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REACTIONS OF THE COBALT(II)-BIPYRIDINE SYSTEM  
IN BASIC AQUEOUS SOLUTION

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE  
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OF THE REQUIREMENTS FOR THE DEGREE OF  
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IN CHEMISTRY  
JANUARY 1968

By

Ronald Carl Conrad

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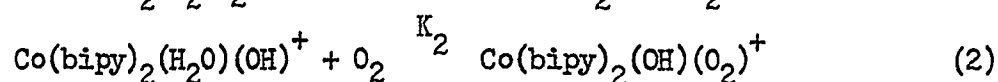
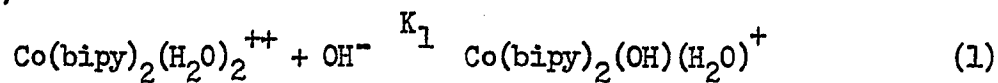
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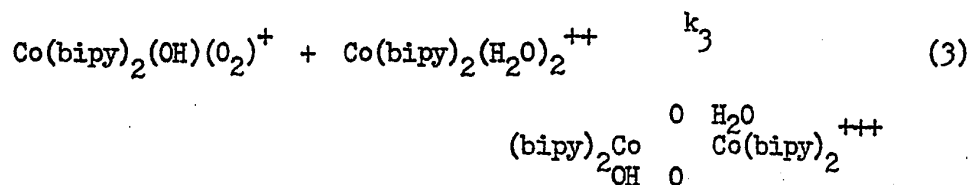
## ABSTRACT

### REACTIONS OF THE Co(II)-BIPYRIDINE SYSTEM IN BASIC AQUEOUS SOLUTION

Basic solutions of  $\text{Co}(\text{bipy})_2^{++}$ , where bipy is 2,2'-bipyridine, react with molecular oxygen, undergoing color changes from the original yellow, rapidly to dark brown, and finally much more slowly to red. Well formed red crystals may be separated from the final solution. The initial reaction involves the reaction of one molecule of hydroxide ion and one molecule of oxygen per two atoms of cobalt.

The pH decrease of the yellow to brown step serves as the basis for monitoring the reaction. Utilizing the pH-stat technique for monitoring the reaction, the fast step of the reaction is indirectly followed as volume of base added versus time. The reaction is found to be first order in both hydroxide ion and oxygen concentration and second order in complex concentration. Magnetic susceptibility measurements showed that the original yellow complex had three unpaired electrons, while the final red complex (both in the solid state and in solution) is diamagnetic. The indications are that the brown intermediate is less paramagnetic than the original yellow complex. The activation energy of the yellow to brown step of the reaction is approximately 11 Kcal mole<sup>-1</sup>. A mechanism which describes this faster reaction follows;





Equations (1) and (2) are quickly established equilibria, followed by the rate determining step, (3), the dimerization of the oxygen carrying compound and the original complex. The rate equation is thus;

$$dx/dt = k_3 K_1 K_2 (\text{cpx})^2 (\text{OH}^-) (\text{O}_2).$$

A spectrophotometric study of the slower brown to red step revealed a pseudo first order decay plus a simple first order decay of the brown intermediate;

$$-dx/dt = k_6 (\text{brown complex})(\text{OH}^-) + k_5 (\text{brown complex}).$$

The analytical and chemical evidence is that the final crystalline red

species is  $\begin{matrix} \text{OH} & \text{O} \\ \text{Co} & \\ \text{OH} & \end{matrix} \text{Co}(\text{bipy})_2(\text{NO}_3)_2 \cdot 1.5 \text{H}_2\text{O}.$

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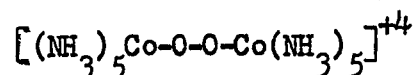
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## I INTRODUCTION

It has been observed that basic solutions of yellow  $\text{Co}(\text{bipy})_3^{++}$  and  $\text{Co}(\text{phen})_3^{++}$  (phen=1,10-phenanthroline and bipy=2,2'-bipyridine) turn brown upon exposure to the atmosphere and upon standing for some time yield a stable red crystalline product. These color changes and concurrent reactions have been attributed to the reaction of a  $\text{Co}(\text{II})$ -bipyridine species with molecular oxygen. No kinetic study of these reactions had been made until the research reported here was undertaken.

The study of oxygen absorbing solutions of cobaltous ions is older than coordination chemistry itself. It was Frey in 1852 who first published results of the air oxidation of ammoniacal solutions of  $\text{Co}(\text{II})$  ions, which resulted in the formation of stable brown salts (1). However, it wasn't until Werner (1910) that the product of Frey's reaction was postulated to be this highly charged dimer containing a peroxy bridge linkage;



This formulation by Werner was the first example of a coordination compound containing a peroxy bridge (2).

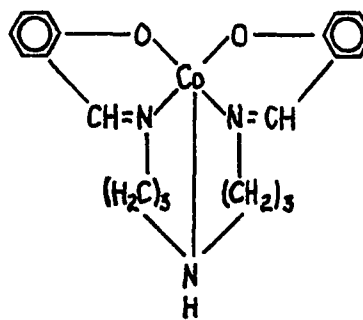
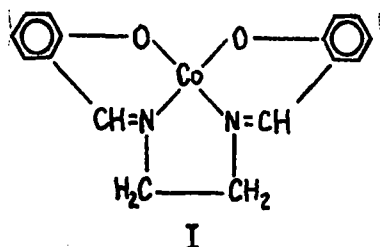
Although many cobaltous compounds in solution are now known to absorb oxygen and to form peroxy linked ions, only a few will absorb oxygen reversibly; that is, will "carry" or "transport" oxygen. The intrinsic interest in these specific ions lies in the catalytic activity of molecular oxygen in oxidizing metal ions, but of more interest to this study is the fact that these oxygenation reactions have been studied very little in basic aqueous solution. The general fascination in reactions of these types lies in the concern for a

model to illustrate the transfer and utilization of molecular oxygen in biological systems. Several of the simpler amino acids and peptides when chelated with Co(II), absorb molecular oxygen reversibly, and it is believed that the elucidation of the mechanism of these reversible reactions may clear up some of the anomalies which remain in the natural oxygen-carriers question--that is, how these oxygen carriers, involving a highly complex set of biological systems, utilize oxygen. However, this research is concerned only with the reaction itself and the elucidation of reaction mechanism. No attempt will be made to relate this to any biological system.

