after mixing; B, 800 seconds; C, 1600 seconds; D, 2000 seconds; E, 2800 seconds

added with silver) was found to have no effect on the reaction. Cobaltous ion was also inert. Iron(II), on the other hand, was a very effective promoter, but its promoting effect was quickly spent. This result suggests that the sulfate radical anion, $SO_4^-\cdot$, is the reactive species. The reaction is more properly described by the scheme below, in which Red and Ox refer to the reduced and oxidized forms of a one-electron

$$\mathrm{Red} + S_2O_8^{2-} \rightarrow \mathrm{Ox} + SO_4^-\cdot + SO_4^{2-} \qquad \text{(XXXII)}$$

$$SO_4^-\cdot + CrNO^{2+} \rightarrow Cr^{3+} + NO + SO_4^{2-} \qquad \text{(XXXIII)}$$

$$SO_4^-\cdot + \mathrm{Red} \rightarrow \mathrm{Ox} + SO_4^{2-} \qquad \text{(XXXIV)}$$

promoter. The rapid loss of promoting power in the iron system could result from reaction XXXIV, which irreversibly destroys both promoter and the reactive intermediate.

Molecular chlorine, bromine, and iodine were rather uninteresting reagents. No reaction could be detected with iodine; less than 10% of the nitrosyl complex was oxidized by excess bromine or chlorine in an hour. No attempt was made to induce a radical pathway for these reactions. Bromate ion was also a very slow oxidant.

Initial experiments with $HCrO_4^-$ indicated that reaction was fairly rapid, occurring in a few minutes, and was strongly retarded by nitrous acid. More careful experiments showed that the rapid reaction does not involve nitrosylchromium. The reactive species is believed to be a hydroxylamine impurity on the basis of a prior report[99] and of chemical tests which indicated that hydroxylamine reacts with acid chromate at similar rates to those measured in the "nitrosyl" reaction. The fast reaction was very noticeable in samples of the nitrosyl complex which had been prepared by bubbling chromous with nitric oxide, less so in samples prepared by adding chromous to the oxide, and not detectable in samples prepared from nitric acid. As such it constitutes a useful test for hydroxylamine contamination.

The stoichiometry of the reaction is not clean. Measurements using freshly purified material of the stoichiometry of the slow (several hours) reaction, based on the decay of the 449 nm peak of the nitrosyl complex, indicates a stoichiometry between those illustrated in reactions XXXV and XXXVI. Further investigation showed that the oxidation of nitrous

$$3\ CrNO^{2+} + Cr^{VI} \rightarrow 4\ Cr^{3+} + 3\ NO \qquad (XXXV)$$

$$3\ CrNO^{2+} + 2\ Cr^{VI} \rightarrow 5\ Cr^{3+} + 3\ HNO_2 \qquad (XXXVI)$$

acid by $HCrO_4^-$ is competitive with the main reaction. Since nitrous acid can undergo at most a two-electron oxidation, while $HCrO_4^-$ must accept three electrons to reach a stable chromium species, at least one chromium intermediate must be generated; the intermediate(s) may react further with the nitrosyl complex. Some intermediate in the system could also be sensitive to oxygen.

The reaction with cerium(IV) also appeared to be quite rapid. The stoichiometry of this reaction was measured in both sulfate and perchlorate solutions by spectrophotometric titrations, cerium being added to chromium. Since both cerium (IV) and chromium(VI) absorb strongly in the near uv, an absorbance enhancement with added cerium is a good indication of the presence of an oxidized metal species. The titration in sulfate was quite straightforward; no uv enhancement was noted until four equivalents of cerium had been added per mole of chromium. This supports the reaction

$$4\ Ce^{IV} + CrNO^{2+} \rightarrow 4\ Ce^{3+} + Cr^{3+} + NO_3^- \qquad \text{(XXXVII)}$$

In perchlorate solution, some chromium(VI) was noted even when only one equivalent of cerium had been added. This results from the possible further oxidation of Cr^{3+} by cerium(IV), a reaction which is much more rapid in perchlorate than in

$$3\ Ce^{IV} + Cr^{3+} \rightarrow 3\ Ce^{3+} + Cr^{VI} \qquad \text{(XXXVIII)}$$

sulfate.[134] It appeared advisable to study the kinetics at high concentrations of $CrNO^{2+}$ to minimize this potential interference.

