A KINETIC STUDY OF THE ELECTRON EXCHANGE BETWEEN THE 12-TUNGSTOCOBALTATE(II) AND THE 12-TUNGSTOCOBALTATE(III) ANIONS IN AQUEOUS SOLUTION

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ABSTRACT

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by Paul G. Rasmussen

The kinetics of the electron exchange reaction between the 12-tungstocobaltate(II) and the 12-tungstocobaltate(III) anions was studied at 0° in aqueous solution. The ions were separated by the selective precipitation of the 12-tungstocobaltate(III) ion with $(Bu)_4NI$ at pH = 5. The reaction was found to be first order with respect to each ion, and second order rate constants of 10^{-2} to 10^{1} $\underline{M}^{-1}sec.^{-1}$ were found depending on experimental conditions. The rate of exchange was found to be a function of the cation present, in particular, the rate in the presence of potassium ion was much greater than that for lithium. The rate was also found to depend on the ionic strength (adjusted with LiCl), and these results were interpreted with the theoretical equations of R. A. Marcus. At constant ionic strength however, the rate was found not to depend on the hydrogen ion concentration for the acid-salt pair of HCl-LiCl. The temperature dependence of the rate was studied and the parameters of activation were obtained. The reaction was also studied in dioxane-water mixtures and the effect of dielectric constant on the rate was determined. In the light of the data obtained, an outer-sphere mechanism is postulated for the system and the results are compared to the theoretical predictions of R. A. Marcus.

A preliminary study was made of the electron paramagnetic resonance spectra of the 12-tungstocobaltate(II) and 12-tungstocobaltate(III) ions, diluted in a host-lattice of potassium 12-tungstosilicate. To obtain a signal, it was necessary to go to very low temperatures ($\sim$ 1°K). No hyperfine splittings were observed in the spectrum of either compound.

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I. INTRODUCTION

Kinetic and mechanistic work in inorganic chemistry has been greatly stimulated in recent years by the availability of radioisotopes(1). The very high efficiencies with which radioactivity may be detected, allows the use of tracer methods, and such methods have been extensively applied to self-diffusion studies and isotopic exchange reactions as well as to the more conventional kinetic systems. Some of the isotope exchange reactions that have been studied have been of the type where simple electron exchange is a possible mechanism. An example is the manganate-permanganate system:

$$\overset{*}{MnO_4}^{-} + MnO_4^{=} \rightleftharpoons MnO_4^{-} + \overset{*}{MnO_4}^{=}$$

studied by Sheppard and Wahl (2). There is good evidence in this case that there is no interpenetration of the coordination spheres (27). An example of a similar cationic system is that of the iron 1-10 phenanthroline complexes (47):

$$\overset{*}{Fe}(phen)_3^{++} + Fe(phen)_3^{+++} \rightleftharpoons Fe(phen)_3^{++} + \overset{*}{Fe}(phen)_3^{+++}$$

which has also been studied by Wahl and his students. Electron exchange in these systems is considered as a barrier penetration phenomena and the activated complex is designated as an outer-sphere complex. Unfortunately, relatively few of the systems which have been studied can be unambiguously classified as being of this simple mechanistic type, and additional data regarding the effect of various ligands and ion atmospheres is desirable.

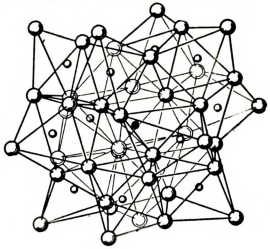
This investigation is concerned with what is believed to be a new example of an electron exchange reaction which proceeds by an "outer-sphere" mechanism. The reactants involved are the 12-tungstocobaltate(II) and the 12-tungstocobaltate(III) anions. These heteropoly acid anions are known to have a "Keggin" (3) type of structure in which the central cobalt atom is surrounded by tungsten-oxygen octahedra sharing corners and edges. (See Fig. 1) Such species are substitutionally inert, and have large formation constants in acid solution (10).

In addition to kinetic considerations, a study of this system seemed desirable because there were no previous reports of electron exchange work on heterpoly complexes in the literature, and because the ability of the central atom electrons to penetrate the tungsten-oxygen "cage" was unknown. Certainly the heteropoly complex cannot aid electron exchange by "conduction" through conjugated ligands like the cyanide or phenanthroline complexes can. If there is not strong overlap between the reactants in the activated complex, then a recent theory due to R. A. Marcus (3,4) should be applicable for predicting the rate of electron exchange, and a test of the theory is possible.

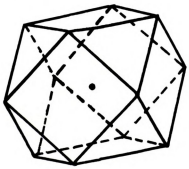
Experimentally, the study was carried out by using ^{60}Co and the usual tracer methods. A major experimental problem in an investigation of this sort is the determining of a rapid, effective means of separating two ions that differ only by one unit of charge. Various methods have been cited in the literature on electron exchange, including solvent extraction, ion exchange chromatography, precipitation, and diffusion. In this system, tetra-n-butyl ammonium ion was found to be an effective reagent for the selective precipitation of the cobalt(III)

anion in the presence of the cobalt(II) anion and an acetate buffer. Although this method leads to various amounts of separation induced exchange, it was found to be reproducible for a given set of conditions, so the induced exchange would not affect the results.(23) The counting of the precipitated samples was done with a windowless gas flow counter. A McKay plot (23) of the data so obtained yields a straight line with slope proportional to the rate of electron exchange.

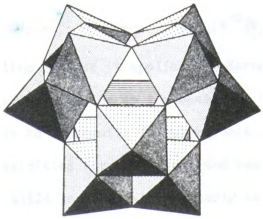
Figure 1. The "Keggin" structure for heterpoly ions
(All figures to the same scale.)



A. Spatial diagram of atoms; ○ Oxygen, ○ Tungsten, ● Cobalt.



B. Cubo-octahedron formed by tungsten atoms at the vertices.



C. Polyhedral diagram, note central tetrahedron.

II. HISTORICAL

A. Heteropolyacid Chemistry

The discovery of the large group of compounds designated heteropolyacids was due to Marignac (6), who found in 1861 that tungstic and silicic acids reacted in solution to form stable compounds which could readily be crystallized out. The heteropoly acids and their salts are a unique group of compounds in which vanadium, molybdenum, tungsten or other heavy addenda atoms combine with oxygen and various hetero atoms to form complex, high molecular weight anions. Heteropoly compounds are commonly classified by the ratio of addenda atoms to hetero atoms. Although all the integral species have been reported from 12:1 to 1:1, species with ratios of 12:1, 9:1 and 6:1 are by far the most numerous.

The determination of the structures of these compounds has evolved slowly over the years and is still the subject of current research. Around the turn of the century, Rosenheim, and later Miolati, attempted to write systematic formulae for the heterpoly ions by considering them as derivatives of a parent acid as follows:

$$H_{12-n}[X^{+n}O_6] + 6W_2O_7^{-2} \longrightarrow H_{12-n}[X^{+n}(W_2O_7)_6]$$

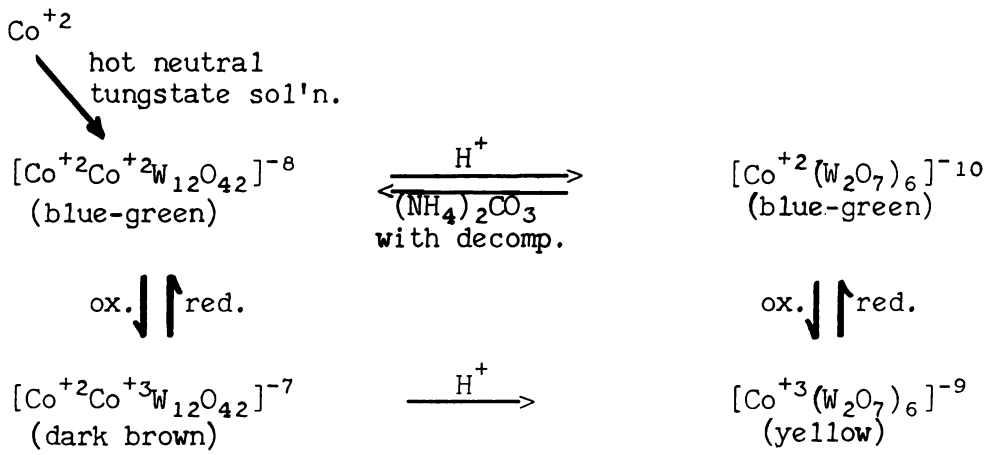
This system was appealing because it applied the Werner coordination theory to what was considered to be an ion analogous to the dichromate ion. Although it leads to systematic formulae, this method does not predict the correct basicities for the anions, and real knowledge of the spatial structure was still lacking. In the early thirties, Pauling applied his empirical bonding rules to the problem and proposed a

structural model for the 12-tungstophosphate(V) ion. Although the gross features of Pauling's structure were correct, the X-ray diffraction work of Keggin(3) showed in detail the oxygen sharing properties of the octahedra involved. Recently, his model has been verified and exact structural parameters found for the compounds used in the present study by Eriks and Yannoni (37). The "Keggin" structure (See Fig. 1) locates the tetrahedrally coordinated hetero atom in the center of a cubo-octahedron with tungsten atoms at the vertices. Each tungsten atom is in a slightly distorted octahedron of oxygen atoms. Four clusters of (W_3O_{13}) tetrahedrally surround the central atom. Each cluster is made up of three octahedra sharing edges in such a way that an oxygen of the central metal atom is common to all of them. The four clusters are bound together by sharing corner oxygens. The over-all formula is then $[X^nO_4W_{12}O_{36}]^{8-n}$ for a heteropoly anion with the "Keggin" structure.

Some general properties common to this class of compounds are: (7)

1. Very high molecular weights - to over 4000.
2. Extraordinary solubility in water.
3. Precipitated by cations such as tetra-alkyl ammonium, rubidium, cesium, and guanidinium ions.
4. Colors which range through the spectrum as well as colorless compounds.
5. Strong oxidizing and reducing properties in many anions.
6. High degree of hydration in the crystalline state.
7. Degradable by alkali.

To the general class of heteropoly anions, belong several members first prepared and characterized by Baker and McCutcheon in 1956 (8). These authors reported the following preparative scheme for the 12-tungstocobaltates.



They note that the relatively late discovery of these compounds is probably due to the unusual circumstance of their formation in neutral solution, whereas most heteropoly tungstates form in acid. In later papers (9,10), Baker and Simmons report further on the structures of the monocobalt compounds. The main features of the "Keggin" structure are preserved; the central cobalt atom is tetrahedrally coordinated, and the formulae are revised to the following:

$$[Co^{+2}O_4W_{12}O_{36}]^{-6} \quad \underset{\text{red.}}{\overset{\text{ox.}}{\rightleftharpoons}} \quad [Co^{+3}O_4W_{12}O_{36}]^{-5}$$

I II

They found by careful dehydration experiments that all the water of crystallization could be removed without destroying the heteropoly ion. This would seem to indicate that there is little vacant space within the ion, and indeed, a study of the ionic radii shows that the oxygen atoms in the heteropoly structure are very nearly close-packed. This feature as well as other structural aspects is discussed elsewhere (24).

The oxidation and reduction were found to take place reversibly in 1N H_2SO_4 at a potential of -1.07 volts indicating small stabilization for the tripositive oxidation state. The bulk magnetic susceptibility was also determined (25) and the applicability of the Curie-Weiss law

rigorously verified. The reported values for magnetic moment were 4.25 and 5.07 Bohr Magnetons for I and II respectively. Finally, they found, in work pertinent to this investigation, that there was no evidence for dissociation of either monocobalt species as determined by cryoscopy in fused $Na_2SO_4 \cdot 10H_2O$ (33). It is the electron exchange between the monocobalt redox pair (hereafter referred to as I and II respectively) that is the subject of this thesis. Recently, several review articles have appeared that may serve to apprise the reader of modern developments in the area of heteropoly chemistry (11, 12, 13).