The research embracing absorption of molecular oxygen by complexes consists of two distinguishable areas; that of physiologists and biochemists, the latter involving those biological systems which exhibit oxygen transport, such as hemoglobin, hemerythrin, dimidazoleproto chromochrome, vitamin B<sub>12</sub>, catalase, oxygenase and related compounds. The other branch implicates much simpler ligand species such as glycylglycine, histidine, salicylaldehydethylenediamine, ethylenediamine, triethylenetetramine, and finally bipyridine and phenanthroline. Although the concern here is only with Co(II) compounds, other metal ions which exhibit an ability to carry oxygen when complexed to simple ligand species are Fe, Ir, Ni and Cu (3).

The first synthetic reversible oxygen-carrying chelate was prepared by Pfeiffer and associates in 1933 (4). Pfeiffer noticed that one of his compounds, cobaltous bis-salicylaldehydethylenediamine (BSAD), turned from a red to a blackish color upon exposure for a few days to the atmosphere. Later in 1938 Tsumaki (5) discovered absorp-

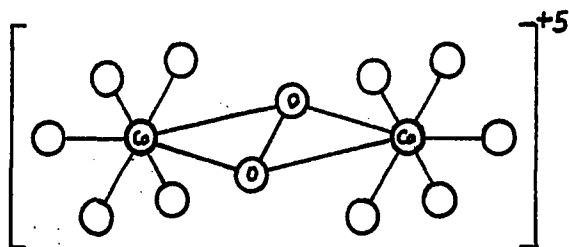
tion of oxygen to be responsible for this discoloration. He learned that upon heating this darkened compound in a stream of  $\text{CO}_2$ , the oxygen could be driven off and the original red compound recovered. This research concerning Co(II) (BSAD) was extensively continued by Calvin, Wilmarth, Barkeley, and associates who published in 1946 an important series of papers which showed that there were actually two types of Co(BSAD) compounds and that both types were oxygen carriers in the solid state as well as in solution (6).



Type I chelate carries one molecule of  $\text{O}_2$  per two atoms of Co, and x-ray studies have shown that Type I molecules are coplanar and arranged in layers. The active crystal is so arranged as to provide holes in the lattice large enough to accommodate  $\text{O}_2$ . Moreover, the interconnection with other holes is such that the  $\text{O}_2$  molecule has access to the whole crystal. The original paramagnetism (one unpaired electron) of the unoxxygenated compounds is lost as  $\text{O}_2$  is added and vanishes when the molecule is fully charged with  $\text{O}_2$ . Type II active chelates initially contain three unpaired electrons which then diminish to one unpaired electron as the capacity of one  $\text{O}_2$  to one Co is reached. The kinetic studies of the formation of these compounds in the

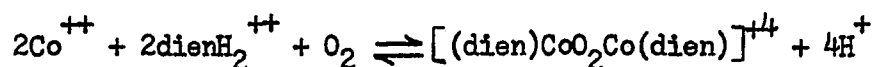
solid state show a first order rate dependence with respect to the complexes in most cases, and in all cases first order with respect to  $P_{O_2}$ . The same results were obtained using non-aqueous solvents such as quinoline, pyridine, methylbenzoate, and 2-methylnaphthalene. The importance of these experiments lies in the fact that they fully describe the first synthetic oxygen carrying chelates and that these chelates have the ability to carry oxygen in the solid state as well as in solution.

Of the simpler ligands, ethylenediamine (en), diethylenetriamine (dien), and triethylenetetramine (trien), when bound to Co(II), exhibit oxygen carrying properties (7). The  $Co(dien)^{++}$  ion is yellow in basic solution but as it is exposed to the atmosphere the solution color changes to brown. Lowering the pH to one, however, causes the reappearance of the yellow color with the oxygen being released. This color reversal indicates that the prime reaction is not just a simple irreversible oxidation of Co(II) to Co(III), for, if on the other hand, a high pH is maintained over long periods, slow changes are detected spectrally in the brown solution and these changes are not reversible with acid. This final red-brown complex has been isolated and shown to contain the simple ion  $Co(H_2O)_3(dien)^{+++}$ , while the brown intermediate is postulated to be a bridged binuclear complex with the O-O axis perpendicular to the Co-Co axis, utilizing steric considerations in accordance with the postulations of Vlcek (8). To support this, Brosset and Vannerberg (9) used x-ray studies to show that in the u-peroxo pentammine-Co complex the molecule had this steric formulation;



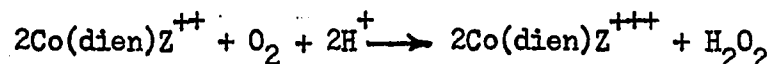
In yet another study Bekaroglu and Fallab (7) were mainly concerned with the factors which influence the stabilization of  $O_2$ -adducts, and they discovered that simple amines such as en, dien and trien produced stable  $O_2$ -adducts while more complex ligands as nitrilotriacetate (NTA) or ethylenediaminetetracetic acid (ETDA) resulted in none. On the other hand, by adding en to solutions of Co(II) and NTA, oxygen-carrying properties were induced. Conversely, if with a  $Co(en)_2^{++}$  compound, the fifth and sixth positions (originally filled by solvent molecules) were occupied instead by oxalate, malonate or glycinate,  $O_2$ -carrying properties were once again lost. These additional ligands would, of course, have the effect of blocking the fifth and sixth positions which in the oxygen-carrying complexes are filled by bridging oxygen groups. Bekaroglu surmised, then, that at least three N-ligand atoms must be present and that O-binding chelates destabilize the bridged complex.

