

lations of signs of B terms of molecules of low symmetry using the standard perturbation formula^{2,3} are not as hopeless as has been believed (e.g., ref 3). In semiempirical model calculations, the exact (FCI) results are origin independent. Even the nonvanishing origin dependence of approximate results is insignificantly small if large enough CI is used, at least for the PPP model. Convergence of approximate to FCI results is quite fast. Simple pictorial rationalization of the signs of B terms is possible in terms of HMO's of the molecule. On the negative side, it must be emphasized that meaningful predictions are possible only for the few lowest energy electronic transitions. However, the signs of the B terms of these low-energy bands are correctly predicted already by the simple PPP model, at least for π -electron chromophores of nonalternant hydrocarbons. It appears likely that the model will also work for substituted derivatives and heterocyclic analogs of alternant as well as nonalternant hydrocarbons, since the exact pairing property is lost in all of these. This is now being tested.

After the completion of this manuscript it has come to our attention that a π -electron calculation on several heterocycles and their derivatives by a method similar to that used by us has just appeared.³¹ It was claimed that the calculated B terms are origin independent since all SCF singly excited configurations were used but no

(31) D. W. Miles and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **70**, 3754 (1973).

proof was given of this statement. According to the analysis presented here and in ref 21, this is not sufficient in itself to guarantee origin independence, since the proper commutation relation between r and H and relation 3 also need to be satisfied.

Further improvement in the semiempirical model will be required for π -electron calculations on alternant hydrocarbons. Finally, for many chromophores, the π -electron approximation will have to be abandoned but the increased size of CI will then make it harder to examine origin dependence and convergence to exact solutions and we hope to obtain additional experience with π -electron models first.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. The initial point of our programming work was an SCF-CI PPP program written by Mr. John Downing (ref 20), which in turn profited greatly from use of a subroutine using an algorithm of ref 32, kindly provided by Professor Frank E. Harris. We are grateful to Dr. Charles R. Flynn for preparation of 6,6-dimethylfulvene and to Professor Henry Eyring for kind permission to use his MCD instrument. The MCD spectra used in this paper were taken by Miss Patti L. Case and Mr. Michael R. Whipple. Finally, we are obliged to Dr. L. Seamans for a copy of his program and a fruitful discussion.

(32) F. E. Harris, *J. Chem. Phys.*, **46**, 2769 (1967).

Mechanism of Halide Substitution in Dichloro- μ -tetrapropionato-dirhenium(III)^{1a}

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Abstract: Kinetic and equilibrium measurements are reported for the reaction $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{Cl}_2 + \text{Br}^- = \text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{ClBr} + \text{Cl}^-$ in acetonitrile. The reaction is reversible with $K = (1.1 \pm 0.1) \times 10^{-2}$ at 25.0° . The forward rate constant in the anhydrous solvent is given by the expression $k_f = A[\text{Br}^-]/([\text{Cl}^-] + B[\text{Br}^-])$ with $A = 3.4 \times 10^{-5} \text{ sec}^{-1}$ and $B = 4.1 \times 10^{-2}$ at 25° , which is interpreted in terms of a two-step mechanism involving loss of Cl^- prior to entry of Br^- . The reaction is subject to strong catalysis by traces of neutral donor molecules including water. The second stepwise replacement of Cl^- by Br^- has an equilibrium constant determined only approximately as $(4 \pm 2) \times 10^{-3}$.

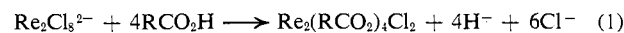
The structural and reaction chemistry of Re(III) complexes was elucidated several years ago largely through the efforts of Cotton and his coworkers. The dimeric Re(III) complex $\text{Re}_2\text{Cl}_8^{2-}$ was identified,² and it was noted³ that refluxing this ion in the carboxylic acid solvent readily converts it to the given carboxylato halide complex of Taha and Wilkinson.⁴

(1) (a) Based on the Ph.D. Thesis of T. R. W., Iowa State University, 1972; (b) National Science Foundation Trainee, 1968–1969; National Science Foundation Predoctoral Fellow, 1969–1972.

(2) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(3) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967).

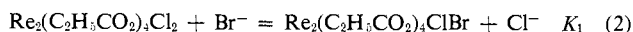
(4) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).