B. Electron Exchange Studies

Since the late nineteen forties, electron exchange kinetics has been a remarkably active area of research. The early work is well summarized up to 1950 by A. C. Wahl and N. A. Bonner (14). At that time there were insufficient data available, however, to allow a quantitative explanation of the factors controlling the rates of electron exchange. Experimental work since 1950 has shown that no single mechanism is generally operative in inorganic redox reactions and that ligands and media play important roles. The system most extensively studied has been Fe(II)-Fe(III). The effects of acid, fluoride ion, sulfate ion, phosphate ion, organic acid anions, temperature, heavy water, alcohol, and other agents on the rate have all been examined. (38,39,40,41,42) From these studies and those on a number of other systems including many net reaction systems, it appears that the possible mechanisms for redox reactions fall into two broad categories. Under the title of "strong over-lap mechanisms" are the atom transfer and some ligand bridge mechanisms. Although these two possibilities have been distinguished in favorable cases, there is often an ambiguity. Atom transfer can be ruled out in the so-called "conduction" mechanisms in which ligands such as para-phthalic acid greatly accelerate the rate, due to the ease with which the electron can traverse the conjugated set of π orbitals. The strong over-lap mechanisms, in either case, are viewed as directly involving the primary coordination spheres of the reactants. In weak-overlap mechanisms, this is not true, and the reactants are inert to ligand substitution. In these cases, the electron transfer is considered as a quantum mechanical barrier penetration. The activated complex is designated as an outer-sphere

complex although its exact nature is difficult to assess. Relatively few of the electron exchange systems studied have been assigned weak-overlap mechanisms and most of these are very fast. Examples of weak-overlap systems include MnO_4^--$MnO_4^=$, $Fe(phen)_3^{++}$-$Fe(phen)_3^{+++}$, $Os(dipy)_3^{++}$-$Os(dipy)_3^{+++}$, $Fe(CN)_6^{-3}$-$Fe(CN)_6^{-4}$, and $IrCl_6^{-2}$-$IrCl_6^{-3}$. (1)

Theoretical approaches to the problem are varied and contradictory. Libby (15) has stressed the importance of the Franck-Condon principle and the ligand rearrangements necessary in electron exchange. R. J. Marcus, Zwolinski and Eyring (16) have treated the barrier penetration aspects of the problem. Their results require calibration, however, with an experimental system. R. A. Marcus (4, 5) has dealt with the weak-overlap case and has derived rate expressions with no adjustable parameters. He has included in his derivation, terms that account for the rearrangement energy on going from reactant to product in cases where this is appropriate. Hush (25) derives in his so-called adiabatic theory, results that are in substantial agreement with those of R. A. Marcus by using an electron reaction coordinate parameter. Laidler (26) proposes a "non-adiabatic" theory which is similar in approach to that of Marcus, Zwolinski and Eyring. Agreement between experimental data and any of the theories is only fair, and a thorough critique of the various approaches as well as additional experimental data would be desirable. The work of R. A. Marcus has gained the widest acceptance at present and his model will be applied to the system involved in this investigation in a following section. Electron exchange between heteropoly anions should be an excellent example of the weak-overlap type of mechanism because of the presumed non-lability of the discrete species in solution and their large

size. Unfortunately, however, a detailed knowledge of the transition state is not obtainable in general from rate studies alone. Several review articles have summarized the available experimental work in recent years (17,18,19,20,21).

III. THEORETICAL

A. The Rate Law For the Exchange Process

For a stable homogeneous phase, in which all the atoms of a particular oxidation state are chemically equivalent, and the half-life of the tracer is long compared to the exchange time, the McKay equation (23) gives the rate of growth of radioactivity in an initially unlabeled species as:

$$(1 - X/X_\infty) = \exp[- \frac{a + b}{ab} Rt] \qquad (1)$$

t = time

a,b = total concentration of each reactant

X = activity in initially inactive species at time t

X_∞ = activity in initially inactive species after infinite time

R = rate of exchange process.

This law is followed, regardless of the mechanism of the reaction between the species involved. The equation may be rewritten as:

$$2.303 \log(1 - X/X_\infty) = - \frac{a + b}{ab} Rt \qquad (2)$$

From which it is apparent, that a plot of log $(1 - X/X_\infty)$ <u>versus</u> time should be linear. The half-time, $t_{1/2}$ is easily obtained from a graph and R is calculated:

$$R = \frac{ab}{a + b} (0.693/t_{1/2}) \qquad (3)$$

To determine the reaction order with respect to a reactant, the rate R is equated to a general rate law:

$$R = k_r[a]^{\alpha}[b]^{\beta}[c]^{\gamma} \cdots \qquad (4)$$

then:

$$\left(\frac{\partial \log R}{\partial \log [a]}\right)_{[b],[c]} = \alpha \qquad (5)$$

therefore a plot of log R versus log [a] for fixed [b] and [c] will have a slope of α, the order with respect species a. The rest of the exponents may be similarly determined. A simpler but less rigorous procedure, is to assume a value for α, β, γ etc. and then calculate k_r, the rate constant, using the rates obtained for various values of a, b, c etc. If k_r remains constant within experimental error, the assumed order is adopted. While this method works well for simple systems, clearly it must be applied with some caution.

Frequently, the reactants in an electron exchange reaction system can only be incompletely separated, or a rapid exchange may occur during the separation. These effects result in an apparent zero time exchange. Zero time exchange can occur to the extent of 100% in which case one does not know whether the reaction itself is rapid or whether the separation method is at fault. If the apparent zero time exchange is less than 100%, however, Prestwood and Wahl (22) have shown that the slope of log $(1 - X/X_{\infty})$ versus time is unaffected and the rate may still be obtained. This result depends of course on the apparent zero time exchange remaining constant for a given set of conditions.

B. Theoretical Prediction of the Rate Constant

Of the current theories mentioned in the introduction of this thesis, the author feels that the one due to R. A. Marcus fits the experimental data the most satisfactorily and is the most complete. Therefore it will be used as a model for comparison with the present experimental system of heteropoly anions. The Marcus theory predicts the rate of electron exchange for the weak-overlap case i.e. when orbital overlap between the reactants is small in the activated complex. Experimentally this situation obtains when the first coordination sphere of the reactants is non-labile and when the ions are large and weakly solvated. These conditions appear applicable to 12-tungstocobaltate ions.

The following equations summarize the results of the Marcus theory. For a detailed development, the reader is referred to the original papers (4,5). The factor $\exp[-\kappa r]$ will not be found in these papers, however. Its inclusion was suggested to the author (49) as a correction for the effects due to the large sizes of the ions. For heterpoly ions it is a poor approximation to compute the energy of interaction on the basis of point charges even at quite low ionic strengths. In the limit of zero ionic strength, the $\exp[-\kappa r]$ term approaches unity and the original equation of Marcus is obtained.

$$k_r = Z \exp[- \Delta F^{*}/RT] \qquad (6)$$

$$\Delta F^{*} = \frac{e_1 e_2}{D_s r} \exp[-\kappa r] + m^2\lambda \qquad (7)$$

where: k_r = rate constant

Z = collision number in solution equals about 10^{11}

T = absolute temperature (Kelvin)

D_s = dielectric constant of solvent

ΔF^{*} = free energy of activation (Gibbs)

e_1, e_2 = charges on the reactants

r = distance of closest approach of the reactants

m = derived constant equal to -0.5 for electron exchange reactions

κ = "Debye-Hückel kappa" equal to $(5.03 \times 10^9)\sqrt{\mu/D_s T}$

μ = ionic strength.

$$\lambda = \lambda_o + \lambda_i \tag{8}$$

$$\lambda_o = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right)(\Delta e)^2 \tag{9}$$

$$\lambda_i = \sum_j \frac{K_j K_j^p}{K_j + K_j^p} (\Delta q_j^o)^2 \tag{10}$$

where:

λ_o = "lambda outer"; contribution to λ of surroundings of activated complex

λ_i = "lambda inner"; contribution to λ of changes in first coordination sphere.

$r = a_1 + a_2$

n = refractive index of the solvent

Δe = amount of charge transferred as a result of the reaction

K_j, K_j^p = force constants of jth vibrational coordinate for a species as reactant and product respectively.

Δq_j^o = change in the bond distances and angles in the inner coordination sphere of each reactant.

The summation is over the j normal modes of each reactant, and over all bonds involved in a particular mode.

To apply the above to the 12-tungstocobaltate system, we must estimate several of the terms in the equation for λ_i. For a regular tetrahedron such as the central $Co(II)O_4$ - $Co(III)O_4$ tetrahedra of these

heteropoly ions, only one of the j normal coordinates involves significant deformation on going from reactant to product. (28) This is the one that corresponds most closely to bond stretching. For the others, the Δq_j^o's are very nearly zero in a case where the reactants and products are so similar. In order to estimate the contribution to λ_i of this singly degenerate normal mode, we need to know the equilibrium bond length change Δq^o as well as the force constant of the bond in each reactant. Using the crystal radii of Pauling (29) and his ligancy correction from six to four, we obtain:

Co(II)-O 1.97 Å

Co(III)-O 1.87 Å.

It is reassuring to note that X-ray diffraction work has found the Co(III)-O distance to be 1.88 Å in $K_5[Co(III)O_4W_{12}O_{36}]$ in good agreement with the above. (37) For consistency we use the two calculated values and obtain for Δq^o the value of 0.10 Å. To evaluate the force constants, we make use of an empirical rule of Badger (30):

$$(C/K)^{1/3} = r_e - d_{ij} \qquad (11)$$

where: C = an empirical constant equal to 0.125 for a bond between a first row atom and a third row atom.

d_{ij} = an empirical constant equal to 1.06 for a bond between a first row atom and a third row atom.

r_e = equilibrium bond length in Angstroms.

K = force constant of bond in megadynes per centimeter.

According to the above rule, the force constants are thus:

Co(II)-O $K = 1.66 \times 10^5$ dynes/cm.

Co(III)-O $K = 2.27 \times 10^5$ dynes/cm.

Substitution of the above factors into the equation for λ_i yields:

$$\lambda_i = 7.68 \times 10^{-13} \text{ ergs} \qquad (12)$$

Proceeding to evaluate the equations for λ_0 and λ, we note that $a_1 = a_2$ for electron exchange reactions, and that $r \lesssim 10$ Å from X-ray diffraction work on $K_5[Co(III)O_4W_{12}O_{36}]$. (37) At 0° $D_s = 88.0$ and $n = 1.333$ for water, and $e_1e_2 = (8)(4.8 \times 10^{-10})^2$ e.s.u.. The value of 8 for the charge product is obtained from the data on ionic strength variation. (See Results section of this thesis). Substitution of these values gives:

$$\lambda_0 = 12.7 \times 10^{-13} \text{ ergs} \qquad (13)$$

$$\Delta F^{\ddagger} = 10.4 \text{ kcal/mole} \qquad (14)$$

$$k_r = 4.7 \times 10^2 \text{ M}^{-1}\text{sec.}^{-1} \qquad (15)$$

This value for the rate constant is for infinitely dilute solution, and it will be compared to the extrapolated experimental value in the Discussion section of this thesis.

IV. EXPERIMENTAL

A. Preparation of Reagents

The potassium salt of anion I was prepared with reagent grade chemicals* used without further purification in the method of Baker.(8) Approximately 0.5 millicurie of 5.2y ^{60}Co was added to the $Co(acetate)_2 \cdot 4H_2O$. The tracer was obtained from Oak Ridge National Laboratory as the chloride, and was converted to the acetate by repeated evaporations with acetic acid. Anion II was prepared by electrolysis of a 0.02M solution of anion I in the anode compartment of an "H" cell. An "H" cell was used to prevent hydrogen formed at the cathode from reducing anion II. The two compartments of the "H" cell were separated by a glass frit which allows the electrical contact to be maintained. The electrolysis was carried out at a platinum anode with an applied potential of 4.5 volts. The entire cell was immersed in water at 80°. This procedure avoids the contamination of the stock solution by chemical oxidizing agents such as $Na_2S_2O_8$ or PbO_2 which were previously used.(8) The color change from blue-green to yellow that accompanies the oxidation serves as a convenient indicator of the extent of reaction. The visible region absorption spectra of the compounds so prepared agree with those obtained by Simmons. (33) To convert the stock solutions prepared from the potassium salts to solutions of the lithium salts, they were passed

*KCl; $Co(acetate)_2 \cdot 4H_2O$ from J. T. Baker Co.
$Na_2WO_4 \cdot H_2O$ from Mallinckrodt Chemical Works.

over a column of Dowex 50 X 12 ion exchange resin which had been converted to the lithium form. The effectiveness of this procedure was checked by flame photometric analysis which indicated that less than 10 ppm Na^+ and K^+ were present. In addition to exchanging K^+ for Li^+, this operation has the desirable effect of removing any cationic cobalt which may be present.

The quenching reagent was prepared by mixing 75% by volume of a solution saturated at 25° with (Matheson, Coleman and Bell) $(Bu)_4NI$ and 25% by volume sodium acetate-acetic acid buffer solution 0.1 M in acid and salt, plus 0.1% by weight "Celite" filter aid. It is of interest to note that without the presence of the buffer, $(Bu)_4NI$ precipitates both of the heteropoly ions, and in the runs in which extra acid was added, additional sodium acetate was required also. Early attempts at using $(CH_3)_4NI$ in the quench led to higher percentages of induced exchange and very finely divided precipitates. The solutions of various acidities and ionic strengths were prepared by appropriate dilutions of the stock solutions along with the addition of HCl and LiCl. (Baker "Analyzed" Reagents) The 1-4 dioxane used in the dioxane-water mixtures was distilled from $LiAlH_4$, to remove the peroxides, and stored under nitrogen. Since the density of dioxane is $1.03\frac{20}{4}$, volumetric dilution was suitable for the preparation of the solutions. All water that was used in this investigation had been distilled from a tin lined still and passed over a mixed resin bed. Conductivity measurements indicated a metal ion concentration of less than one part per million in the effluent water.