Furthermore, Bekaroglu and Fallab made equilibrium measurements for the reaction;



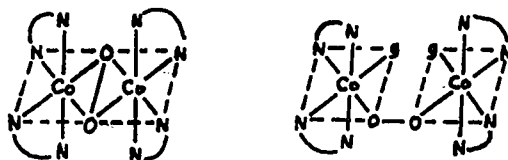
At  $25^\circ$  the log of the equilibrium constant is 6.80. The brown intermediate was found to be diamagnetic, and it also showed a broad

absorption band extending from 350-450m $\mu$ . The presence of accessory anions as  $\text{CH}_3\text{COO}^-$ ,  $\text{HPO}_4^{=}$ ,  $\text{C}_2\text{O}_4^{--}$ ,  $\text{HP}_2\text{O}_7^{-3}$ , caused red-violet solutions to arise, taking days in the case of  $\text{CH}_3\text{COO}^-$  ions but only minutes in the case of  $\text{HP}_2\text{O}_7^{-3}$ . In each case the anion was incorporated in the coordination sphere while cobalt terminated in the (III) oxidation state. The auxiliary ion concentration term appeared in the rate equation. The reactions were studied exclusively in acid solution, utilizing phosphate buffers, and rate studies of the decay of the brown species showed that  $dx/dt=k(A)$ , where A was the intermediate. The method of initial rates was necessary owing to deviations from first order after only a small reaction time, for the forward reaction was being retarded in some manner--possibly by back formation of the initial reactant. A postulation, by Erdem, (10) for the overall reaction is the following equation:



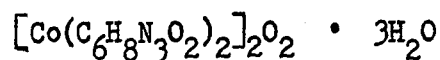
This is where Z is an accessory ion mentioned above. It is of some interest to note here that adding  $\text{H}_2\text{O}_2$  fails to have any influence upon the rate. This, perhaps, means that  $\text{H}_2\text{O}_2$  cannot oxidize Co(II) under these conditions. Erdem states that the oxidation electron transfer arises from a transfer of electrons from Co(II) to oxygen resulting in Co(III) and the still coordinated peroxide ion. It is just this step which is the irreversible one in the reaction, as the binuclear complex then dissociates to  $\text{Co}(\text{III})\text{Z}^{+++}$  and  $\text{H}_2\text{O}_2$ . The slow rate of the reaction can be understood in terms of a slow rearrangement and displacement of atomic nuclei, and the high activation energy of 20 Kcal mole<sup>-1</sup> lends support to this hypothesis.

Burk (11), et. al. found in 1946 that the histidine complex of Co(II) possessed oxygen carrying properties, and Hearon (12) continued this investigation of Co(II)-histidine, exploring the reaction extensively. His findings showed that two molecules of bis-histinato Co(II) combine with 1 molecule of oxygen. Moreover, the initial pink compound was converted upon oxygenation to a brown oxygen-carrying complex, and this same step was accompanied by a change in number of unpaired electrons--from three (pink) to one (brown). Hearon, then, proposed the following structures for the intermediate:



G in the proposed structure is either a carboxyl or a water group. Hearon was unable to isolate the oxygen-carrier.

However, in 1962 Sano and Tanabe (13) claimed to have isolated the oxygen-carrying complex of Co(II)-histidine from a cold alcoholic solution. Isolation from neutral solutions yielded a high purity product (not contaminated by Co(III) ions) represented by the empirical formula;



Infra-red spectroscopy was utilized to elucidate the structure of the oxygen-carrying compound, and the fact that two different car-

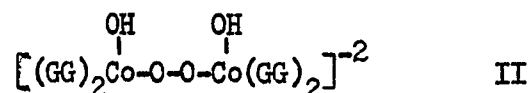
boxyl stretching vibrations were evident, indicated that for each histidine molecule, one carboxyl group coordinated and one remained free. This left one position open on each octahedron so that the oxygen bridge could form. Leberman (14) had previously proved that the unoxxygenated complex was bis-coordinated and that the histidine acted as a tridentate. In addition, Earnshaw's (15) magnetic data and the visible and ultra-violet spectra lend support to an octahedral structure for the bis-histidine Co(II) complex. Finally, Sano found the brown compound to be quite hygroscopic, thermally unstable (decomposing at  $90^{\circ}$ ), and upon decomposition to yield no qualitative test for released oxygen.

Gilbert, Otey, and Price (16), upon introducing oxygen into alkaline solutions of Co(II) glycyldydroalanine, found that a yellow-brown solution resulted which changed slowly with time to a red solution that absorbed at 515 m $\mu$ . The same sequence of reactions occurred with Co(II) plus glycyll and glycyll-alanine, as well as with glycyll-glycine. Oxygen absorption experiments were undertaken which showed a rapid oxygen uptake approaching a maximum after 15 minutes with a total oxygen absorption of 1 mole of oxygen per 2 moles of Co(II). The brown to red color change was not accompanied by additional oxygen absorption. Increasing the hydroxide concentration in the solution increases the yield of the final red product. Reversibility of the yellow to brown step was shown by the release of 10% of the consumed oxygen by lowering the pH of a brown solution to 2.6 with HCl. Moreover, no reaction at all was observed with the careful exclusion of oxygen from the reaction vessel--even after fifty hours had passed. The isolated final red product corresponded analytically to 2 moles of

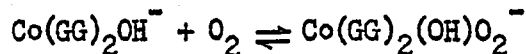
peptide per mole of Co and 0.5 moles of oxygen. No kinetic analysis was made on the oxygen-uptake data.