At the time we began work on the problem of the mechanism of halide ion substitution in these dinuclear Re(III) complexes, a useful first study appeared to be the reactions of either $\text{Re}_2\text{Cl}_8^{2-}$ or $\text{Re}_2(\text{RCO}_2)_4\text{Cl}_2$ with another halide ion. The former reaction appeared too complex a system in which to make the first attempt at a meaningful resolution of the mechanism, not only because eight steps are involved in the conversion of $\text{Re}_2\text{Cl}_8^{2-}$ to, say, $\text{Re}_2\text{Br}_8^{2-}$ but also because the intermediate mixed ligand complexes can exist in a number of isomeric forms. Moreover, relatively high concentrations of halide ions are required to prevent loss of

halide (in methanol, 0.1 *F* HCl² and 0.4 *F* HBr,⁵ respectively), thereby restricting the range of halide concentrations. Hynes⁵ has since reported on certain substitution reactions of the octahalo complexes; some of the complexities we anticipated were in fact observed.

We decided to concentrate instead on the halide substitution reactions of the tetracarboxylato complexes because of the much smaller number of reactions possible. In this paper we report on kinetic studies of the reaction of Re₂(C₂H₃CO₂)₄Cl₂ with bromide ion in acetonitrile. The propionato complex was chosen simply for reasons of solubility and stability in acetonitrile. The reaction proceeds in two distinct stages, corresponding to the successive replacement of the two chloride ions.



In the course of these studies a marked catalysis by traces of water was observed, although no Re(III) complex other than the indicated dihalo species was detected at significant concentration at any stage during the reaction. This observation prompted an examination of the effects of other neutral molecules, and most of the substances examined also were efficient catalysts. Kinetic studies were carried out to examine these effects as well.

Experimental Section

Materials. Octachlorodirhenate(III) ion was prepared from potassium perrhenate by reduction with 50% hypophosphorous acid at 90° for 12 hr and was isolated at the tetrabutylammonium salt as described by Cotton, *et al.*⁶ This complex was converted to the dichloro-*μ*-tetraacetato compound by refluxing in acetic acid-acetic anhydride under nitrogen. Subsequent conversion to dichloro-*μ*-tetrapropionato-dirhenium(III) was accomplished by heating 0.5 g of the tetraacetato compound in propionic acid (100 ml)-propionic anhydride (50 ml) under nitrogen in a distillation apparatus so as to distill 50 ml of liquid from the reaction flask over a 3–6-hr period. The solution was cooled in an ice bath and the orange solid was filtered under nitrogen and recrystallized from acetonitrile.

Anal. Calcd for Re₂C₁₂H₂₀O₅Cl₂: C, 19.58; H, 2.72. Found:⁷ C, 19.31; H, 2.72.

In acetonitrile, absorption maxima for Re₂(C₂H₃CO₂)₄Cl₂ were found at λ 396 and 497 nm with ε₃₉₆/ε₄₉₇ 1.03 (lit.⁸ 396, 497 nm, with ε₃₉₆/ε₄₉₇ 1.06).

Commercial samples (Eastman) of tetraethylammonium bromide were purified by the method of Supin;⁹ the chloride was reprecipitated from acetonitrile by addition of benzene or ether. Stock solutions of the dried bromide salt in acetonitrile were analyzed after a fourfold dilution with water by a direct Volhard titration.¹⁰ Before titration, the chloride was first converted to the bromide using a column of Dowex 1-X8 resin in the bromide form; this method was tested with a standard solution of potassium chloride of similar concentration in 50% acetonitrile.

Tetraethylammonium perchlorate was prepared by mixing concentrated aqueous solutions of Et₄NBr and NaClO₄. The resulting precipitate was recrystallized twice from conductivity water, yielding a sample which gave a negative test for bromide ion. The dried sample was shown to be anhydrous by the absence of a nmr

(5) M. J. Hynes, *J. Inorg. Nucl. Chem.*, **34**, 366 (1972).

(6) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

(7) Analyses were performed by the Analytical Services Group of the Ames Laboratory.

(8) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **5**, 1798 (1966).

(9) G. S. Supin, *Zh. Anal. Khim.*, **16**, 359 (1961).

(10) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1966, pp 261–262.

peak (CD₃CN) for water and by thermogravimetric analysis; the weight loss upon heating to 170° was only 0.04%.

Anal. Calcd for C₈H₂₀NClO₄: C, 41.8; H, 8.7. Found:⁷ C, 41.4; H, 9.0.

Acetonitrile was purified by distillation from sodium carbonate and potassium permanganate; the middle fraction was taken, dried over phosphorus pentoxide, and redistilled.¹¹ The middle fraction of the distillate was used for stock solutions or was further dried either by vacuum distillation onto Linde 4a molecular sieves which had been activated by heating to 280° under dynamic vacuum for 12–15 hr or by vacuum distillation from P₄O₁₀ onto more P₄O₁₀. It was stored under vacuum over the drying agent for distillation into the reaction cell as described subsequently.