Four sets of kinetic data were taken at 25° in 1 M $HClO_4$, with cerium(IV) concentrations from 2×10^{-5} to 2×10^{-4} M and $CrNO^{2+}$ concentrations from 2×10^{-4} M to 5×10^{-3} M, obtained from the nitric acid preparation or from the addition of chromous to nitric oxide, both with and without pretreatment with cerium(IV) or nitrous acid to remove hydroxylamine. The reaction was followed in the uv where cerium(IV) absorbs strongly (λ_{max} 290 nm, ε 1800 M^{-1} cm^{-1}).[135,136] Several problems were noted, including:

1. Marked non-reproducibility, with measured rates differing from one batch of material to another and sometimes from day to day with the same batch.

2. Absorbance change 1/4 to 1/2 the size expected, based on the known molar absorptivities and the calibration of the photomultiplier voltage changes.

3. Non-linearity of pseudo-first-order kinetic plots even though large excesses of the nitrosyl complex were employed.

4. Failure of freshly chromatographed $CrNO^{2+}$ to improve the situation.

The non-reproducibility is certainly reminiscent of trace catalysis. An effort was made to locate possible impurities, especially in the nitric acid preparations. Qualitative analysis by arc emission spectroscopy[137] revealed a small trace of silver in one solution of 0.01 M $CrNO^{2+}$. Precipitation tests with HCl revealed that the solution contained less than 10^{-4} M silver. Higginson and coworkers[138] have reported that the rate constant for the cerium(IV)-silver(I) reaction is 0.1 M^{-1} s^{-1} at 25° and 4.5 M ionic strength (rather higher than the 1 M used here). This reaction should be negligible in comparison with the nitrosyl reaction, which is complete in less than five seconds. An analysis of the perchloric acid stock solution found 10^{-6} M Fe^{2+}, again probably negligible in terms of its effect on cerium ($k = 700\ M^{-1}\ s^{-1}$ at 0°).[139] A trace-metal analysis detected a few redox-inert elements, such as magnesium and nickel. The cerium(IV)-chromium(III) reaction was examined; it appeared to be too slow to affect the main reaction. In addition, no rate effects were noted when Cr^{3+} was added to a reaction solution. A search for nonmetallic impurities was also unsuccessful. Spot tests with $HCrO_4^-$ for hydroxylamine were negative. Nitrous acid can be detected by its reaction with sulfamic acid.[140]

$$NH_2SO_3^- + HNO_2 \rightarrow N_2 + H_2O + HSO_4^- \qquad \text{(XLIX)}$$

Nitrogen evolution was apparent with 10^{-4} M nitrous acid in 1 M perchloric acid; the test was indecisive when applied to the solutions of the nitrosyl complex. This suggests that the concentration of nitrous acid is less than 10^{-4} M, which can be compared with the chromium concentration of 0.01 M.

The problem of the small absorbance changes was examined briefly. Samples of the cerium solution taken from the reservoir syringe of the stopped flow before and after an experiment had approximately the expected absorbances and had decayed less than 5% over the time needed for the experiments; decomposition of the cerium solutions is therefore ruled out.

Some insight into the shape of the traces was gained from an examination of the reaction between cerium(IV) and nitrous acid. In perchloric acid the reaction is rapid but measurable; at 10^{-4} M cerium and 10^{-3} M nitrous acid, a rough estimate of k is 2 x 10^5 M^{-1} s^{-1}. At much lower concentrations of nitrous acid, so that cerium(IV) is in excess, the reaction occurs on a similar time scale to that noted for the nitrosyl reaction. Since this reaction could occur as a secondary reaction in the overall reaction, it is possible that the nitrosyl reaction has a variable stoichiometry under concentration conditions apparently suitable for kinetics. At comparatively high concentrations of cerium(IV) (nitrosylchromium still in excess), a slow tailing was noted in the traces; in some of these product solutions, chromium(VI) was detected spectrally.

A further purification technique has been noted. Ardon and Herman[99] have crystallized nitrosylchromium as a sulfate by evaporating solutions of the complex in sulfuric acid in a vacuum desiccator over sodium hydroxide. Moore and Basolo[141] have accomplished the same end by extracting water with alcohol-ether mixtures. These methods were not successful in this study because the solutions of the complex were too dilute. The Moore method produced only a few milligrams of solid before the solution decomposed; if more concentrated solutions (0.05 M or so) were obtained initially, the chances for success should be much better. A solution of the crystals would then need to be freed of sulfate by ion-exchange purification.