Tanford, Kirk, and Chantooni (17), however, did study the kinetics of the reactions of Co(II)-glycylglycine and oxygen in alkaline solution. They noted that at lower pH regions (pH=7-8) the final red product was formed directly and there was very little brown intermediate detected. However, at higher pH regions, the intensely colored brown intermediate was formed; this led to the same ultimate red product as obtained at lower pH, and conformed to the product found previously by Gilbert, Otey, and Price.

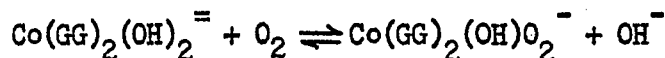
At pH=9.5 the formation of the intermediate was essentially instantaneous (spectrophotometrically) as no spectral changes at 365 mμ (where the extinction coefficient equals 8000 per complex) could be observed initially at any pH greater than 9.5. No evidence was found for any other active forms. Initial rates were utilized in the calculation of the rate constants, and at low pH values the reaction was directly proportional to the oxygen partial pressure and to the 3/2 power of the complex. In addition, there was a strong (order of 2.5) dependence on the hydroxide ion indicating that the OH<sup>-</sup> itself is consumed in the reaction. Tanford, therefore, assumes that Co(GG)<sup>-</sup> alone cannot react with molecular oxygen, and that it is the hydroxy compound--either Co(GG)OH<sup>-</sup> or Co(GG)(OH)<sub>2</sub><sup>=</sup>, which is the active species, and that the intermediate in the reaction is of the following type;



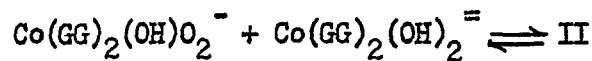
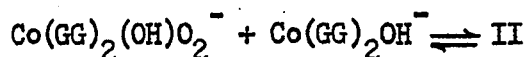
Thus, his reaction mechanism at lower pH would be as follows;



or



Since  $\text{Co(GG)}_2(\text{OH})\text{O}_2^-$  contains an unpaired electron and would be relatively reactive, a binuclear species would rapidly form in either of two ways;



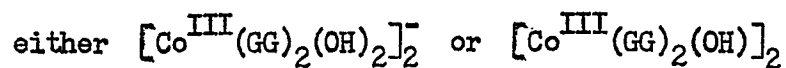
where II is the brown compound.

II would decay at once to the final red product, for it was shown that the formation of that final red product was equal to the rate of the oxygen-uptake. This final reaction presumes the formation of a second Co-Co bridge and is likely to be slow. Hence, elimination of at least one hydroxide ion is required.

The rate studies in alkaline solution were concerned mainly with the brown to red step. The brown intermediate is increasingly stable with increasing pH, while in decaying to the ultimate red product, it follows a first order decay constant. The decay constant is independent of the oxygen partial pressure and above pH=11 is independent of hydroxide ion. However, below pH=11, the rate depends linearly on the  $\text{OH}^-$  ion--increasing with decreasing pH. There is also a dependence on ionic strength, the rate increasing with increasing ionic strength. On the basis of such rate data as this, Tanford and his associates postulated the following species as the ultimate product of these oxidation reactions;



Co atoms, hydroxide groups were actually involved, and the general formula for the product was;

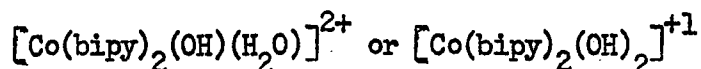


Finally, there has been some important work done on the Co(II)-bipyridine systems, in every case applying polarographic techniques to the study of the system. Waind and Martin (20) in 1958 studied the low valence stabilization of  $\text{Co}(\text{bipy})_3^+$ , first by preparing the ion in the salt form, and then by recognizing its existence as the two-step reduction product of  $\text{Co}(\text{bipy})_3^{+++}$  at the dropping mercury electrode.

A. Vlcek (21) in 1958 also investigated the reduction of  $\text{Co}(\text{bipy})_3^{+++}$  at the dropping mercury electrode finding a simple one step reduction to  $\text{Co}(\text{bipy})_3^{++}$  followed by a much more complicated additional reduction to Co(I) and Co(0).

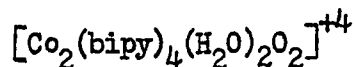
Moreover, directly related publications appeared in the early '60's by several Italian authors, Silvestroni (22) in 1960 and Cabani (23) in 1962. The former author noticed that a basic solution of Co(II) ions and bipyridine, when exposed to air, changed from a yellow to a brown color, and finally to a red color upon further standing. They determined polarographically that a Co(II)-bipyridine solution would reversibly absorb oxygen at neutral or slightly alkaline pH. Oxygen absorbance increased as the ratio of bipyridine to Co(II) approached 2.2-2.5, and decreased at higher ratios. Maximum oxygen absorbance was also attained with ever increasing pH. However, at much higher pH's than 8 the oxygenated product would become unstable and oxidize irreversibly to a final cobaltic species. The same final co-

baltic species could be obtained by subjecting  $\text{Co}(\text{bipy})_3^{+++}$  to prolonged contact with hydroxide ions. This final red cobaltic species was found to absorb in the visible region at around 306 and 520  $\mu$ . These wavelengths of maximum absorption were close to the absorbances obtained with solutions of the oxidation products of  $\text{Co}(\text{II})$ -glycylglycine and  $\text{Co}(\text{II})$ -bihistidine. As the final product, Silvestroni and Ceciarelli postulated the following possible structures for the cation;