Urea was recrystallized from acetone, mp 132–133°. Commercial acetamide was recrystallized twice from methanol to give an odorless solid, mp 80.5–81.5°. Tetrahydrofuran was dried and stored *in vacuo* over lithium aluminum hydride; propionitrile and pyridine were dried over barium oxide and stored under vacuum over molecular sieves.¹² *N,N'*-Dimethylformamide was refluxed for 1 hr, dried over phosphorus pentoxide, and vacuum distilled from the oxide onto molecular sieves over which it was stored in the dark. Commercial tetramethylurea, after treatment with phosphorus pentoxide to remove an amine impurity, was vacuum distilled onto molecular sieves.

Kinetic and Equilibrium Measurements. Spectra were measured using a Cary Model 14 spectrophotometer, which was also used for the equilibrium measurements and most kinetics determinations. A few more rapid reactions were studied using a Durrum stopped-flow instrument. The slower kinetic determinations utilized a specially constructed, two-compartment quartz cell which could be evacuated on a vacuum line.

The general procedure for the kinetics experiments under "anhydrous conditions" was as follows. Known volumes of stock solutions of the rhenium complex and of the halide salts were added to the different arms of the reaction cell. The acetonitrile was removed on a vacuum line, and the solid residue was pumped on for a further 5 min. The specially dried solvent described earlier was distilled into the cell from a reservoir on the vacuum line. At this point the cell was closed off with a vacuum stopcock, removed from the vacuum line, and thermostated in a 25° bath. The reactions were started by pouring the solutions from one arm of the cell to the other. After a mixing time of *ca.* 20 sec, the absorbance at an appropriate wavelength was recorded continuously as a function of time.

The volume of each reaction solution was measured accurately at the end of the run to permit the computation of the exact concentrations present, which depended upon the quantity of acetonitrile transferred in the final distillation.

Urea and acetamide were added as solutions in acetonitrile in the same manner as the halides. Water was transferred from a 50-μl syringe to 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, and from there into the reaction cell. The line was heated to *ca.* 80° with heating tape to assist in the transfer of the higher boiling liquids.

Kinetic Data. The rate constants for reaction 2 were evaluated under conditions where an equilibrium was attained with appreciable concentrations of both the dichloro and bromochloro complexes. The concentrations of both Cl⁻ and Br⁻ being in large excess over the rhenium complexes, the kinetics were simplified to that of a pair of opposing pseudo-first-order reactions, as described by the equation

$$\ln [(C_t - C_\infty)/(C_0 - C_\infty)] = -k_{\text{obsd}}t \quad (4)$$

in which C₀, C_t, and C_∞ represent the respective concentrations of Re₂(C₂H₃CO₂)₄Cl₂ initially, at time *t* during the rate measurement, and at equilibrium. The data were treated in accord with eq 4 utilizing absorbance readings directly in place of concentrations. The data for every experiment when treated according to eq 4 gave plots which were linear to at least 80% completion. The net rate of approach to equilibrium (*k*_{obsd} of eq 4) may be further resolved into the contributions of forward and reverse reaction rates by use of

(11) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

(12) The samples of THF, propionitrile, and pyridine were generously provided by R. Hoxmeier and M. King.

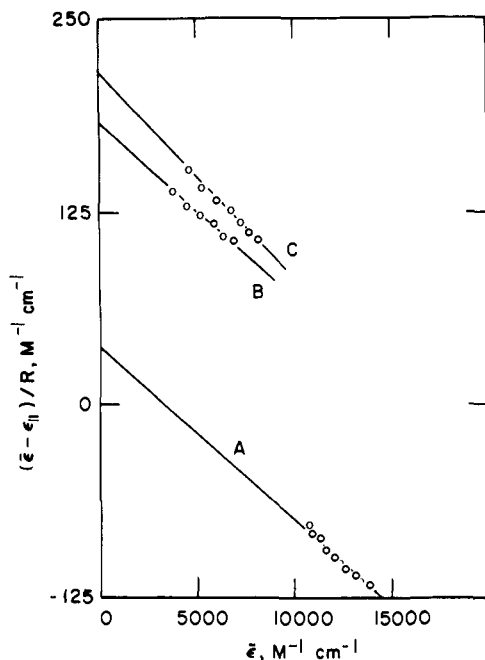


Figure 1. A plot to determine K_1 in acetonitrile at 25.0° according to eq 8 at λ 272 (A), 300 (B), and 305 nm (C).