The reaction was briefly examined in the presence of 0.02 M HSO_4^-. The reaction was slower by about a factor of five than in perchlorate solution. The predominant cerium species are sulfate complexes,[142] which also react more slowly with Cr^{3+} than do the aquo and hydroxo complexes present in perchloric acid.[134] The problems of non-reproducibility and curved plots were also noted in these runs.

DISCUSSION

An extensive discussion of the mechanisms of oxidation and reduction of nitrosylchromium ion is prevented by the failure to obtain quantitative kinetic data for the reactions, but the observations at hand do allow some points to be made.

The reductions with chromous and vanadous warrant some comment. The chromous reaction is definitely complex, as indicated by the absorbance traces; the complexity undoubtedly arises from the further reduction of intermediates, such as hydroxylamine.[143-145] Although the vanadous reaction was not studied spectrally, the apparent stoichiometry indicates possible complexity there too. Secondary reactions were also noted in some of the oxidations.

The bulk of the discussion will be devoted to the oxidations, about which several points can be raised. First, no evidence was found for the intermediate formation of chromium (II); had it formed, its rapid reaction with oxygen or some of the oxidants used in this study[116] would have produced $Cr(OH)_2Cr^{4+}$, which was not detected as a product of any oxidation. This result offers some support to the notion that nitrosylchromium ion behaves chemically like a chromium(III) complex.

The second observation is that no concrete evidence was obtained for the formation of a nitrochromium(III) intermediate. The spectrum of this complex was expected to have a maximum between 545 nm[146] (the maximum for the ammine complex $CrNH_3^{3+}$) and 525 nm[147] (the maximum for the cyano complex $CrCN^{2+}$), based on the relative positions of ammonia, $-NO_2^-$, and $-CN^-$ in the spectrochemical series. However, no such band was noted in the experiments. Ion-exchange experiments also failed to detect a nitro complex in reaction solutions. The nitro complex might well have formed in the reaction of nitrosylchromium with ozone or hydrogen peroxide, in which the oxidant loses an oxygen atom. The results imply that the nitro complex does not form or decomposes too rapidly to be detected.

The slowness of most of the reactions is noteworthy. Free NO^- and its conjugate acid HNO are not known in aqueous solution, but it might be expected that their oxidation by some of the reagents used in this study would be rather fast. The nitrous acid-hydrogen peroxide reaction is fast;[148] a similar oxidation of NO^- or HNO should also occur readily. The slowness of the reactions of $CrNO^{2+}$ is quite in keeping with the slow reactions of coordinated ligands relative to the free ligands described in the Introduction.

The rate of oxidation depends on the type of reagent. The one-electron reagent cerium(IV) is far more reactive than the two-electron reagents, even those which are better oxidants than cerium(IV). The results of the peroxodisulfate reaction, which is fairly rapid in the presence of a good one-electron promoter and negligible in its absence, are also impressive in this regard.

Finally, in all cases the reactions necessarily involve a ligand substitution at some stage, since the chromium-nitrogen bond is not retained in the final product. One mechanism is redox-catalyzed aquation, which was noted by Ogard and Taube[149] for the aquation of chlorochromium(III) catalyzed by manganese(III). Their mechanism is the three-step scheme

$$CrCl^{2+} + Mn(III) \rightarrow CrCl^{3+} + Mn^{2+} \qquad (XL)$$

$$CrCl^{3+} \rightarrow Cr^{IV} + Cl^{-} \qquad (XLI)$$

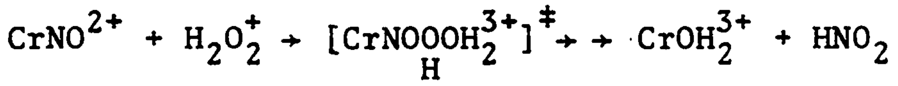
$$Cr^{IV} + Mn^{2+} \rightarrow Cr^{3+} + Mn^{III} \qquad (XLII)$$

Another possibility is direct substitution at chromium(III). Although most of these reactions are more rapid than a classical substitution on chromium(III),[13,126,127] this is not sufficient reason to rule out direct substitution. Reaction XXVIII also requires a substitution; although redox catalysis is not possible, the reaction is complete in seconds under laboratory conditions.[133] This reaction illustrates that rapid substitution is possible even in an inert system if a good leaving group is present.