Cabani made a most important examination of both  $\text{Co}(\text{II})$  and  $\text{Co}(\text{III})$  complexes of bipyridine and their reaction products resulting from reaction with molecular oxygen. Cabani established that acidic solutions of  $\text{Co}(\text{bipy})_3^{++}$  upon exposure to oxygen, slowly yielded the  $\text{Co}(\text{bipy})_3^{+++}$  ion. Conversely, a basic solution of  $\text{Co}(\text{bipy})_3^{+++}$  slowly led to the final red species, as Silvestroni had observed before. Like Silvestroni, Cabani stated that the optimum conditions for the formation of the oxygenated species were a high pH and a bipyridine/ $\text{Co}(\text{II})$  ratio of between 2.2-2.5. Again, like Silvestroni, Cabani found that at higher pH values the oxygenation reaction was rapidly followed by an oxidation of  $\text{Co}(\text{II})$  to  $\text{Co}(\text{III})$ .

Cabani also measured manometrically the amount of oxygen absorbed at different pH's and by coupling this with polarographic data, arrived at the ratio of oxygen molecules bound to  $\text{Co}(\text{II})$  in the intermediate-- on the average it was equal to 0.5. Cabani believed that the intermediate had the following formula;



In addition, Cabani tested the oxygen-carrying properties of the

cobaltous, ion-bipyridine system by alternately oxygenating and deoxygenating slightly basic solutions of Co(II) and bipyridine, with air and nitrogen respectively. This could be repeated several times with little net oxidation to Co(III). Polarograms obtained both before and after oxygenation and deoxygenation established the pattern of these continuing cycles. Cabani believes that the actual oxygen carrying species in the solution is the  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  ion. For the ultimate product of the reaction, he agrees with those proposed by Silvestroni and Ceciarelli previously.

Ritter (24) in 1962 found that in the preparation of  $\text{Co}(\text{bipy})_3\text{Cl}_3$ , by oxidizing  $\text{Co}(\text{bipy})_3\text{Cl}_2$  with 30%  $\text{H}_2\text{O}_2$ , instead of the expected orange product, he received a dark brown solution which upon the addition of HCl regenerated the original yellow solution. The same oxygenation reaction could be effected with oxygen gas. Upon standing for several days and with some evaporation, long, needle-like red crystals separated out. Ritter attempted to measure the rate of oxygen-uptake of the yellow compound by manometric measurements, but his attempts were generally unsuccessful. However, he did establish that maximum absorbance occurred when the ratio of bipyridine to cobaltous ion was two; and further, that as oxygen was absorbed, the pH decreased but as oxygen was released the pH went up again.

Ritter dissolved the red crystals in 1 M  $\text{HNO}_3$ , and heated at  $65^\circ$  for 24 hours. By adjusting the pH to 4.4 with NaOH, a new red compound could be isolated after slow evaporation and refrigeration. This second red compound was many times more soluble than that of the original red compound. It could also be titrated with 0.01 M NaOH and yielded

equivalent points of 593 and 297. The compound  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_3$  would have equivalence points at 594 and 297. Elemental analysis indicated the existence of this di-aquo compound also. By adjusting the pH of a solution of the di-aquo compound to 13.4, slender red needles of the original oxidation product were recovered again.

Over the course of this recovery the pH fell from 13.4 to 8.0. Ritter also proved that oxygen had to be present for the yellow to brown sequence of the reaction to take place.

## II EXPERIMENTAL

### A. pH-stat Measurements

All pH-stat measurements were made with a Radiometer Automatic Titrator, Type TTT1c. The method of running experiments was to first dissolve the calculated bipyridine (reagent grade-Matheson Coleman and Bell) in one drop of 4 M HNO<sub>3</sub>. This was volumetrically transferred to a 50 ml volumetric flask with a 0.5 M solution of NaNO<sub>3</sub> (to maintain an essentially constant ionic strength throughout the reaction). This volume was then transferred to the reaction vessel which was then immersed in an oil bath regulated by a Precision Scientific mercury thermostat. The reaction vessel remained in the oil bath at least 15 minutes while temperature equilibration was attained. Constant temperature could be maintained to  $\pm 0.1^{\circ}$  C. Concurrently with the temperature equilibration, oxygen was bubbled through the solution in order to saturate the system. Vigorous paddle stirring efficiently pulverized the gas bubbles producing a large surface area of gas. Hydroxide ion (1.00 M NaOH) was next added through a hole in the top of the reaction vessel until the required pH (usually between pH=8-9.30) was reached. Several minutes later the required volume of Co(II) ion was injected into the reaction solution by a 100 ul capacity syringe fitted with a Cheney adaptor. The injection of the Co(II) ion signalled time zero and the pH-stat monitoring of the reaction was initiated. Stirring was achieved by means of a high speed paddle stirrer. The initial reactive species in acid solution is  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})^{++}$ , and the reaction of this species was followed automatically by recording the amount of hydroxide

ion which was added to keep the pH constant, as a function of time. The reaction was followed over several half lives and at 28° C. took approximately 10 minutes. A calibrated, 0.50 ml micrometer driven syringe was used to maintain constant pH.

The amount of Co(II) injected in the various experiments was of the order of 0.01938 mmoles which in 50 ml of solution gave molar concentrations to the order of magnitude of  $10^{-4}$ .