equations which introduce explicitly the equilibrium constant for reaction 2, K_1 . The equations are

$$k_f = \frac{k_{\text{obsd}}}{1 + (K_1 R)^{-1}}; \quad k_r = \frac{k_{\text{obsd}}}{1 + K_1 R} \quad (5)$$

with $R = [\text{Br}^-]/[\text{Cl}^-]$. The expressions in eq 5 remain valid irrespective of the form of the dependence upon $[\text{Br}^-]$ and $[\text{Cl}^-]$ shown by the apparent rate constants k_f and k_r (and irrespective therefore of the mechanism). The procedure whereby the kinetic data are considered in terms of one or the other expressions in eq 5 offers the advantage that the number of unknown parameters is reduced by one owing to the explicit introduction of the value of the equilibrium constant K_1 , which was determined independently.

Results

Spectral and Equilibrium Studies. The uv absorption spectrum of $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{Cl}_2$ in acetonitrile shifts to that of the dibromo compound upon addition of Et_4NBr . The change takes place without the preservation of isosbestic points, suggesting the formation of the mixed halide compound $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{BrCl}$. However, at low values of the concentration ratio $[\text{Br}^-]/[\text{Cl}^-]$ (designated hereafter as R) isosbestic points were maintained (to approximately $R \leq 80$). These observations are consistent with the occurrence of the two stepwise equilibria shown in eq 2 and 3, and suggest $K_1 > K_2$. The importance of only the first equilibrium at $R < \sim 80$ was also indicated by a measurement of the absorbance as a function of time and wavelength in an experiment with $R = 60$. Isosbestic points were maintained at 257 and 284 nm throughout the reaction suggesting that only the dichloro and bromochloro compounds were present. The absorbance data, when tested for the number of species present using the plots suggested by Coleman, Varga, and Mastin,¹³ indicated the presence of only two absorbing species during the course of the reaction under these conditions.

Quantitative spectral measurements were made to determine values of K_1 and K_2 in acetonitrile at 25°.

(13) J. S. Coleman, L. P. Varga, and S. H. Mastin, *Inorg. Chem.*, **9**, 1015 (1970).

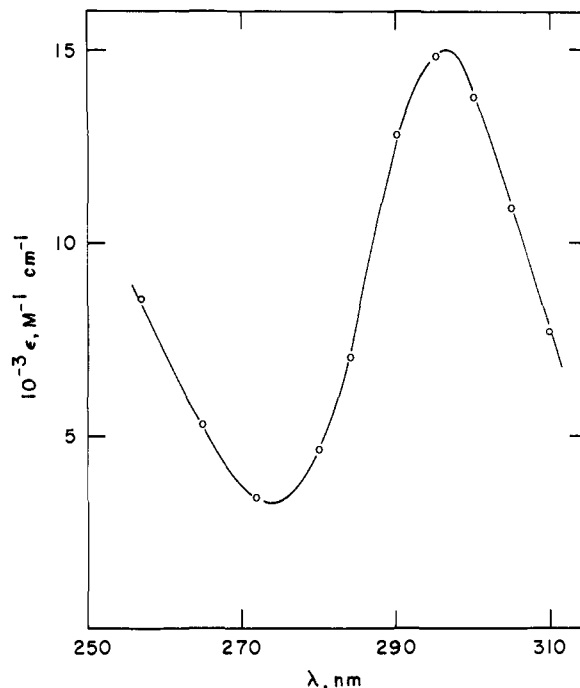


Figure 2. Derived absorption spectrum of the mixed ligand complex $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{ClBr}$ in acetonitrile.

The absorbance of solutions containing various values of R can be expressed in terms of the three rhenium complexes as

$$D = \bar{\epsilon} b C_T = \epsilon_{11}[\text{ClRe}_2\text{Cl}] + \epsilon_{12}[\text{BrRe}_2\text{Cl}] + \epsilon_{22}[\text{BrRe}_2\text{Br}] \quad (6)$$

Introducing the equilibrium expressions from eq 2 and 3, $\bar{\epsilon}$ is given by

$$\bar{\epsilon} = \frac{\epsilon_{11} + K_1 \epsilon_{12} R + K_1 K_2 \epsilon_{22} R^2}{1 + K_1 R + K_1 K_2 R^2} \quad (7)$$