B. Analytical Methods

The stock solution of anion II was analyzed by potentiometric titration with ferrous ammonium sulfate which was itself standardized against potassium dichromate. (48) The reduction is quantitative and rapid as can easily be demonstrated by rapidly adding excess ferrous ion to a solution of anion II and noting the color change. The color is not sufficiently intense, however, to serve as an indicator. Therefore, a platinum indicator electrode and a saturated calomel reference electrode were used to follow the reaction potentiometrically. The anion I solutions were similarly analyzed by first oxidizing an aliquot electrolytically as described in the preparative section, and then titrating as for the anion II solutions. This method has several advantages over analysis on the solid material. It requires no knowledge of the somewhat uncertain number of cations or protons present in these acid salts, or of the number of waters of crystallization, but gives the concentrations of the anions (I or II) directly.

The radiochemical assay of the separated precipitates was done with a windowless gas-flow counter using helium-isobutane as the counting gas and an applied potential of 1400 volts.

Although anion II is a strong oxidizing agent, its solutions were found not to decompose with time, as long as dust and other easily oxidized materials were carefully excluded, and the solutions were not heated in the presence of chloride ion which may then reduce them. The solutions of anion II were easily checked by determining their absorbancy at 638 mμ where anion I has a substantial absorption maximum and anion II is transparent. (See Appendix II)

C. Procedure

The reaction was initiated by the addition of 1 ml. of anion II solution to 1 ml. of anion I solution. The pipets used were stored at 0° by placing them in a cylinder which was immersed in a bath at 0.0° ± 0.1 The solutions were delivered in blackened test tubes to prevent photocatalysis, although no evidence for such catalysis was found. Each point in a run represents an individual reaction mixture since some of the half-times were short and several minutes were required to carry out the separation. Anion II was selectively precipitated from the reaction mixture by the rapid addition of 1 ml. of quenching reagent stored at 0°. (The composition of the quenching reagent is described above.) Two-tenths of a minute were allowed for the complete formation of the precipitate, and then the mixture was filtered by suction on a 2 cm. circle of Whatman #540 filter paper in a funnel with a removable chimney. At temperatures above 0° slightly less quench was required in order to prevent the precipitation of both anions. The quality of the separation can readily be judged by the color of the precipitate, which should be light yellow. If coprecipitation of anion I is extensive (as it is if the separation is attempted at too low a pH) the color of the precipitate becomes green. The devising of a rapid, reproducible, separation of anion I and anion II, which are large and identical except for one unit of charge, was the most difficult experimental part of this investigation. No separation has previously been reported. After filtration, the precipitates were air dried on the filter papers, which were kept from curling by placing small lengths of 2 cm. diameter copper tubing over them. The radioactivity of the dried samples was counted. The

infinite-time samples were allowed to equilibrate, and then quenched and filtered after more than ten half-times had elapsed. Separation induced exchange to the extent of about 20% was observed in most series. All operations were carried out in as standard a manner as possible in order to minimize random errors. Weighing of the precipitates in order to determine the absolute activity did not lead to increased precision in the results and this procedure was abandoned.

D. Errors

The sources or error in this investigation are of two types, the usual random errors of laboratory work and the errors associated with radiochemical assay. Radiochemical assay errors or counting errors are dealt with in detail in texts on radiochemistry. (31,32) The salient points are these: 1) radioactive decay follows a Poisson distribution law; 2) for such a process the probable error is determined by the number of counts rather than by the length of the counting period; 3) the probable error can be reduced below and given value by observing a sufficient number of counts. In this study, approximately 10,000 counts were measured for each sample. It can be shown that this leads to a standard deviation in the number of counts observed of ± 1%.

Unfortunately, random errors from another source were larger and more difficult to control. The most serious source of error was the separation method itself. Both positive and negative errors are possible since the precipitation of anion II may be incomplete, or the precipitate may be contaminated by occlusion and coprecipitation of the anion I compound. Because of these factors, a single point in a given kinetic run has a relative standard deviation of about ± 7%. Although attempts by various methods to reduce this scatter were not particularly successful, the rate constants are not in error by this amount for two reasons: 1) the rate is calculated from the slope of a straight line on a semi-log plot and not from individual points; 2) the infinite time point which does affect the slope (see part A of this section) was determined in triplicate for each run.

In addition to the two sources of error discussed above, there were the normal errors of quantitative procedures, and the errors in the measurements of times and temperature. The timing errors were probably the least significant, as shown by the linearity of the data for a series in which the half-time was only 0.73 minutes. In most runs, the temperature was held at $0.0^{\circ} \pm 0.1$ with ice in equilibrium with water at 0° in a dewar flask. Similar control was possible for the runs at slightly higher temperatures by the use of an insulated refrigerator bath controlled by a bimetallic probe and an electric relay, in which the regulation was to at least $\pm 0.1^{\circ}$.

V. RESULTS

A. Determination of the Kinetic Order

An essential first step in any kinetic study is the establishment of the rate dependence on the concentration variables. Although electron exchange reactions are most often second order, first order in each reacting species, there are several other cases. The Ag(I) - Ag(II) exchange (34) and the U(IV) - U(VI) exchange (43) are well known examples where a simple second order rate law does not hold. By assuming that:

$$R = k_r[I][II] \tag{16}$$

and determining R from the McKay equation (see section III-A of this thesis) the rate constants of table I were calculated for various concentrations of anion I and II. The half-times used in the McKay equation to calculate R were obtained from plots such as figure 1 which shows some typical rate data. From the variation in the rate constants, it was found that :

$$R = k_r[I]^{1.0\pm.01}[II]^{1.0\pm.01} \tag{17}$$

For the concentrations and conditions listed in table I, the half-time was approximately 11 minutes.

Table I. Dependence of the rate constant on reactant concentrations.

Ionic Strength Adjusted to 0.6 with LiCl; Temperature 0°; pH = 2; Li salts of anions I and II

[I]	[II]	k_r ($\underline{M}.^{-1}$ sec.$^{-1}$)
0.0007	0.0018	0.63
0.0009	0.0015	0.64
0.0011	0.0012	0.63
0.0014	0.0010	0.65
0.0016	0.0007	0.61
		0.63 ± .016

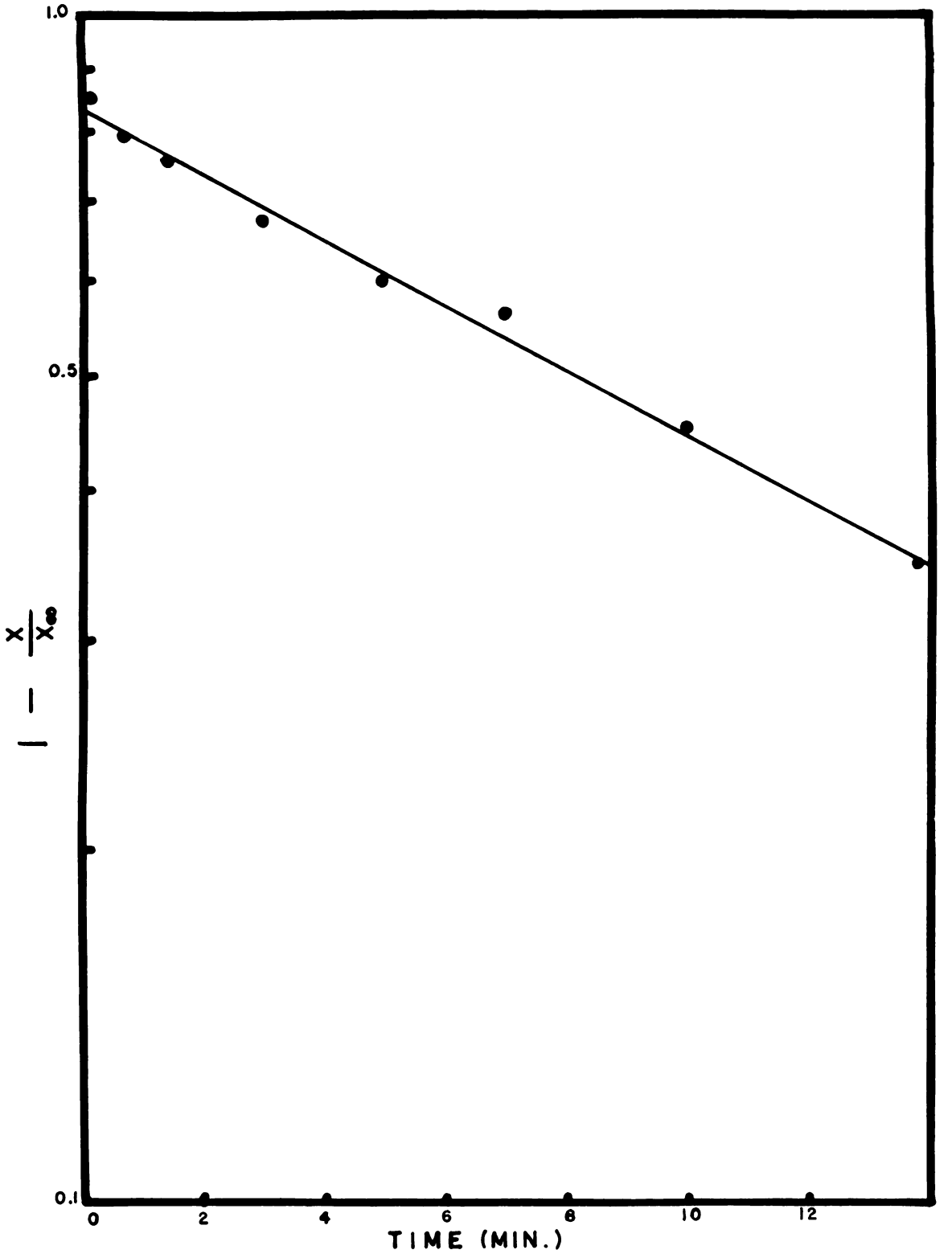


Figure 2. Exchange curve for some typical rate data. Temperature 0°; 0.41 LiCl; [I] = 1.14×10^{-3}M; [II] = 1.22×10^{-3}M; $k_r = 0.44$ (M^{-1} sec.$^{-1}$).

B. Dependence of the Rate on Hydrogen Ion Concentration.

Because the heteropoly acid salts used in this investigation can ionize to varying degrees depending on the ion atmosphere, it is important to know how the hydrogen ion concentration affects the rate of exchange. The hydrogen ion concentration was varied from 0.025 M to 0.80 M with HCl while the ionic strength was maintained constant at 1.02 with LiCl. The acid-salt pair of HCl-LiCl is a useful one because the mean activity coefficients for these two materials are nearly identical throughout this concentration range in water solution. Within experimental error of ± 6% in the rate constant, the exchange rate was independent of hydrogen ion conentration at constant ionic strength. (Table II below). This indicates that protons are not a necessary part of the activated complex, and that neither a Grotthuss type of proton jump mechanism, nor H atom transfer contributes significantly to the rate, since the ionic mobility of H^+ is 340 cm./sec./volt while that of Li^+ is only 37 cm./sec./volt. (35).

Table II. Dependence of rate on HCl concentration.

Ionic strength 1.02 adjusted with LiCl; [I] = 1.08 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; Temperature 0°.

[HCl]	k_r($M^{-1}sec.^{-1}$)
0.025	1.05
0.200	0.98
0.400	1.03
0.600	0.93
0.800	1.09

C. Dependence of the Rate on Ionic Strength

The rate was found to have a marked dependence on the ionic strength. This is not surprising in view of the large charges of like sign on the ions. Simple coulombic considerations would predict that increasing the density of the ion atmosphere around such ions would aid them in approaching each other close enough to allow electron transfer to occur. The ionic strength was varied from 0.01_5 to 0.81 by the addition of LiCl, and the resulting effects on the rate constants are given in table III. Results of this nature may be described by the Brönsted-Bjerrum equation (36) if the ionic strength is very low. For large ions at moderate ionic strengths, a plot of $\log k_r$ vs $\sqrt{\mu}$ will not be linear as would be the case if the Brönsted-Bjerrum equation were followed. (Figure 3). We note, however, that the deviation from linearity is in the direction expected if the additive term in $\sqrt{\mu}$ in the denominator of the Debye-Hückel is neglected as is done in the Brönsted-Bjerrum approximation. Alternatively, the same data may be interpreted with the Marcus equations (Section II-A). This treatment indicates that a plot of $\log k_r$ vs $e^{-\kappa r}$ (Figure 4) should also be linear but this relationship will hold for somewhat higher ionic strengths than the limiting Brönsted-Bjerrum expression.

From the slope of the line in figure 4, a charge product of $Z_1Z_2 = 8$ can be calculated. This would seem to be a reasonable value for ions in solution that have formal charges of five and six.