#### B. Ultra-violet Spectra

The visible and ultra-violet spectra of the specific compounds in aqueous solution were taken on a Beckmann Model DB recording spectrophotometer, over the wavelength region from 600 down to 220 mu. One cm cells were used.

#### C. Preparation of the Final Red Species in Crystalline Form

Two moles of bipyridine dissolved in nitric acid are added to one mole of  $\text{Co}(\text{NO}_3)_2$ . To the solution is added 0.25 M NaOH until a pH between 8 and 10 is reached. Next, 0.5 ml of 3%  $\text{H}_2\text{O}_2$  is added to the reaction solution, or pure oxygen is bubbled through the solution for a period of one-half hour. The original yellow color of the solution immediately turns to a dark brown. The reaction beaker is then placed on a small heater and warmed at 60° C. for one day. Additional hydroxide ion is added to keep the pH up around the value of 10. Slender, needle-like red crystals then separate out of the solution before much evaporation has taken place. The red needles are washed with ice cold distilled water. In air they retain their shiny luster indefinitely. Washing with acetone will cause a crumbling of the crystal along with a loss of luster. Drying the crystal above  $\text{H}_2\text{SO}_4$  will likewise evoke

crumbling and loss of luster. The crystal is insoluble in common organic solvents as acetone and ethyl alcohol.

D. Quantitative Drying of the Red Species

The final red species was quantitatively dried in this manner; after washing the isolated red crystals, they were recrystallized from hot distilled water several times and then air dried. They were next weighed and placed in a vacuum desiccator over concentrated  $H_2SO_4$  overnight. They were then weighed again. This initial drying was followed by treatment in a vacuum drying pistol at temperatures of  $50^\circ$  and  $80^\circ$  C. respectively, weighing the crystals again at appropriate times.

E. Conductivity Measurements

The conductivity measurements on the red species were done in aqueous solution using an Industrial Instruments Model RC-1682 conductivity bridge with accompanying platinum coated electrodes. Standardized 0.02 M KCl was employed to obtain the cell constant and the measurements were obtained in the usual manner.

F. Magnetic Susceptibility Measurements

A Gouy type magnetic susceptibility balance was assembled to measure susceptibilities of solid samples and solutions. A Mettler balance capable of weighing to 0.01 mg was employed to measure the change in force resulting from placing the sample in and out of the magnetic field. From the balance pan was hung a non-magnetic chain, containing at its terminus a sterling silver ring. The sample tube was attached to the ring by means of a free swinging copper wire, which could be fastened to the Pyrex sample tubes. The Gouy tube was then lowered

down an adapted condenser through which circulated distilled constant temperature water from a constant temperature bath. The condenser served not only to maintain a constant temperature in the sample tube but also to eliminate air currents which would disturb the measurements. The Gouy tube was fixed between the 2 inch poles of a Varian Electromagnet, Model V-4004. The distance between the poles was 2.5 inches and this pole gap was maintained over all the experiments.

With these experimental conditions a theoretical magnetic field strength of 10 kilogauss was possible. The Gouy tube was positioned so that its lower tip was placed at the very center of the pole gap and at the theoretical center of the field, while the upper section of the tube extended well above the maximum of the magnetic field. Solid  $\text{Hg}(\text{Co}(\text{CNS})_4)$ , as recommended by Figgis and Nyholm (25) was utilized to calculate the tube constants for the solid sample fields, while a concentrated aqueous solution of  $\text{NiCl}_2$  (26) was employed to calculate the tube constants for the solution tubes. The  $\text{NiCl}_2$  solution was standardized according to the procedure of Foulk, Moyer, and MacNevin (27).

#### G. Visible Spectra Kinetic Measurements

The brown to red step of the reaction was studied spectrally, using a Spectronic 20 Colorimeter-Spectrophotometer to study the changes in absorbance at 450 m $\mu$ . The procedure for preparing  $\text{Co}(\text{bipy})(\text{H}_2\text{O})_2^{++}$  in solution was the same as that used in the pH-stat measurements. As the yellow to brown segment of the reaction proceeded, samples were removed periodically from the reaction vessel, and the absorbance measurements taken. A maximum absorbance at 450 m $\mu$  was soon reached, followed soon afterwards by a decrease of the absorbance at the same

wavelength as the brown species started to decay. The pH was maintained constant by employing the pH-stat apparatus. As before, the reaction vessel was immersed in an oil bath and all above measurements were made at 50° C. A temperature rate study was also done on this reaction.

#### H. Standardizations of Reagents

The 0.1 M NaOH was standardized according to normal procedures utilizing potassium-acid phthalate as the primary standard. The Co(II) solution was standardized using the procedure of Vogel (28), but with the following changes; The ammonium thiocyanate was not added until the Co(II) solution was near its boiling point. The pyridine was added while the solution was actually boiling, and this resulted in large well-formed crystals instead of the smaller more microcrystalline like crystals obtained in the standard procedure. This procedure, then, should increase the accuracy of the determination.

### III EXPERIMENTAL RESULTS

The main section of this research is involved with kinetic studies of the yellow to brown step of the reaction, by use of the pH-stat technique. Ritter had discovered in his oxygen absorption experiments that as oxygen is absorbed, the pH of the solution decreases, but as oxygen is released, the pH goes up again. Accompanying this was the color change from yellow to brown or from brown to yellow respectively. Since the pH decrease paralleled the oxygen absorption, it was felt the reaction of  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  with molecular oxygen in basic aqueous solution could be followed using the pH-stat method. That is to say, by maintaining the pH constant by addition of base through a micrometer driven calibrated syringe, and recording the amount of base added as a function of time, the reaction of the bis-bipyridine Co(II) complex with molecular oxygen could be indirectly followed. It had been shown previously by both Cabani and Ritter, and was confirmed again in this study, that a ratio of bipyridine to Co(II) close to two yielded a solution for the maximum absorbance rate of oxygen, hence it was felt that by making up solutions wherein the bipyridine/Co(II) ratio was two, the reacting species concentration was maximized. Although the dominant species in solution will be the bis-bipyridine Co(II) complex, there will undoubtedly be some of the tris-bipyridine complex in solution also. However, since one bipyridine has been shown to undergo fast exchange (29), the subsequent aquation of the product of the dissociation of the tris compound is probably fast.