If the formation of the dibromo compound can be neglected at $R \leq 80$, eq 7 can be rearranged to the simpler form

$$\frac{\bar{\epsilon} - \epsilon_{11}}{R} = \epsilon_{12} K_1 - \bar{\epsilon} K_1 \quad (8)$$

From a plot of the left-hand side of eq 8 vs. $\bar{\epsilon}$, values of ϵ_{12} and K_1 can be computed. Plots at three wavelengths are given in Figure 1; the data at 272 nm give $K_1 = 0.011 \pm 0.001$. The values of K_1 determined at other wavelengths are in reasonable agreement, although considerable scatter is noted, reflecting inaccuracies associated with reading absorbances from the shoulders of absorption peaks. Another source of error is the second substitution step, although its effect is small in this wavelength region.

The values of ϵ_{12} determined from such a plot at each wavelength generate the spectrum of the intermediate bromochloro compound, as shown in Figure 2. Spectral measurements at higher values of R (up to $R = 181$) gave the approximate value $K_2 \sim 0.004 \pm 0.002$, based on the use of eq 7 with the values of ϵ_{12} and K_1 computed in the experiments at $R < 80$.

The equilibrium studies were carried out in distilled acetonitrile without special provision for the removal of traces of water. The absorbance intensities and equilib-

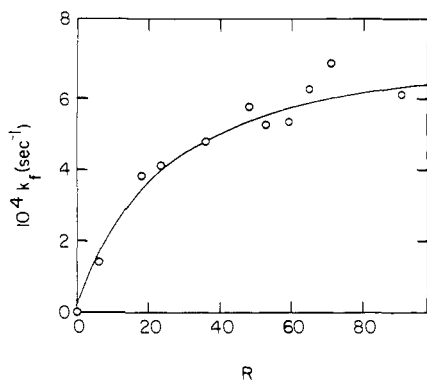


Figure 3. Variation of k_f in acetonitrile at 25.0° with the ratio $R = [\text{Br}^-]/[\text{Cl}^-]$.

rium properties were not at all sensitive to the presence of these small traces of moisture, however, in contrast to the kinetic parameters (see below).

Kinetic Studies in the Absence of Water. Preliminary measurements pointed toward a strong catalytic effect of water, although subsequent careful spectral studies proved that neither the species present nor the equilibria were affected by the addition of a small quantity of water. Basically, two choices were possible: experiments in which every possible trace of water had been removed or in which the concentration of water was deliberately maintained at some fixed value, relatively high to ensure its constancy when reactant concentrations were varied from run to run. The first approach was adopted for the experiments described in this section.

Using the procedure given in the Experimental Section, kinetic measurements were made in the presumed absence of water using P_4O_{10} -dried solvent. Typical starting concentrations were $1\text{--}4 \times 10^{-5} \text{ M}$ $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{Cl}_2$, 10^{-4} M Cl^- , and 10^{-2} M Br^- ; the halide ions were added as their tetraethylammonium salts. The pseudo-first-order rate constant for the approach to equilibrium in the first halide substitution step was evaluated over a range of Cl^- and Br^- concentrations.¹⁴ The qualitative effects were most surprising; *the observed rate constants increased with $[\text{Cl}^-]$, a product of the reaction, and decreased with $[\text{Br}^-]$, a reactant.*¹⁵

The value of k_{obsd} (eq 4) was converted to k_f according to eq 5 using the experimental value, $K_1 = 0.011$. Values of k_f (and k_r) proved to be dependent only upon R , the ratio of halide concentrations, and not upon the individual concentrations. As an example of this, rate constants at $R = 59$ were determined over the ranges $[\text{Cl}^-]$, $0.7\text{--}3.1 \times 10^{-4} \text{ M}$, and $[\text{Br}^-]$, $4.0\text{--}18 \times 10^{-3} \text{ M}$. The average rate constant was $k_{\text{obsd}} = (1.31 \pm 0.16) \times 10^{-3} \text{ sec}^{-1}$ (or $k_f = (5.75 \pm 0.60) \times 10^{-4} \text{ sec}^{-1}$), where the indicated uncertainty is the standard deviation of 14 experiments. The variation of k_f with R , depicted in Figure 3, suggests a relation of the form

$$k_f = \frac{AR}{1 + BR} \quad (9)$$

such that a plot of R/k_f vs. R should be linear with an intercept $1/A$ and a slope B/A . The plot is shown in

(14) The original equilibrium data and the rate constants for individual experiments are presented in the thesis cited.^{1a}

(15) A similar effect of entering group upon k_{obsd} was noted in the reaction of $\text{Co}(\text{CN})_5(\text{SO}_3)(\text{H}_2\text{O})^{3-}$ with I^- : J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta*, 5, 7 (1971).