Table III. Dependence of the rate constant on ionic strength.

Ionic strength adjusted with LiCl; Temperature 0°; [I] = 1.14×10^{-3} M; [II] = 1.22×10^{-3} M.

μ	$\sqrt{\mu}$	κr	$e^{-\kappa r}$	k_r (M^{-1} $sec.^{-1}$)
0.01_5	0.122	0.396	0.670	0.03
0.05	0.224	0.727	0.481	0.07
0.21	0.459	1.489	0.225	0.31
0.41	0.641	2.080	0.125	0.44
0.61	0.783	2.541	0.079	0.64
0.81	0.901	2.924	0.053	0.96

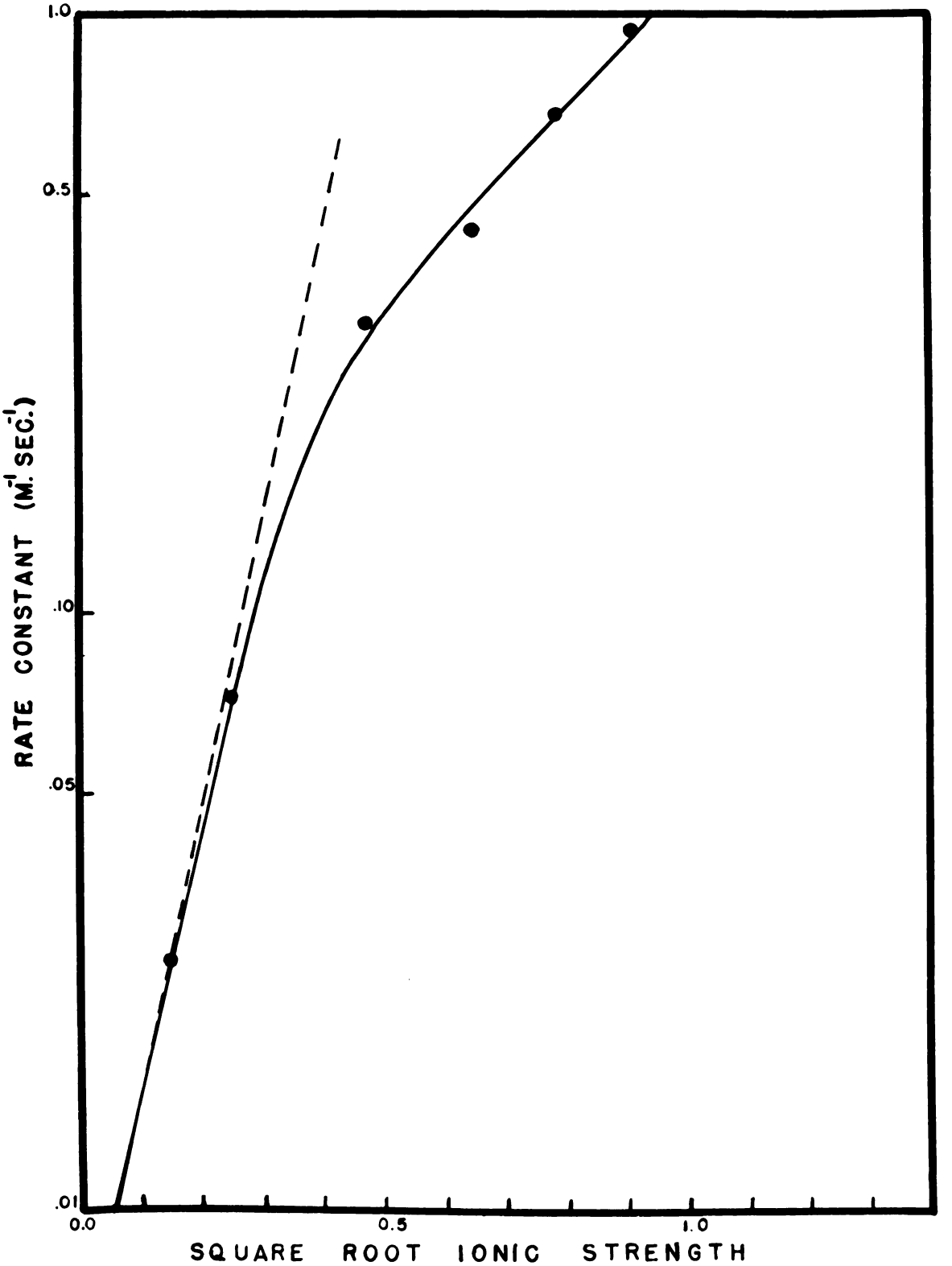


Figure 3. Graph of log k_r vs $\sqrt{\mu}$.

Temperature 0°; Ionic strength adjusted with LiCl; [I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M.

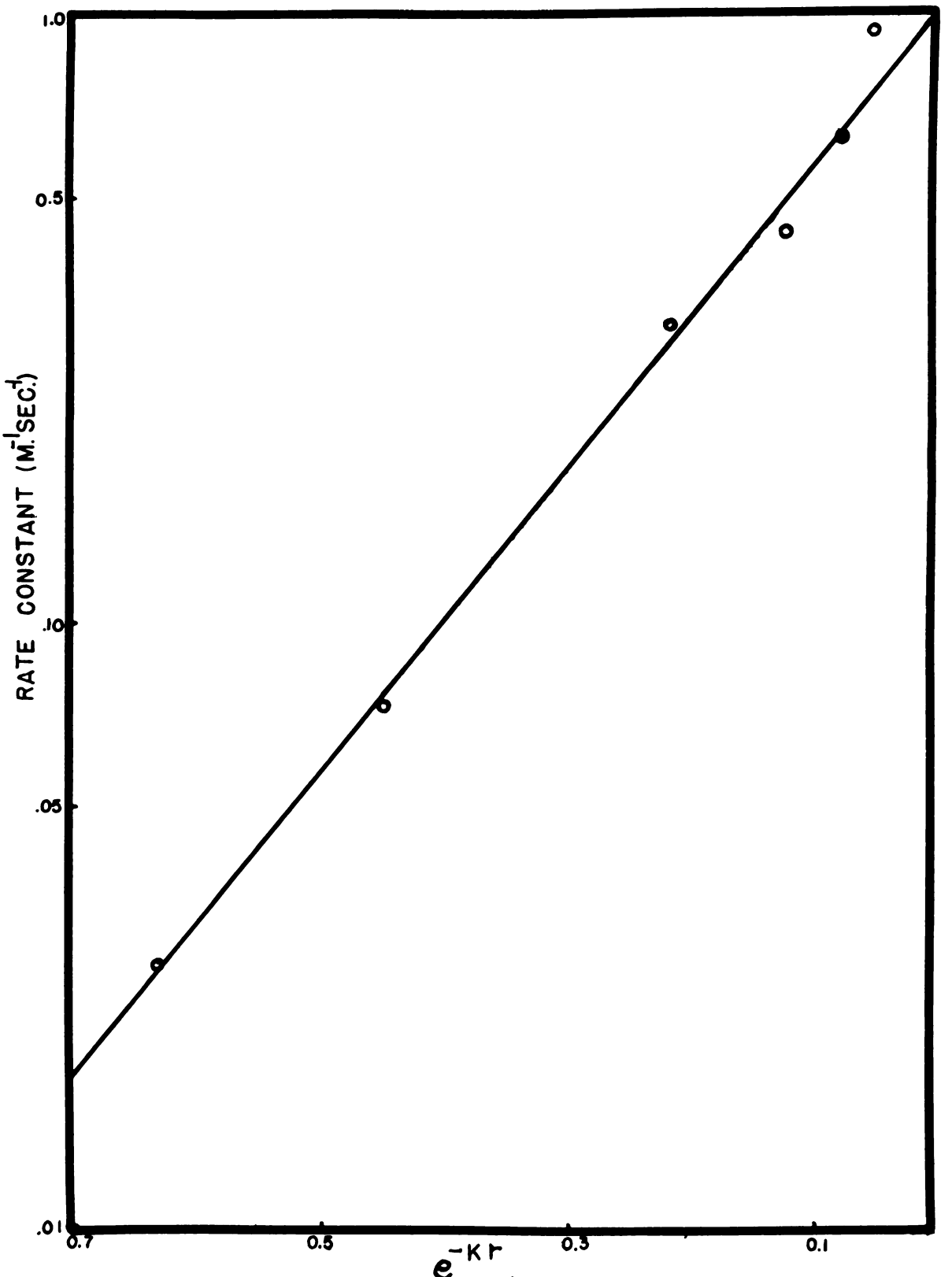


Figure 4. Graph of log k_r vs $e^{-\kappa r}$.

$\kappa r = 3.24\sqrt{\mu}$ for water solutions at 0°; Ionic strength adjusted with LiCl; [I] = 1.14×10^{-3}M; [II] = 1.22×10^{-3}M.

D. Dependence of the Rate on Temperature.

The temperature dependence of the rate was studied at several ionic strengths and the parameters of activation were obtained. The activation energy is a function of ionic strength and an approximate extrapolation to zero ionic strength was possible. (Table IV) The dependence of the energy and entropy of activation on ionic strength for reactions between ions in solution, is a matter frequently ignored in experimental papers on the subject, a fact which undoubtedly has lead to fallacious conclusions when comparisons between various systems are made. The results of this investigation demonstrate the futility of any such conclusions that are based on slight differences in the activation parameters, especially when they are for solutions of different strength. The data on the temperature dependence of the rate may be interpreted by the transition state equation (36):

$$k_r = (kT/h)\exp[\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/R\,T] \qquad (18)$$

where:

k_r = the rate constant

k = Boltzmann's constant

T = the absolute temperature

$\Delta S^{\ddagger}$ = the entropy of activation per mole

$\Delta H^{\ddagger}$ = the enthalpy of activation per mole

R = gas constant per mole

E_a = activation energy per mole

for a reaction in solution:

$$\Delta H^{\ddagger} = E_a - RT \qquad (19)$$

The activation energies were obtained from the slope of the lines in Figure 4, but the entropies were calculated from the above equation because the extrapolation of 1/T to zero is very long. The results are summarized in Table IV.

Table IV. Dependence of the rate constant on temperature and ionic strength. The parameters of activation.

Ionic strength adjusted with LiCl; [I] = 1.14×10^{-3}M, [II] = 1.22×10^{-3}M.

μ	k_r($M^{-1}sec.^{-1}$)	Temp.	E_a kcal/mole	ΔS e.u.
0.21	0.31	00.0		
0.21	0.48	12.7	5.0 ± 0.5	-44.0 ± 2
0.21	0.72	25.0		
0.05	0.07	00.0		
0.05	0.13	12.7	8.0 ± 1	-35.4 ± 1
0.05	0.34	25.0		
0.01_5	0.03	00.0		
0.01_5	0.08	12.7	12.8 ± 2	-19.7 ± 1
0.01_5	0.24	25.0		
0.00	--	--	18 (extrapolated)	