Fairly dilute concentrations of the complex were used, with the

concentration of Co(II) in solution being of the order of magnitude of  $10^{-4}$  moles liter<sup>-1</sup>. This concentration range was chosen for several reasons. First of all, the reaction velocity is fairly fast and low concentrations of the complex allow easier monitoring of the reaction. Secondly, the Co(II) concentration is governed by the fact that at higher pH regions an insoluble species comes out of solution, probably the quite insoluble Co(II) hydroxide. Finally, it was felt that if the reaction was allowed to proceed at too quick a rate, there might enter in a complicating factor involving the concentration of oxygen in solution. The molar concentration of dissolved oxygen ( $1.23 \times 10^{-3}$  M at 25° C.) (30) is several times greater than the Co(II) concentration and with presaturation of solution with gas and excellent stirring, the oxygen concentration should remain constant for reactions which react at reasonable rates. However, if excessively fast reactions are run, it is possible that the concentration of dissolved oxygen might be less than saturation and the overall reaction would therefore be controlled by the dissolution of oxygen gas. Since  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$ , itself, slowly oxidizes to the Co(III) species upon standing in the atmosphere, as was observed in this research, solutions are reacted within one hour of preparation.

In all the reactions the order of mixing was not varied, with the dilute basic bipyridine solutions being prepared and saturated with oxygen, and then the reaction being initiated by injecting the Co(II) into the solution with a syringe. Since the formation of the bipyridine-Co(II) complexes is essentially instantaneous (31), it was felt that this order of mixing could achieve the highest accuracy for

monitoring the reactions. In as much as the reaction is quite fast, it was imperative that the pH-stat monitoring be initiated immediately.

The sensitivity of the reaction to hydroxide ion is such that the reactions must be run at relatively low hydroxide ion concentrations,  $3.0-20.0 \times 10^{-6} \text{ M}$ . At these higher hydroxide ion concentrations and with  $1.96 \times 10^{-6} \text{ M Co(II)}$  concentrations, the limit of the instrument is approached (that is, addition of syringe base in a reproducible manner).

As mentioned above, even though the amount of oxygen dissolved in solution is quite small ( $1.23 \times 10^{-3} \text{ M}$  at  $25^{\circ} \text{ C.}$ ), the experimental conditions were such that the concentration of dissolved oxygen was surmised to be constant throughout the reaction. The reaction solutions were all presaturated with oxygen and the oxygen flow through the solution continued throughout the reaction. Furthermore, since the oxygen delivery tube and the high speed paddle stirrer were in close proximity, the oxygen bubbles were efficiently pulverized, presenting a large surface area of oxygen available for absorption.

Since the pH was kept constant by the titrimeter and as the oxygen concentration was maintained constant during the reaction, the reaction rate could be isolated to dependence on the changing concentration of the bis-bipyridine Co(II) species. A plot of  $1/(A/2-X)$  versus  $t$ , where  $A$  is the initial concentration of complex and  $X$  is the concentration of binuclear intermediate which has formed at time  $t$ , yielded a straight line which was indicative of second order dependence on the complex.

On the other hand, if the order with respect to hydroxide ion was desired, a series of reactions could be completed in which the same

concentration of Co(II) and the same oxygenating agent were used in every case. However, the pH would be altered for the various experiments and a series of  $k_{\text{obs}}$  (observed rate constants) could be found which were dependent on the hydroxide ion concentration. The observed rate constants were then plotted versus the hydroxide ion concentration and if a straight line was obtained, the order with respect to hydroxide ion is one. Likewise a plot of  $\log(k_{\text{obs}})$  versus  $\log(\text{hydroxide ion})$  would yield a straight line with a slope of one if there is first order base dependence. That is, since;

$$\text{rate} = dx/dt = k_{\text{obs}} (\text{complex})^2 \quad (1)$$

and;

$$k_{\text{obs}} = k_{\text{OH}^-} (\text{OH}^-)^n \quad (2)$$

Taking the logarithm of both sides of (2) results in (3).

$$\log(k_{\text{obs}}) = n \log(\text{OH}^-) + \log(k_{\text{OH}^-}) \quad (3)$$

Plotting  $\log(k_{\text{obs}})$  versus  $\log(\text{OH}^-)$  yields the order with respect to hydroxide ion equal to the slope of the line obtained, with the y intercept being equal to  $\log(k_{\text{OH}^-})$ . In the same manner, the order of the reaction with respect to oxygen could be found. Different gaseous mixtures of oxygen and nitrogen were obtained and series of reactions were undertaken whereby the initial concentrations of hydroxide ion and complex were the same but different oxygen-nitrogen mixtures were bubbled through the reaction solution.