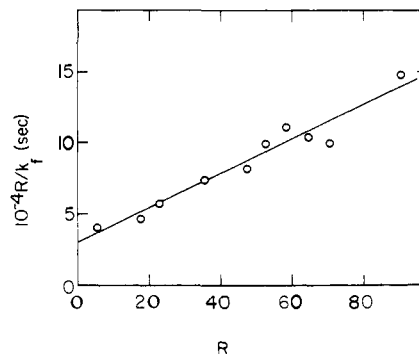


Figure 4. A plot of the kinetic data in acetonitrile according to the linearized form of eq 9.

Figure 4; a least-squares analysis gives the values $A = (3.4 \pm 0.6) \times 10^{-5} \text{ sec}^{-1}$ and $B = 0.041 \pm 0.006$. The expression in eq 9 is consistent with a stepwise dissociation-controlled mechanism, as will be presented in a later section.

The effect of traces of water upon the reaction rate is so pronounced that the possibility remains that the precautions taken here were not sufficient to remove a small residual amount of water. In that event the supposedly anhydrous kinetics measurements would refer, in fact, to data obtained at a small but unknown $[\text{H}_2\text{O}]$. The dependence upon $[\text{H}_2\text{O}]$ which is described in the subsequent section lends some support to this view, in that the quantity of water needed to account for the values of k_{obsd} found in these supposedly anhydrous experiments was quite small, of the order of 0.003 M or 0.005% by volume. Moreover, the scatter in the rate constants determined under these conditions was larger than generally proves to be the case for spectrophotometric rate determinations. This could be accounted for by variation of the concentration of water accidentally present.

Experiments were carried out to determine the rate constants using solutions prepared from acetonitrile dried over molecular sieves. The rate constants were typically two–four times larger than the values obtained using the more rigorous drying technique described above. This rate variation is particularly striking because both solvents would normally be considered “dry.”

Kinetic Studies in the Presence of Water and Other Nucleophiles. Measurement of the dependence of the reaction rates upon $[\text{H}_2\text{O}]$ were undertaken to resolve its striking mechanistic role in this reaction. These studies were extended to include a number of other neutral molecules which also proved to have an accelerating effect on the reaction, in an effort to learn the detailed nature of this catalysis. That the rate effects were truly catalytic was shown by measuring the absorption spectra of the chloro complex and of various chloro–bromo equilibrium solutions. In every case the spectrum remained independent of the concentration of added nucleophile,¹⁶ and corresponded only to the same mixture of $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{Cl}_2$ and $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{BrCl}$ as observed in its absence.

The apparent rate constant, designated $k_{\text{obsd}}^{(\text{N})}$, was evaluated over the range of concentrations 6.5×10^{-3}

(16) However, at much higher concentration of added nucleophile, such as 10% water in acetonitrile or 80% DMF in acetonitrile, the rhenium complexes decomposed.

to $2.4 \times 10^{-2} M$ H_2O and was found to follow a linear dependence upon $[H_2O]$ as shown in Figure 5. Some rate measurements also were carried out in the presence of a still larger excess of water, 5% by volume, corresponding to $2.8 M$ H_2O . These experiments sought conditions where the concentration of water would be high enough that the accidental introduction of traces of water, say through the various $Et_4N^+X^-$ solutions, would be negligible. The reaction occurred quite rapidly under these conditions, with $k_{obsd} \sim 20 \text{ sec}^{-1}$ (compared to $2 \times 10^{-3} \text{ sec}^{-1}$ with comparable concentrations under anhydrous conditions). These determinations indicated that k_{obsd} increased with $[Cl^-]$ and decreased with $[Br^-]$, as was also the case under anhydrous conditions. The rhenium complexes did not prove to be reliably stable in these more aqueous systems,¹⁶ however, and a complete study at high water concentration was not made.