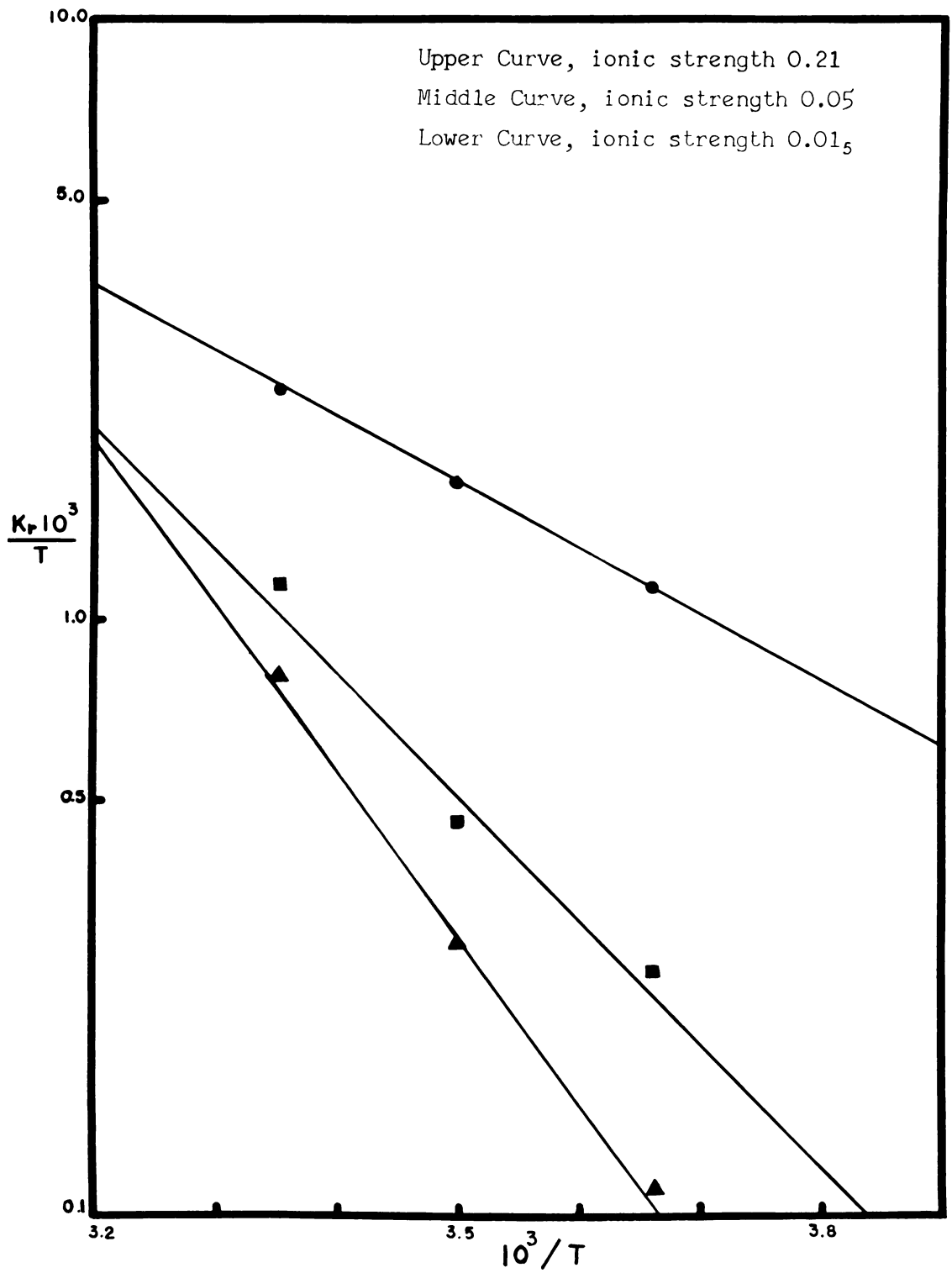


Figure 5. Graph of log $k_r 10^3/T$ vs $10^3/T$.
Ionic strength adjusted with LiCl; [I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M.

E. Specific Cation Effects

Substitution of the lithium cations by potassium ions lead to large increases in the rate of electron exchange, as shown by the data in table V. At 0°, [I] = 1.14×10^{-3} M, [II] = 1.22×10^{-3} M; and [KCl] = 0.3 M, the half-time is only 0.73 minutes. This represents the approximate lower limit of half-times which could be measured by the present techniques. In figure 6 the effects of lithium and potassium ions are compared. We note that not only is the rate constant larger in the presence of potassium, but the rate of increase with concentration is greater. Attempts to prepare solutions of similar heteropoly ion concentrations to those of table V in the presence of even 0.1 M cesium ion led to extensive precipitation of the heteropoly ions.

Table V. Dependence of the rate on various cations.

Temperature 0°; [I] = 1.14×10^{-3} M; [II] = 1.22×10^{-3} M; K^+ as KCl.

Cation	Concentration	k_r ($M^{-1}sec.^{-1}$)
Li	0.01_5	0.03
Li	0.05	0.07
Li	0.21	0.31
Li	0.41	0.44
Li	0.61	0.64
Li	0.81	0.96
K	0.02	0.74
K	0.10	2.21
K	0.30	6.67

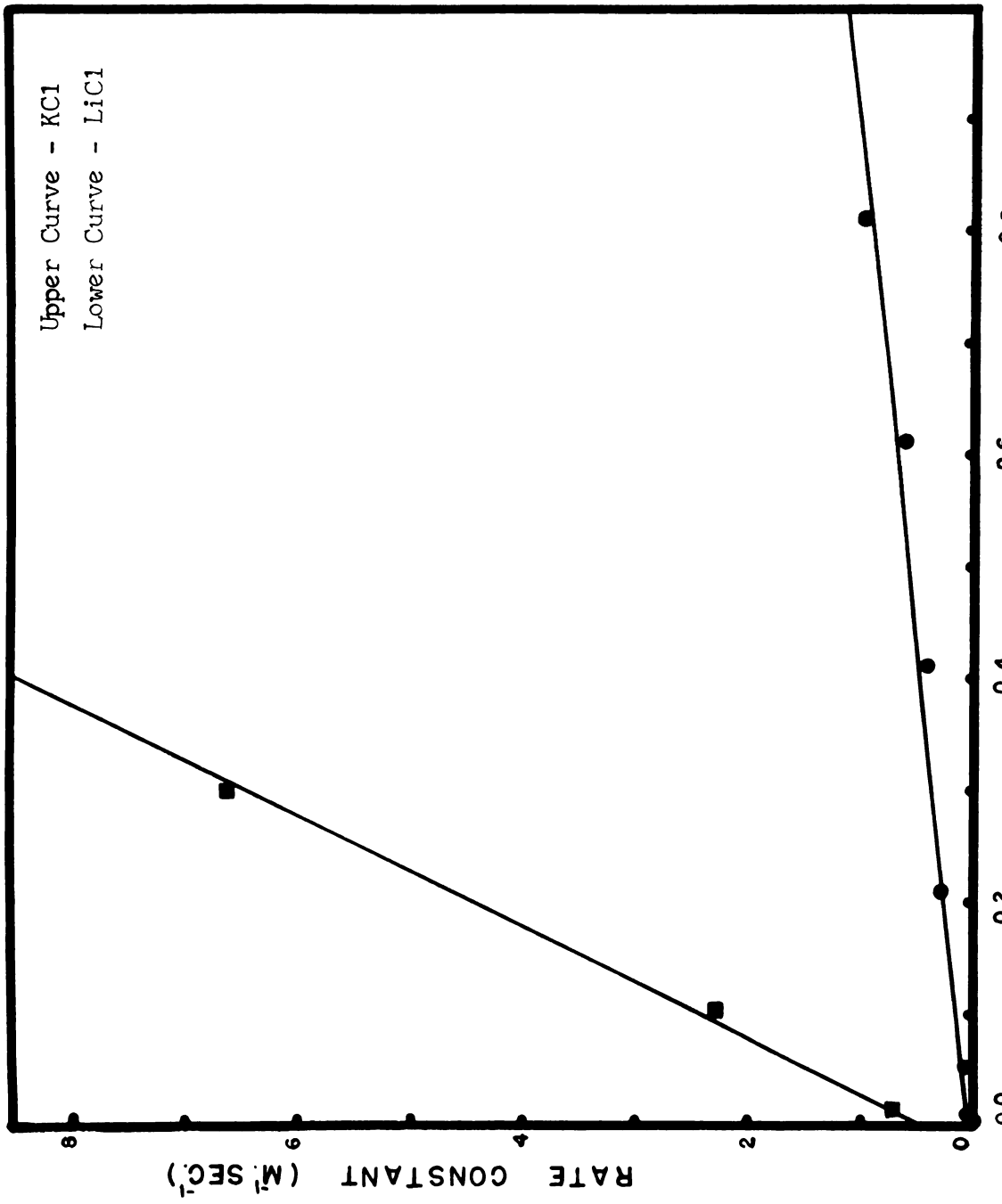


Figure 6. Graph of rate constant vs [MCl]. M = Li, K.
Temperature 0°; [I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M.

F. Dependence of the Rate on Dielectric Constant

In order to determine the effect of dielectric constant on the rate, several series of experiments were made in dioxane-water mixtures. Dioxane is commonly chosen for such studies because it is miscible in all proportions with water, and it has a very low dielectric constant itself so that a wide variation may be obtained. The dielectric constant of the mixtures approximates a linear function of the weight percent dioxane over most of the range. For the sake of comparison with other data from this investigation, it was desirable to work at 0°. The dielectric constant of dioxane-water mixtures is a function of temperature however, and experimental values are not available for 0°. It was possible to estimate them none-the-less. Data at 15°, 25°, 35°, and 45° for dioxane-water mixtures are tabulated for mixtures of various concentrations. (44) By extrapolation of the values for each mixture from 15° down to 0°, a set of data were obtained for 0° from which a plot could be made of weight percent dioxane *vs.* dielectric constant. (Figure 7) As may be seen from the graph, the known value for the dielectric constant of water at 0° falls on the same straight line as the extrapolated values.

As one might expect for a reaction between like charged ions, decreasing the dielectric constant decreased the reaction rate. More quantitatively, the Marcus theory predicts that a plot of $\ln k_r$ *vs.* $1/D_s$ should be linear with a slope proportional to $z_1 z_2$, the charge product of the ions in solution, if the slight dependence of λ on D_s is neglected. From Figure 8, the charge product is found to be 30.

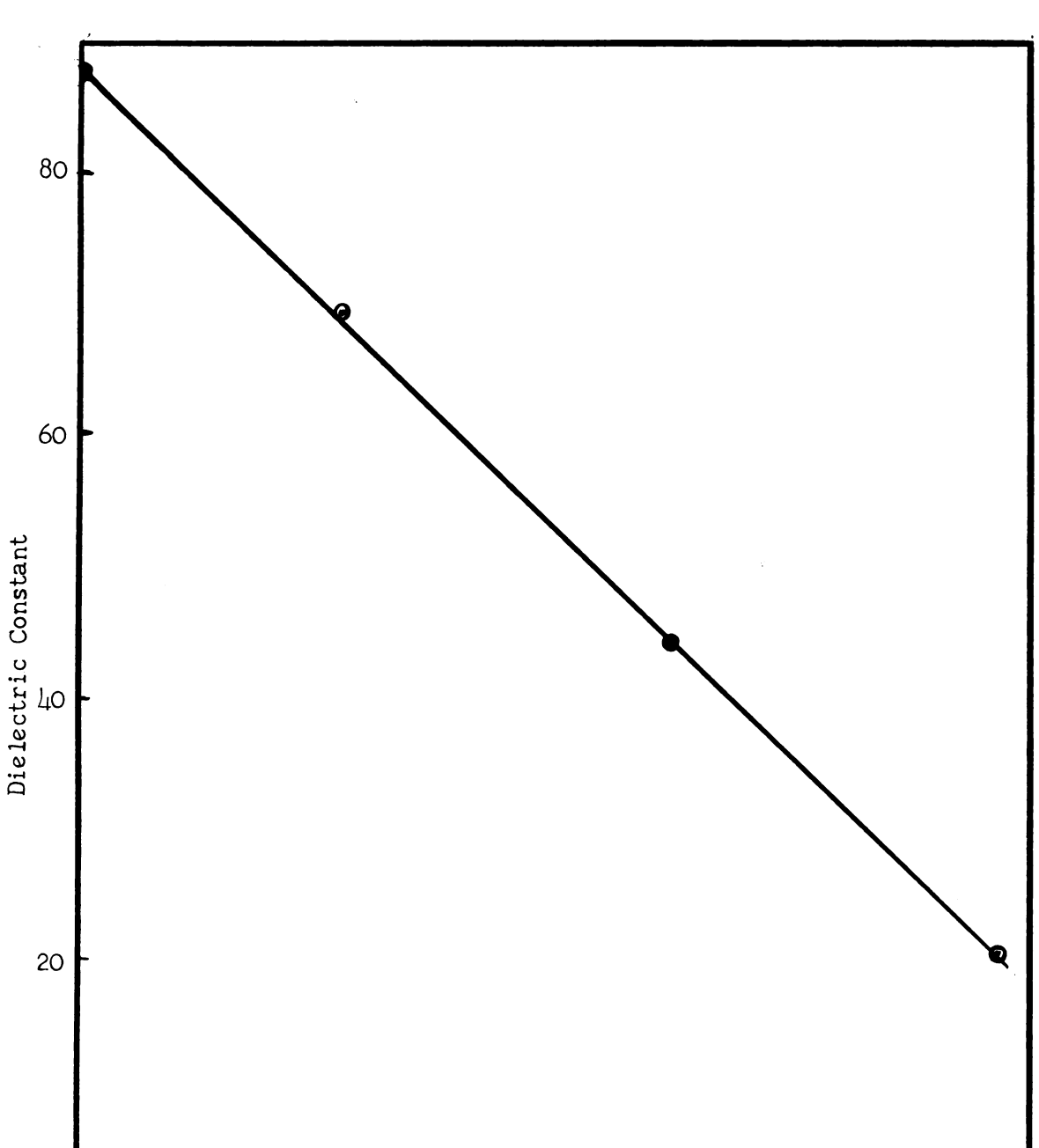


Figure 7. Weight percent dioxane vs. dielectric constant at 0°.

Table VI. Dependence of the rate on the dielectric constant.

Temperature 0°; Ionic strength 0.6, adjusted with LiCl; [I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M.