The observation that chlorochromium(III) is produced in the peroxide reaction in an amount similar to that found by Thompson and Kaufmann[133] for reaction XXVIII suggests that the substitution steps are quite similar; since reaction XXVIII involves substitution at chromium(III), presumably the peroxide reaction does also.

The hydrogen peroxide and peroxodisulfate oxidations can be considered together. A direct comparison of rates does not appear to be too profitable because of the different concentrations of oxidant used in the two reactions. The peroxide reaction could proceed as a simple a mechanism as the scheme

$$H_2O_2 + H^+ = H_3O_2^+ \qquad \text{(XLIII)}$$



$$CrNO^{2+} + H_2O_2^+ \rightarrow [CrNO\underset{H}{O}OH_2^{3+}]^{\ddagger} \rightarrow \rightarrow CrOH_2^{3+} + HNO_2 \qquad \text{(XLIV)}$$

followed by the oxidation of nitrous acid. The failure of one-electron reagents to accelerate the peroxide reaction implies that hydroxyl radical is scavenged before it can oxidize nitrosylchromium or, less likely, that a one-electron path cannot contribute to the peroxide reaction.

A subject of great interest in the literature of chromium (VI) oxidations[150] is whether a reaction proceeds through a series of one- or two-electron transfers, such as the two schemes shown below.

$$\begin{array}{lcl} Cr^{VI} + Red \rightarrow Cr^{V} + Ox & & Cr^{VI} + Red' \rightarrow Cr^{IV} + Ox' \\ Cr^{V} + Red \rightarrow Cr^{IV} + Ox & \text{or} & 2\ Cr^{IV} \rightarrow Cr^{V} + Cr^{III} \\ Cr^{IV} + Red \rightarrow Cr^{III} + Ox & & Cr^{V} + Red' \rightarrow Cr^{III} + Ox' \end{array}$$

giving the net reactions

$$Cr^{VI} + 3\ Red \rightarrow Cr^{III} + 3\ Ox \text{ and } 2\ Cr^{VI} + 3\ Red' \rightarrow 2\ Cr^{III} + 3\ Ox'$$

In the nitrosylchromium oxidation, a stable nitrogen species is known at each level of oxidation, so that either scheme is possible. The slowness of the reaction provides slight support that the reaction proceeds by a two-electron path, complicated by side reactions.

The cerium(IV) and $SO_4^-\cdot$ reactions indicate the effectiveness of a one-electron oxidant. One possible scheme involves the series

$$CrNO^{2+} + Ox \rightarrow CrNO^{3+} + Red \qquad (XLV)$$

$$CrNO^{3+} \rightarrow Cr^{3+} + NO \qquad (XLVII)$$

Further oxidation of the products or of the intermediate $CrNO^{3+}$ would be possible. The intermediate is postulated because $CrNO^{2+}$ does not readily lose the NO group, but loss of an electron would form (possibly after an internal electron transfer) a nitric oxide complex of chromium(III); nitric oxide should be an excellent leaving group.

The primary observation throughout the entire study, however, is that despite far more extensive purification than is normally afforded CrX^{2+} complexes, the complex at hand shows every indication of being sufficiently contaminated with reactive impurities to make quantitative rate studies a hopeless proposition. There are some reactions whose investigation would be interesting: the vanadous reaction, the cerium reaction, possibly one of the catalyzed peroxodisulfate reactions. However, under the concentration conditions needed to suppress side reactions in the cerium system, one ppm (2 x 10^{-5} M) of nitrous acid is intolerable. This is apparently the first study of this complex in which such stringent purity is necessary. Possible solutions include crystallizing the complex or working with completely aquated solutions of the cyano complex, which is crystallized during its preparation;

$$Cr(CN)_5NO^{3-} + 5\ H_3O^+ \rightarrow Cr(H_2O)_5NO^{2+} + 5\ HCN \qquad (XLVII)$$

if HCN reacts with the reagent of interest, it can be removed by ion-exchange. By one of these methods it should be possible to narrow the gap between analytical and chemical purity so that more quantitative work can be done.

PART III. THE REDUCTION OF THE TANTALUM CLUSTER ION ($Ta_6Br_{12}^{3+}$) BY CHROMIUM(II)

This portion of the thesis has been previously published under the title "Kinetic Studies of the Reduction of the Tantalum Halide Cluster Ion ($Ta_6Br_{12}^{3+}$) by Chromium(II)."[151]

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