The catalytic effect of a number of other neutral molecules was also studied. The molecules chosen included acetamide and urea, which are oxygen donors and exhibit hydrogen bonding like water, dimethylformamide and tetramethylurea, which are capable of coordination but not of hydrogen bond formation; THF, which is a more weakly coordinating oxygen donor than most of the others; pyridine, which is a much stronger base; and propionitrile, which is a model for the solvent acetonitrile. The variation of k_{obsd} with $[N]$ at a given value of R is also depicted in Figure 5 for some other groups. In these cases and the others, k_{obsd} showed a linear dependence upon $[N]$ with an intercept common to all the catalytic groups within the experimental error. This can be expressed by the relation

$$k_{obsd}^{(N)} = k_{obsd} + k_N[N] \quad (10)$$

in which $k_{obsd}^{(N)}$ represents the experimental pseudo-first-order rate constant for the approach to equilibrium in the presence of the neutral catalyst and k_{obsd} is the same number in its presumed absence. The slopes of these plots (k_N) represent the catalytic strength of each molecule. The values are given in Table I and are seen

Table I. Summary of Catalytic Rate Constants^a

Catalyst	$k_N, M^{-1} \text{ sec}^{-1}$
H_2O	0.83 ± 0.16
C_5H_5N	0.75 ± 0.17
Urea	0.40 ± 0.02
DMF	0.11 ± 0.01
Acetamide	0.066 ± 0.005
$(NMe_2)_2CO$	0.043 ± 0.008
THF ^b	0.0012 ± 0.0001
C_2H_5CN	$< 5 \times 10^{-4}$

^a In acetonitrile at 25.0° . ^b The concentrations of THF were in the range 0.2–1.0 M , which are such that the solvent composition was altered appreciably.

to decrease in the order $H_2O \sim py > urea > DMF > acetamide > TMU > THF \gg C_2H_5CN$. Although k_{obsd} showed a slight systematic increase with propionitrile concentration, the variation was not outside the range of experimental scatter. Variation of R (in the cases of water and urea) indicated that $k_{obsd}^{(N)}$ also shows the same dependence upon R as given by eq 9.

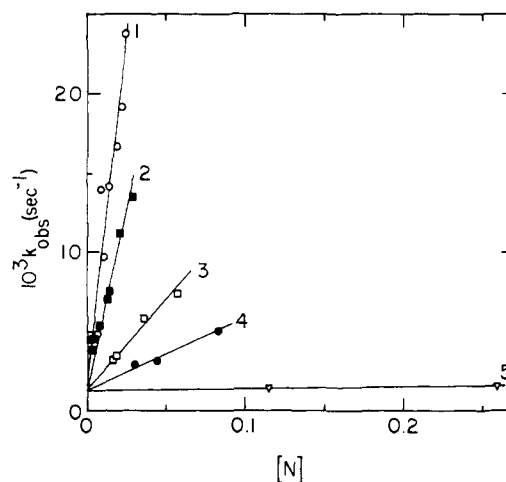
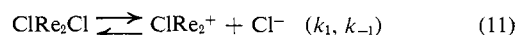


Figure 5. A plot of k_{obsd} vs. $[N]$ for different donor molecules in acetonitrile at 25.0° : 1 = H_2O , 2 = urea, 3 = DMF, 4 = tetramethylurea, 5 = propionitrile.

Effects of Electrolyte Concentration. The addition of Et_4NClO_4 in anhydrous kinetic runs resulted in values of k_{obsd} which were within the experimental error of the values found at the same value of R in its absence. These measurements provided a variation of ionic strength from 0.01 to 0.04 M (computed under the assumption of complete ionization). The results indicate the absence of any significant kinetic salt effect, as well as the absence of a common ion mass-law retardation effect on the halide concentration.¹⁷ Extensive ion pair formation is questionable; if such is the case, however, the ion pairs appear to have essentially the same reactivities as the free halide ions.

Interpretation and Discussion

The rate dependence upon halide ions both in the anhydrous experiments and in the catalytic studies are consistent with the reactions in eq 11 and 12. If the



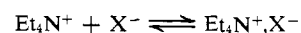
steady-state approximation is applied to the monohalo intermediate which in fact probably contains a solvent molecule or other nucleophile in place of the missing halide (see below), the expression for k_{obsd} as defined in eq 4 is

$$k_{obsd} = \frac{k_1 k_2 [Br^-] + k_{-1} k_{-2} [Cl^-]}{k_{-1} [Cl^-] + k_2 [Br^-]} \quad (13)$$

With the relation $K_1 = k_1 k_2 / k_{-1} k_{-2}$ this expression becomes

$$k_{obsd} = \frac{1 + K_1 R}{(K_1/k_1)R + (1/k_{-2})} \quad (14)$$

(17) An ion-pairing equilibrium can be considered



For the bromide in acetonitrile $K = 14.5 M^{-1}$ has been reported.¹⁸ However, the reported values of constants for R_4N^+ association with halide ions show wide variations in different determinations¹⁹ and must hence be regarded with some caution.