Volume % Dioxane	D_s	$1/D_s$	k_r ($M^{-1}sec.^{-1}$)
0.0	88.0	0.0114	0.63
4.0	84.3	0.0119	0.52
20.0	69.3	0.0144	0.36
32.0	57.0	0.0175	0.26

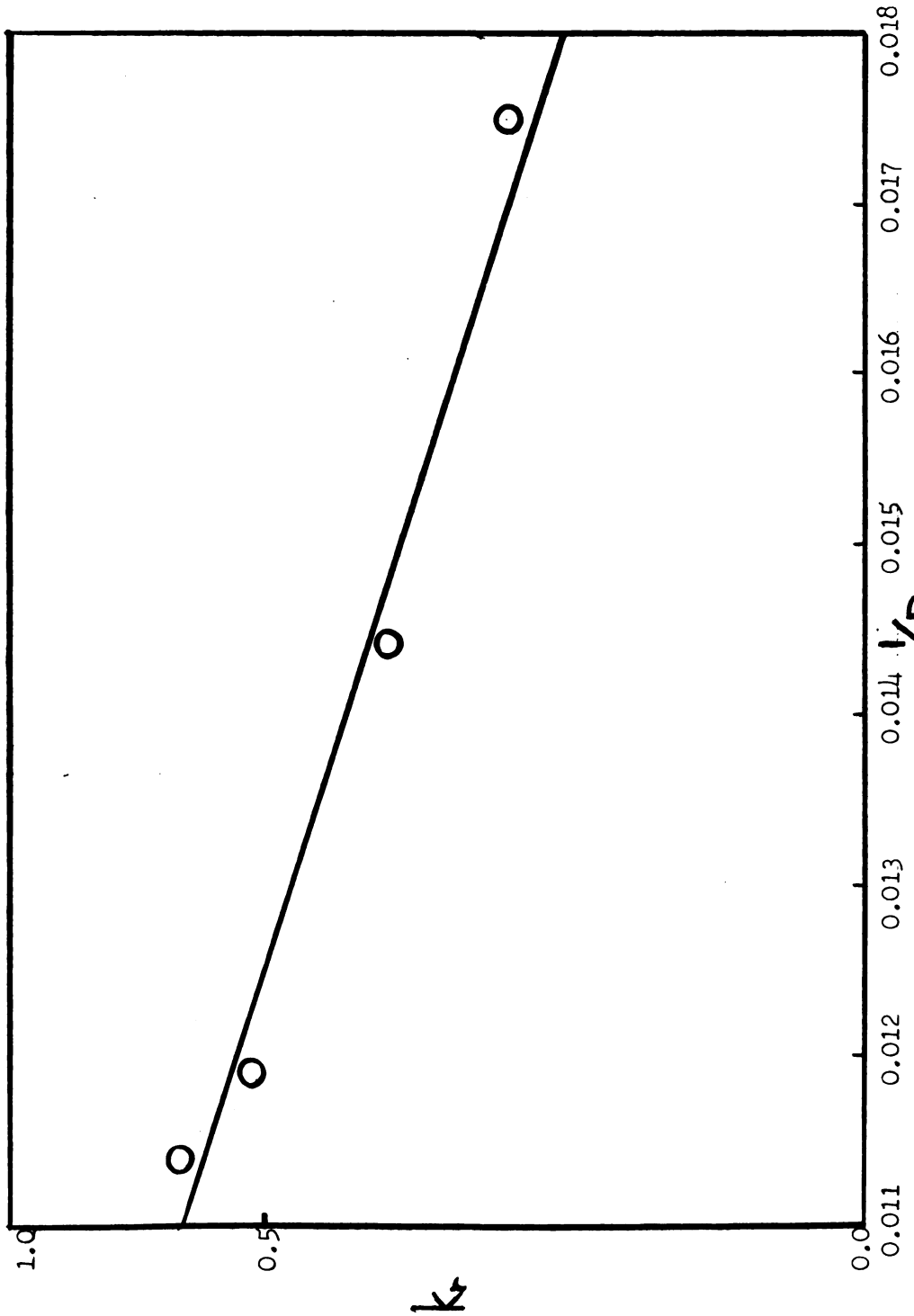


Figure 8. Graph of log k_r vs. $1/D_s$. Ionic strength 0.6 adjusted with LiCl; Temperature 0°; [I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M.

VI. DISCUSSION

It has been found, (33) by cryoscopic studies in $Na_2SO_4 \cdot 10\ H_2O$ (Glauber's salt) that the heteropoly ions used in this investigation show very little tendency to dissociate into $WO_4^=$ or other simple units. This fact, plus the number of bonds between groups implies substitutional inertness with respect to $WO_4^=$ groups and leads one to believe that electron exchange between such ions can only take place via an outer-sphere activated complex in acid solution. If the pH is raised above 7, degradative dissociation does occur with any heteropoly compound. The postulate of an outer-sphere activated complex is supported by the lack of hydrogen ion dependence of the rate, by the negative entropies of activation (-19 to -44 e.u.), and by the simple kinetic order, although individually these factors are not conclusive. Taube (17) has pointed out the difficulties involved in attempting to make parameters of activation diagnostic of mechanism. In this sytem, however, the evidence is not contradictory and the assignment of an outer-sphere mechanism seems appropriate.

The magnitude of the rate constants for this system as well as the possible mechanism is deserving of comment. Most outer-sphere reactions which have been investigated are very rapid, particularly in anionic systems. For example the reaction: (45)

$$W(CN)_8^{-3} + W(CN)_8^{-4} = W(CN)_8^{-3} + W(CN)_8^{-4}$$

has a $10^5 < k_r < 10^8\ \underline{M}^{-1}$ sec.$^{-1}$ as determined from electron spin resonance experiments. The reaction: (46)

$$\overset{*}{Fe}(CN)_6^{-3} + Fe(CN)_6^{-4} = Fe(CN)_6^{-3} + \overset{*}{Fe}(CN)_6^{-4}$$

has been studied by flow methods and a $k = 3.5 \times 10^2\ \underline{M}^{-1}\text{sec.}^{-1}$ was found.

In the light of the above, it is noteworthy that the 12-tungstocobaltate (II - III) system exchanges slowly enough to allow study by conventional techniques. Therefore, a comparison with the theory of Marcus, which is derived for a weak-overlap type of mechanism, is of interest. A summary of the necessary calculations may be found in the section on theory, of this thesis. Several approximations were made in order to obtain a numerical result. From the Marcus theory: (for infinitely dilute water solution)

$$k_r = 4.7 \times 10^2\ \underline{M}^{-1}\text{sec.}^{-1}$$

By extrapolation of the $\log k_r$ *vs.* $e^{-\kappa r}$ to infinite dilution one obtains

$$k_r(\text{expt.}) = 4.5 \times 10^{-3}\ \underline{M}^{-1}\text{sec.}^{-1}$$

The discrepancy between the calculated and the experimental values is substantial, and may be caused by a number of factors. The estimate made of the rearrangement energy necessary for reaction is probably on the low side, since in the approximation used, distortion of the ions as a whole was neglected and attention was concentrated on the central atom and its nearest neighbors. Furthermore, the Marcus treatment assumes that the transmission probability for the electron is unity within the activated complex. This condition may not hold in heteropoly ions where a large number of oxygen and tungsten atoms are present, (see Figure1) which may serve to "insulate" the central cobalt atoms from each other.

Finally, there is some uncertainty in what value to use for the charge product of the ions in solution. This matter is discussed in more detail in the latter part of this section. Although the mechanisms may not be the outer-sphere type, it is of interest to note that the following reactions are very slow: (1)

$$\overset{*}{Co}(NH_3)_6^{+2} + Co(NH_3)_6^{+3} = \overset{*}{Co}(NH_3)_6^{+3} + Co(NH_3)_6^{+2}$$

$$Co(C_2O_4)_3^{-3} + Co(C_2O_4)_3^{-3} = \overset{*}{Co}(C_2O_4)_3^{-4} + Co(C_2O_4)_3^{-3}$$

This may be the result of a large change in the cobalt ligand bond length necessary upon changing oxidation state, or a consequence of the change in the number of unpaired electrons. (Octahedral cobaltous complexes are generally spin free while octahedral cobaltic complexes are spin paired.) This situation does not occur in the present system where both complexes are tetrahedral and spin free. (33) The observed exchange rate is probably affected by several of the factors discussed above and a determination of the contribution of each is not possible at the present time.

While the gross magnitude of the rate is determined by the considerations discussed above, variation from $k_r = 10^{-2}$ to $10^1 \underline{M}^{-1}\text{sec.}^{-1}$ was possible as a result of changes in experimental conditions. In particular, changing the cation from lithium to potassium leads to a large increase in the rate of exchange. In the range studied, the rate is linear in cation concentration, (see Figure 6) so that one might write:

$$R = k_r[M^+][I][II]$$

Such a rate law implies, however, that exactly one cation enters the activated complex, which is not necessarily true for an outer-sphere

mechanism where the activated complex is of uncertain structure. The effect appears to be specific for each cation which might lead one to attribute the results to differences in ionic mobilities in the ions.

The ionic mobility of the potassium ion is 73 cm/sec./volt, while that of lithium is 37 cm/sec./volt. From Table V, however, we see that for a given concentration of cation, the rate constant for potassium is always at least ten times that of lithium. Thus, the rate increase is not linearly associated with the ionic mobilities. It seems preferable to attribute the effects of different cations to the greater ion pairing abilities of the larger ions. Ion pairs can facilitate electron exchange by decreasing coulombic repulsion, and the number of ion pairs will increase rapidly with concentration, as does the rate.

The result of ionic strength variation on the rate may be interpreted in several ways. The Brönsted-Bjerrum equation is often applied to predict the effects of ionic strength for ionic reactions. In the case of large ions and only moderately low ionic strengths, however, this equation is not followed. (Figure 3) The equations of Marcus provide another means of interpreting the data, and the requirements are not as stringent. Figure 4 shows that the linear relationship predicted for $\log k_r$ vs. $e^{-\kappa r}$ is followed quite well, and from the slope of the line, a charge product in solution, $z_1 z_2 = 8$, may be computed.

The charge product can also be calculated from the rate data obtained as a function of dielectric constant. (See Figure 8). In this case, a value of $z_1 z_2 = 30$ is obtained. This value does not agree with the value of eight, obtained from the ionic strength variation data. It seems probable that the value of eight is the more reliable one, since

the validity of the Debye-Hückel treatment in solutions of low dielectric constant and moderate ionic strength is questionable.

An interpretation consistent with the results in water solution is that several cations are closely associated with heteropoly ions even in very dilute solution. These ion groups may then act as a strong electrolyte of somewhat lower charge. Such a conclusion is corroborated by the fact that even unsymmetrical 3-1 electrolytes of complex ions are not "strong" in several cases which have been examined. (50,51) The situation in the mixed solvent system of water-dioxane is more complicated, and defies a clearcut explanation, at present.

In summary, this investigation has led to the following results and conclusions. The rate of electron exchange between the 12-tungstocobaltate (II) and the 12-tungstocobaltate (III) anions is moderately rapid but slow enough to be followed by classical techniques. The exchanging electron is able to penetrate the tungsten-oxygen "cage" of the heteropoly ion, and since the "cage" itself is very stable, the reaction must proceed by an outer-sphere mechanism. The rate law for the exchange is second order, first order in each ion. Hydrogen ions were found to have no special function in the activated complex, as evidenced by the fact that the rate was unaffected by the hydrogen ion concentration at constant ionic strength. In solution the heteropoly ions probably exist in close association with cations so that their high charge is partially neutralized. Thus the presence of K^+ which tends to form ion pairs more readily than Li^+ greatly accelerates the exchange rate. The temperature dependence of the rate is summarized in the thermodynamic parameters of activation which are within the range of values typically observed for

exchange reactions that proceed via an outer-sphere mechanism. The large negative values for the entropies of activation and the catalytic effects of cations, suggest that the closeness of approach of the reactants is very important in determining whether or not electron exchange occurs.

The comparison of the experimental data with the predictions of the Marcus theory is inconclusive. The plots which are predicted to be linear, particularly $\log k_r$ vs. e^{-Kr} are fit fairly well by the data, but the theoretical and experimental rate constants are not in agreement. The decision as to whether this is the result of: substitution of incorrect values for some of the parameters into the equations, misapplication of the theory altogether, or simply an inadequate theoretical treatment, will have to be deferred until data from more experimental systems have been compared to the Marcus theory.

VII. LITERATURE CITED

1. Lewis, J., and R. G. Wilkins, ed. "Modern Coordination Chemistry," Chap. 2, by D. R. Stranks, p. 78-173. Interscience, New York, 1960.

2. Sheppard, J. C. and A. C. Wahl, J. Am. Chem. Soc. 79, 1020 (1957).

3. Keggin, J. F., Proc. Roy. Soc. 144, 75 (1934).

4. Marcus, R. A., J. Chem. Phys. 24, 966 (1956).
   J. Chem. Phys. 26, 867 (1957).
   J. Chem. Phys. 26, 872 (1957).

5. Marcus, R. A., J. Phys. Chem. 67, 853 (1963).

6. Sidgwick, N. V. "Chemical Elements and Their Compounds," Vol. 2, p. 1042. Oxford, 1950.

7. Kline, C. H., "Heteropoly Anions in Science and Industry," Symposium on Structure and Properties of Heteropoly Ions, 130th National Meeting American Chemical Society, Atlantic City, N.J., Sept. 17, 1956.

8. Baker, L. C. W., and T. P. McCutcheon, J. Am. Chem. Soc. 78, 4503 (1956).

9. Baker, L. C. W., and V. E. Simmons, J. Am. Chem. Soc. 81, 4744 (1959).

10. Kirschner, S., ed. "Advances in the Chemistry of Coordination Compounds," p. 604. Proceedings of the 6th I.C.C.C. Wayne State U., Detroit, Mich., Sept. 1961. Macmillan, New York, 1961.

11. Cotton, F. A., ed. "Progress in Inorganic Chemistry," Vol. 4, Chap. 4, "Isopolytungstates", by D. L. Kepert, p. 199. Interscience, New York, 1962.

12. Souchay, P. Pure Applied Chem. 6, 61 (1963).

13. Pascal, P., ed. "Nouvou Traite De Chemie Minerale," Vol XIV, "Heteropolyacids" by L. Malaprade, p. 903. Masson et Cie, Paris, 1959.

14. Wahl, A. C., and N. A. Bonner, ed. "Radioactivity Applied to Chemistry," Chap. 1, by O. E. Meyers and R. J. Prestwood, p. 6. Wiley, New York, 1951.

15. Libby, W. F., J. Phys. Chem. 56, 863 (1952).
   J. Chem. Phys. 38, 420 (1963).

16. Marcus, R. J., B. Zwolinski, and H. Eyring, J. Phys. Chem. 58, 432 (1954).

17. Emeleus, H. J. and A. G. Sharpe, ed., "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Chap. 1 by H. Taube, p. 1-53. Academic Press, New York, 1959.

18. Stranks, D. R., and R. G. Wilkins, Chem. Rev. 57, 743 (1957).

19. "Oxidation-Reduction Reactions in Ionizing Solvents" -- A General Discussion, Discussions Faraday Soc., Vol. 29, 7-169 (1960).

20. Halpern, J., Quart. Rev. (London) Vol XV, No. 2, 207 (1961).

21. Brubaker, C. H., Record Chem. Progr. 24, 181 (1963).

22. Prestwood, R. J. and A. C. Wahl, J. Am. Chem. Soc. 71, 3137 (1949).

23. Mckay, H. A. C., Nature 142, 997 (1938).

24. Baker, L. C. W., Chemical Data Series, Bulletin Cdb-12, Climax Molybdenum Co., 1960.

25. Hush, N. S., Trans, Faraday Soc. 57, 557 (1961).

26. Laidler, K. J., Can. J. Chem. 37, 138 (1959).
Sacher, E., and K. J. Laidler, Trans. Faraday Soc., 59, 396 (1962).

27. Symons, M. C. R., J. Chem. Soc. 3676 (1954).

28. Herzberg, G. "Infrared and Raman Spectra of Polyatomic Molecules," p. 100. D. Van Nostrand Co., New York, 1945.

29. Pauling, L. "Nature of the Chemical Bond," p. 518,538. Cornell University Press, Ithaca, New York, 1960.

30. Badger, R. M., J. Chem. Phys. 2, 128 (1934).
J. Chem. Phys. 3, 710 (1935).

31. Friedlander, G. and J. W. Kennedy "Nuclear and Radiochemistry," John Wiley and Sons, New York, 1955.

32. Overman, R. T. and H. M. Clark "Radioisotope Techniques," McGraw-Hill Co., New York, 1960.

33. Simmons, V. E., Ph.D. Dissertation, Boston University, 1963.

34. Gordon, B. M., and A. C. Wahl, J. Am. Chem. Soc. 80, 273 (1958).

35. Hamer, W. J., ed. "The Structure of Electrolyte Solutions," Chap. 5, by M. Eigen and L. DeMaeyer, p. 66. Wiley, New York, 1959.

36. Frost, A. A. and R. G. Pearson "Kinetics and Mechanisms," 2nd Ed., p. 100. Wiley, New York, 1961.

37. Eriks, K. and N. F. Yannoni, et. al. Acta. Cryst. 13, 1139 (1961).

38. Silverman, J. and R. W. Dodson, J. Phys. Chem. 56, 846 (1952).

39. Hudis, J. and R. W. Dodson, J. Am. Chem. Soc. 78, 911 (1956).

40. Hudis, J. and A. C. Wahl, J. Am. Chem. Soc. 75, 4153 (1953).

41. Sheppard, J. C. and L. C. Brown, J. Phys. Chem. 67, 1025 (1963).

42. Sutin, N., J. Phys. Chem. 64, 1766 (1960).

43. Rona, E. R., J. Am. Chem. Soc. 72, 4339 (1950).

44. Harned, H. S. and B. B. Owen. "The Physical Chemistry of Electrolytic Solutions", 3rd. Ed., Reinhold, New York, 1958, p. 713.

45. Weissman, S. I. and C. S. Garner, J. Am. Chem. Soc. 78, 1072 (1956).

46. Wahl, A. C. and C. D. Deck, J. Am. Chem. Soc. 76, 4054 (1954).

47. Eichler, E. and A. C. Wahl, J. Am. Chem. Soc. 80, 4145 (1958).

48. Blaedel, W. J. and V. W. Meloche. "Elementary Quantitative Analysis," 2nd Ed., p. 473. Harper and Row, 1963.

49. Marcus, R. A., Private communication.

50. Wynveen, R. A., J. L. Dye, and C. H. Brubaker, J. Am. Chem. Soc. 82, 4441 (1960).

51. Groves, K. O., J. L. Dye, and C. H. Brubaker, J. Am. Chem. Soc. 82, 4445 (1960).

52. Griffiths, J. S. and J. Owen, Proc. Roy. Soc. A 226, 96 (1954).

53. Ebsworth, E. A. V. and J. A. Weil, J. Phys. Chem. 63, 1890 (1963).

54. Booth, H. S., Ed., "Inorganic Synthesis," McGraw-Hill, New York, 1939, p. 129.

APPENDIX I

ORIGINAL KINETIC DATA

Dependence of rate on reactant concentrations.

t (min.)	X (c/6 min.)	$X_\infty - X^*$
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; pH = 1.6; 0.6M LiCl; Temperature 0°; $t_{1/2}$ = 8.0 min.		
0.12	1571	10926
1.50	3279	9218
3.01	3999	8498
4.51	5155	7342
6.01	5833	6664
8.03	7130	5367
10.00	7338	4659
12.02	7981	4516
14.01	9307	3190
∞	12497	--
[I] = 9 x 10^{-4}M; [II] = 1.5 x 10^{-3}M; pH = 1.6; 0.6M LiCl; Temperature 0°; $t_{1/2}$ = 7.8 min.		
0.15	1482	10917
0.21	1610	10789
1.04	2550	9849
3.01	3635	8764
5.02	5507	6894
7.02	6478	5921
∞	12399	--
[I] = 7 x 10^{-4}M; [II] = 1.8 x 10^{-3}M; pH = 1.6; 0.6 M LiCl; Temperature 0°; $t_{1/2}$ = 8.0 min.		
0.15	1225	8506
2.02	2516	7215
4.04	3338	6393
6.03	4524	5207
8.01	5425	4306
10.00	5496	4235
12.01	5532	4199
14.01	7315	2416
∞	9731	--

*The value of X_∞ is experimentally determined. The listed value is the average of triplicate determinations.

Dependence of rate on reactant concentrations. (Cont.)

t (min.)	X (c/6 min.)	$X_\infty - X^*$
[I] = 1.4 x 10^{-3}M; [II] = 1.0 x 10^{-3}M; pH = 1.6; M LiCl; Temperature 0°; $t_{1/2}$ = 7.7 min.		
0.13	1939	11236
2.01	4427	8748
4.01	5998	7177
6.01	7123	6052
8.01	7370	5805
10.00	8014	5161
12.01	9342	3833
14.00	10578	2597
∞	13175	--
[I] = 1.6 x 10^{-3}M; [II] = 7 x 10^{-4}M; pH = 1.6; M LiCl; Temperature 0°; $t_{1/2}$ = 8.2		
2.02	4004	8226
5.02	5199	7031
8.26	7393	4837
10.42	8158	4072
12.82	8725	3505
∞	12230	--

Dependence of rate on hydrogen ion concentration.

t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.08 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.025 M HCl; 1.0 M LiCl; Temperature 0°; $t_{1/2}$ = 4.8 min.		
0.13	2432	15697
0.72	3826	14303
1.57	5972	12157
2.91	8507	9622
5.03	10889	7240
10.17	14265	3864
∞	18129	--
[I] = 1.08 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.8 M HCl; 0.2 M LiCl; Temperature 0°; $t_{1/2}$ = 4.6		
0.12	11393	12100
0.48	11881	11612
1.03	14691	8802
1.53	14930	8563
2.02	13928	9565
3.05	14558	8935
5.07	17474	6019
8.03	19779	3714
∞	23493	--
[I] = 1.08 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M HCl; 0.4 M LiCl; Temperature 0°; $t_{1/2}$ = 5.4 min.		
0.15	3653	12692
0.52	4524	11821
1.06	5437	10908
2.59	6933	9412
5.04	9118	7227
7.23	11558	4787
10.12	12872	3473
∞	16345	--

Dependence of rate on hydrogen ion concentration. (Cont.)

t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.08×10^{-3}M; [II] = 1.22×10^{-3}M; 0.4 M HCl; 0.6 M LiCl; Temperature 0°; $t_{1/2}$ = 4.9 min.		
0.18	1988	13538
0.62	3267	12259
1.11	4109	11417
2.09	5429	10097
3.07	6765	8761
4.09	7259	8267
5.08	9077	6449
5.44	9406	6120
6.95	10316	5210
8.59	10596	4930
∞	15526	--
[I] = 1.08×10^{-3}M; [II] = 1.22×10^{-3}M; 0.2 M HCl; 0.8 M LiCl; Temperature 0°; $t_{1/2}$ = 5.1.		
0.12	1820	15489
0.52	2865	14514
1.05	3546	13833
1.55	4548	12831
2.06	5076	12303
3.12	6930	10449
4.10	7194	10185
5.08	9567	7812
6.08	9123	8256
8.05	10983	6396
∞	17379	--

Dependence of rate on ionic strength

[I] = 1.14×10^{-3}M; [II] = 1.22×10^{-3}M; 0.8 M LiCl; Temperature 0°; $t_{1/2}$ = 5.1 min.		
0.12	1928	13407
0.54	3240	12095
2.08	5286	10049
4.01	7748	7587
7.04	10145	5190
10.02	13133	2202
∞	15335	--

Dependence of rate on ionic strength. (Cont.)

t (min.)	X (c/6 min.)	X_∞ - X
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M LiCl; Temperature 0°; $t_{1/2}$ = 7.6 min.		
0.12	2193	13341
0.65	3040	12494
1.07	3320	12214
2.08	4502	11032
3.07	4826	10708
5.04	6506	9028
7.04	7547	7987
9.07	9897	5637
11.57	11807	3727
13.71	11690	3844
∞	15534	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.4 M LiCl; Temperature 0°; $t_{1/2}$ = 11.0 min.		
0.15	2181	12895
0.77	3049	12027
1.52	3614	11462
3.06	4940	10136
5.06	6024	9052
7.05	6558	8518
10.07	8264	6812
13.85	9826	5250
18.92	10752	4324
∞	15076	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.2 M LiCl; Temperature 0°; $t_{1/2}$ = 15.7 min.		
0.12	2330	12067
1.11	3238	11159
3.08	4329	10068
5.04	4579	9818
8.02	6655	7742
11.07	7376	7021
14.02	8102	6295
∞	14397	--

Dependence of rate on ionic strength. (Cont.)

t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.0 M LiCl; Temperature 0°; $t_{1/2}$ = 180 min.		
0.13	3293	6224
2.51	3599	5918
7.62	3666	5851
15.07	3876	5641
25.06	3649	5868
30.01	4411	5106
46.11	4362	5155
60.05	4818	4699
92.78	5000	4517
131.04	5987	3530
∞	9517	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.05 M LiCl; Temperature 0° $t_{1/2}$ = 66.4 min.		
1.48	3325	8248
5.34	4206	7367
10.34	5054	6519
25.22	5585	5988
42.06	6586	4987
61.10	7220	4353
∞	11573	--

Dependence of rate on temperature.