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Upon application of eq 5, the expression for k_f is

$$k_f = \frac{(k_1 k_2 / k_{-1}) R}{1 + (k_2 / k_{-1}) R} \quad (15)$$

which is of the same form as the experimental expression in eq 9. The rate constants appropriate to eq 10 and 11 in acetonitrile at 25.0° are thus $k_1 = (8.1 \pm 0.7) \times 10^{-4} \text{ sec}^{-1}$, $k_2 / k_{-1} = (4.1 \pm 0.6) \times 10^{-2}$, and (with K_1) $k_{-2} = (3.0 \pm 0.3) \times 10^{-3} \text{ sec}^{-1}$.

It should be noted that this scheme is entirely consistent with the unanticipated rate accelerating effect of the product Cl^- and rate retarding effect of the reactant Br^- . Differentiation of eq 13 with respect to the halide concentrations indicates that $(\partial k_{\text{obsd}} / \partial [\text{Cl}^-])_{[\text{Br}^-]}$ and $(\partial k_{\text{obsd}} / \partial [\text{Br}^-])_{[\text{Cl}^-]}$ must have opposite signs, depending upon the relative magnitude of k_{-1} and k_{-2} ; the dependences noted here will result if $k_{-2} > k_1$.¹⁵ This is, in fact, exactly the expected order of dissociation-controlled rate constants; the specific rate of dissociation of Br^- from ClRe_2Br (k_{-2}) should be much greater than that of Cl^- from ClRe_2Cl (k_1), considering that the $\text{Re}-\text{Cl}$ bond is thermodynamically the more stable.

The effects of the catalytic groups appear to be ascribable to their nucleophilic character, in particular to their ability to stabilize the coordinatively unsaturated intermediate of the proposed mechanism. Assuming a common mechanism for all the catalysts, the effects cannot be due to hydrogen bonding between N and the leaving Cl^- , because pyridine, tetramethylurea, and DMF, which cannot hydrogen bond to anions, are nonetheless effective catalysts. Also, DMF and acetonitrile, which have similar dipole moments and dielectric constants, differ markedly in catalytic effect (considering propionitrile), suggesting that the catalysis is not simply a medium effect.

The suggested mechanism entails the intermediate $\text{Re}_2(\text{C}_2\text{H}_5\text{CO}_2)_4\text{ClN}^+$ in eq 11 and 12, such that both k_1 and k_{-2} , and thus also k_{obsd} as in eq 13, show a linear dependence upon $[\text{N}]$. In support of this suggestion, the catalytic rate constants of Table I show a rough correlation with the basicity of N (measured toward the harder acid H^+ in aqueous sulfuric acid).²⁰ Solvento

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complexes are quite common intermediates in substitution reactions; Tobe and Watts²¹ have summarized their role in Co(III) substitutions. No direct proof can be offered whether the rate constants in supposedly anhydrous acetonitrile do in fact correspond to this process or whether they might represent the reaction of residual traces of water ($\sim 0.003 \text{ M H}_2\text{O}$, 0.005% by volume would be needed to account for the data). This small quantity of water might well have been retained by the hygroscopic halide salts despite the extensive drying procedures. It is entirely possible, therefore, that the substitution reactions would not occur at all in the complete absence of a donor catalyst; certainly acetonitrile is far less effective as a catalyst than water, pyridine, or the amides.

Despite the major role of N, the reaction rate appears to be limited by dissociation of the leaving group. Bonding models of the dinuclear rhenium complexes indicate that there is no vacant orbital to bond to an incoming group (thus similar to octahedral Co(III) complexes where dissociative control is believed to operate and unlike the Pt(II) case where the reactions proceed by an associative pathway), leading to the expectation that bond-breaking processes should predominate. The spread in reactivity of the donors is relatively small, suggesting that primary control resides in $\text{Re}-\text{Cl}$ bond breaking. The higher rate of $\text{Re}-\text{Br}$ substitution ($k_{-2} = 3.0 \times 10^{-3} \text{ sec}^{-1}$) compared to $\text{Re}-\text{Cl}$ ($k_1 = 8.1 \times 10^{-4} \text{ sec}^{-1}$) is consistent with a bond-breaking process in that the Re(III) center is clearly a hard acid (note $K_1 = 0.011$). Finally, were the role of N to displace Cl^- associatively, Br^- (which appears to be a more reactive nucleophile than the polar solvents such as DMF²²) would be expected to associatively displace Cl^- more readily still, contrary to observation.

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