[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.0 M LiCl; Temperature 25°; $t_{1/2}$ = 20.3 min.		
0.26	1331	10525
5.02	4015	7841
10.10	5424	6432
15.02	6261	5595
25.02	6907	4949
34.91	8935	2921
∞	11856	--

Dependence of rate on temperature. (Cont.)

t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M LiCl; Temperature 25°; $t_{1/2}$ = 14.5 min.		
0.17	2002	13617
0.77	2183	13436
1.56	2775	12844
3.02	3262	12357
5.03	4638	10981
7.52	5281	10338
10.53	7310	8309
13.97	6967	8652
∞	15619	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.2 M LiCl; Temperature 25°; $t_{1/2}$ = 6.77 min.		
0.10	1623	14352
0.41	2356	13619
0.84	3057	12918
1.32	3702	12273
2.02	4459	11516
3.02	5802	10173
4.02	6448	9527
5.03	7250	8725
7.00	9161	6814
∞	15975	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.2 M LiCl; Temperature 12.7°; $t_{1/2}$ = 10.3 min.		
0.15	1468	13796
0.62	2484	12780
1.18	3094	12170
2.01	3351	11913
3.01	3994	11270
5.17	5650	9614
7.09	5631	9633
10.02	8631	6631
13.72	9656	5608
∞	15264	--

Dependence of rate on temperature. (Cont.)

t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.05 M LiCl; Temperature 12.7°; $t_{1/2}$ = 37.0 min.		
1.01	1862	13700
2.55	2978	12584
5.05	4108	11454
8.09	4104	11458
12.85	5086	10476
17.05	5219	10343
23.08	6248	9314
30.07	7726	7836
42.83	10137	5425
60.07	11151	4411
∞	15562	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.0 M LiCl; Temperature 12.7°; $t_{1/2}$ = 60 min.		
2.01	3419	10777
10.01	5991	8205
15.05	6808	7388
20.01	7640	6556
30.57	8003	6193
45.07	8977	5219
55.08	9143	5053
∞	14196	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.0 M LiCl; Temperature 12.7°; $t_{1/2}$ = 58 min.		
2.70	4130	10785
7.00	6736	8179
14.70	8753	6162
25.12	9786	5129
35.40	10068	4847
52.20	11494	3421
66.10	11765	3150
∞	14915	--

Dependence of rate on specific cation.

t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.33 x 10^{-3}M; [II] = 1.79 x 10^{-3}M; (K^+ salts) 0.0 M KCl; Temperature 0°; $t_{1/2}$ = 5.0 min.		
0.15	4246	12254
0.45	5693	10807
1.30	7251	9249
3.00	8521	7979
5.01	10774	5726
∞	16500	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.10 M KCl; Temperature 0°; $t_{1/2}$ = 2.2 min.		
0.13	2278	11292
0.58	3653	9917
1.11	5181	8389
2.02	7229	6341
3.03	7453	6117
∞	13570	--
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.30 M KCl; Temperature 0°; $t_{1/2}$ = 0.73 min.		
0.08	3015	11068
0.09	3437	10646
0.17	3785	10298
0.29	5368	8715
0.41	6053	8029
0.61	7278	6805
0.80	8477	5606
1.11	10565	3518
1.42	10427	3656
∞	14083	--

Dependence of rate on dielectric constant.

[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M LiCl; Temperature 0°; 0 % Dioxane; $t_{1/2}$ = 8.0 min.

t (min.)	X (c/6 min.)	X_∞ - X
0.12	1571	10926
1.50	3279	9218
3.01	3999	8498
4.51	5155	7342
6.01	5833	6664
8.03	7130	5367
10.00	7838	4659
12.02	7981	4516
14.01	9307	3190
∞	12497	--

[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M LiCl; Temperature 0°; 4 % Dioxane; $t_{1/2}$ = 9.6 min.

0.13	1461	10937
2.02	3858	8540
4.01	4453	7945
6.03	5196	7202
8.04	6445	5953
10.03	7146	4872
12.03	8194	4204
14.00	8426	3972
∞	12398	--

[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M LiCl; Temperature 0°; 20% Dioxane; $t_{1/2}$ = 14.0 min.

0.10	1423	11206
2.02	2664	9965
4.02	3970	8659
6.02	4728	7901
8.03	5217	7412
10.02	5597	7032
12.01	6398	6231
14.00	6953	5676
18.22	7384	5245
22.10	8962	3667
∞	12629	--

Dependence of rate on dielectric constant. (Cont.)

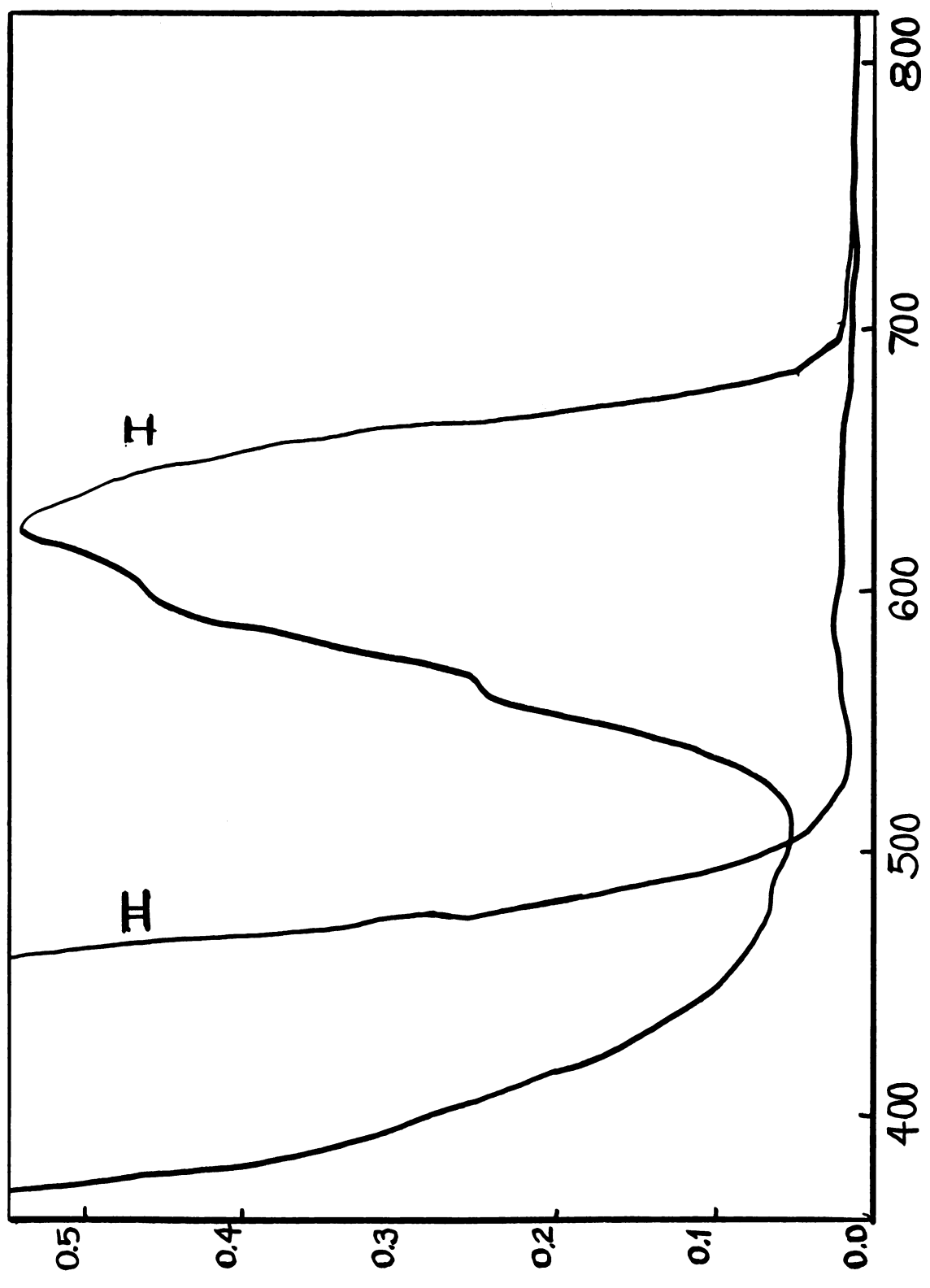
t (min.)	X (c/6 min.)	$X_\infty - X$
[I] = 1.14 x 10^{-3}M; [II] = 1.22 x 10^{-3}M; 0.6 M LiCl; Temperature 0°; 32% Dioxane; $t_{1/2}$ = 19.1 min.		
2.01	1885	7046
4.01	2630	6301
6.02	3120	5811
8.02	3587	5344
10.00	4122	4809
12.04	3947	4984
14.03	4434	4497
16.01	4965	3966
18.02	4888	4043
20.00	5564	3367
22.01	5653	3278
24.02	5624	3307
26.02	5537	3394
28.00	6609	2322
∞	8931	--

APPENDIX II

Visible Region Absorption Spectra of Anion I [12- tungstocobaltate (II)] and Anion II [12-tungstocobaltate (III)] in Water Solution. pH = 2.

abscissa: wavelength in millimicrons

ordinate: absorbance


H
H
0.5
0.4
0.3
0.2
0.1
0.0
400
500
600
700
800

APPENDIX III

A preliminary study of the electron paramagnetic resonance spectra of the 12-tungstocobaltate (II) and 12-tungstocobaltate (III) ions.

An investigation of the electron exchange between the 12-tungstocobaltate (II) and the 12-tungstocobaltate (III) anions has been described in this thesis. The results of this investigation show that an electron that is formally associated with the central or hetero atom of such a complex, can readily pass through the "cage" of addenda atoms and associate with another ion. This suggests that there is extensive electron delocalization in such a complex, and further elucidation of the electronic structure would be of interest. One of the few methods for the direct determination of electron density is from measurement of the hyperfine coupling constants in electron paramagnetic resonance (EPR) experiments. A well known example of such a study is the $IrCl_6^{-2}$ ion, which has one unpaired electron. (52) Hyperfine splittings were found both from the Ir and from the Cl nuclei. From the magnitude of the splittings, it was deduced that the unpaired electron spends about 70% of its time on the Ir nucleus and about 5% on each chlorine. Ebsworth and Weil have observed the EPR signal from $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{+5}$ (53) in water solution, and from the hyperfine structure proved the equivalence of the two cobalt atoms within the ion. Both the 12-tungstocobaltate (II) and the 12-tungstocobaltate (III) ions are paramagnetic, and have been shown to have three and four unpaired electrons respectively. Further, the graphs of magnetic susceptibility vs. temperature show no evidence of spin aligning interactions down to liquid nitrogen temperatures. Therefore, a preliminary study was undertaken to determine whether or not EPR experiments might provide new data about the electronic structure of these complexes. Experimental work was done on two instruments; a commercial model, Varian 4502, which could be operated down to liquid

nitrogen temperature, and an apparatus constructed by the Michigan State University physics department which is designed for use down to liquid helium temperature. Both instruments employ X-band microwave frequency sources. ($\sim$ 9000 megacycles).

Examination of the EPR spectra of the powdered potassium salts of the ions gave no detectable absorption lines either at room temperature or at liquid nitrogen temperature. Solutions of these salts, examined in a specially designed quartz solution cell also gave negative results. Single crystals of these salts showed no resonance absorptions down to 78°K with the possible exception of the Co(II) compound which gave a broad baseline depression. In order to lengthen the spin-lattice relaxation times, the search was carried on at approximately 1°K, obtained by pumping on liquid helium. At this temperature, the cobalt (II) compound gave a resonance absorption line over 2000 gauss wide with no fine structure. It was decided that spin-spin relaxation was the cause of the line broadening, and therefore a diamagnetic host-lattice was sought for these compounds. The colorless potassium salt of 12-tungstosilicic acid proved to be suitable for this purpose. (The synthesis of this acid has been described. (54) Large hexagonal prisms of this compound could easily be grown from solutions containing 1% by weight of either of the heteropoly cobalt compounds. Visual inspection of the crystals so formed, indicated that they were homogeneous. From the colors of these crystals it appeared that they contained approximately as much of the cobalt compounds as the solution from which they were grown. A single crystal of potassium 12-tungstosilicate containing 1% of the 12-tungstocobaltate (II) ion gave a single resonance line at 1°K. This line appeared very close to the DPPH reference line, and its position

changed slightly as the static magnetic field was rotated, although its intensity remained approximately the same. No fine structure was observed. A similar crystal containing the 12-tungstocobaltate (III) ion showed three resonance lines. The center line appeared at a field strength of about 3000 gauss and did not shift as the static magnetic field was rotated. The other two lines varied in distance from the center line depending on the angle of the static field with respect to the hexagonal crystal axis. Rotation through ninety degrees caused these two lines, if initially coalesced with the center line, to diverge from it to a maximum distance of less than 1000 gauss each way, and to again coalesce with it. For no angle of the static field did any of the lines show resolvable fine structure.

It seems unlikely that the spectra of these compounds will yield sufficient detail to make further study of them worthwhile, at least from the point of view of a chemist. The hoped for comparison of the nuclear hyperfine splittings for the cobalt atoms in the two different oxidation states is out of the question since no hyperfine structure was observed. The reason for the failure to observe these splittings is not clear, although it is probably related to the number of unpaired electrons in these complexes.