Owing to the fact that the initial reaction is quite fast and is itself followed by a second slower reaction which is also hydroxide ion active (takes hydroxide ion out of solution or generates a proton), a second procedure for analyzing data was undertaken. This was to

measure the actual initial slope of the pH-stat curves obtained in the monitoring of the reaction. This involved choosing a point on the curve very close to the commencement of the reaction, and actually measuring the tangent to the line at this point and hence the slope. This slope, then, veritably represented the moles of complex reacting at this time. Since  $dx/dt$  is directly proportional to  $k_{obs}$ , one could use  $dx/dt$  itself, in lieu of  $k_{obs}$  and again by obtaining a series of points at different pH values, could plot  $dx/dt$  versus  $(OH^-)$  in order to secure the dependence on the different reactants. The point chosen in all cases occurred at ten seconds after the start of the reaction. It was difficult to choose any earlier point due to the inaccuracy of the points in the initial stages of the reaction. The error of measuring the slope at a certain point is, of course, admittedly great, but in most instances good curves were obtained. This method of analysis will be referred to as the method of "initial slopes" and its value rests on the fact that its points occur at the outset of the reaction, and before any complicating reactions can effect the rate. For it is this problem of consecutive reactions which probably cause deviations from the second order plots after approximately 50% of the reaction in those reactions, run at higher pH values.

B. The Order of the Reaction with Respect to Hydroxide Ion

The great bulk of the pH-stat experiments which were performed, were attempts to measure the rates of the reaction at various initial hydroxide ion concentrations. In these measurements the initial Co(II) concentrations and the oxygenating agent's composition would be the same for a series of reactions, but the hydroxide ion concentration would be

different for each separate reaction.

Then by plotting the second order rate constants versus initial hydroxide ion concentration, a curve should be obtained which would be a straight line if the order with respect to hydroxide ion is one, or by plotting  $\log k_{\text{obs}}$  versus  $\log(\text{OH}^-)$  a straight line with a slope equal to one indicates first order dependence on hydroxide ion. In Figures I and II are the plots of  $k_{\text{obs}}$  versus  $(\text{OH}^-)$  and  $\log(k_{\text{obs}})$  versus pH respectively. These figures are based on the data tabulated in Table I. Although there is some scatter in these curves, it can be observed that Figure I is linear and has a slope (as calculated by least squares analysis) equal to  $4.17 \pm 0.18 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$ . The slope of the  $\log(k_{\text{obs}})$  versus  $\log(\text{OH}^-)$  is equal to  $1.01 \pm 0.11$ . As noted above, by measuring the slope of the plot of  $k_{\text{obs}}$  versus hydroxide ion concentration, the  $k_{\text{OH}^-}$  of the reaction could be found. That is, the rate will be proportional to the complex concentration, the hydroxide ion concentration, and the oxygen "concentration."

$$\text{rate} = dx/dt = k_{\text{obs}} (\text{complex})^n (\text{OH}^-)^n (\text{O}_2)^n$$

The rate constant which is measured is  $k_{\text{obs}}$  and, since only the hydroxide ion concentration is varied over this series of reactions, the  $k_{\text{obs}}$  would be equal to  $k_{\text{OH}^-}(\text{OH}^-)$ .

Similarly, straight lines may be established by graphing the "initial slopes" versus hydroxide ion concentration. In Figures III and IV, which correspond to Tables II and III, are found these types of graphs at diverse initial concentrations. Additional figures of this type can be found in the discussion of the experimental data involving the effect of ionic strength on the rate. The fact that

both classes of graphs yield essentially straight lines, is indicative of the first order nature of the reaction with respect to hydroxide ion. That the "initial slopes" at higher hydroxide ion concentrations appear to deviate negatively from the slope of the "initial slopes" versus  $(OH^-)$  straight line may be attributed to several circumstances. First of all, it was recognized in several experiments run at higher pH values and with higher initial complex concentration, that a faint turbidity clouded the solution. This can perhaps be ascribed to the solubility product of  $Co(OH)_2$  being exceeded, hence lowering the amount of the initial species,  $Co(bipy)_2(H_2O)_2^{++}$  at these higher pH values. However, since most of the  $Co(II)$  should be coordinated to bipyridine, it is unlikely that much of the  $Co(II)$  would be available for the formation of the hydroxide. Concurrently, and perhaps more likely at these higher pH values, is the potentiality that the di-hydroxy species can form-- $Co(bipy)_2(OH)_2$ , which is unreactive. There is some likelihood that this di-hydroxy species would be the precipitate since it is a neutral species. At these higher pH regions, the oxidation of the  $Co(II)$  species to the  $Co(III)$  species (which would again be unreactive) would lower the concentration of the active  $Co(II)$  complexes. Finally, because of the high velocity of the reaction at higher pH values, the oxygen concentration might be less than its saturation value, ultimately lowering the speed of the reaction.

Table I

Order of Reaction With Respect to  $(\text{OH})^-$  --  $k_{\text{obs}}$  vs.  $(\text{OH})^-$ 

$\text{Co(II)} = 5.81 \times 10^{-4} \text{ M}$     Pure  $\text{O}_2$      $0.5 \text{ M NaNO}_3$      $T = 26.9^\circ \text{ C.}$   
 $\text{bipy} = 11.62 \times 10^{-4} \text{ M}$

$(\text{OH})^- \times 10^6 \text{ M}$	pH	$k_{\text{obs}} (\text{M}^{-1} \text{ sec}^{-1})$
3.71	8.57	1.33
4.47	8.65	1.64
5.01	8.70	2.11
5.01	8.70	2.10
5.25	8.72	2.16
5.62	8.75	1.77
5.75	8.76	1.70
6.17	8.79	2.36
6.46	8.81	1.89
6.76	8.83	2.78
6.92	8.84	2.78
6.92	8.84	2.85
7.24	8.86	2.72
7.59	8.88	2.63
7.76	8.89	2.70
8.51	8.93	4.10
8.71	8.94	3.48
8.71	8.94	3.38
8.91	8.95	3.27
10.23	9.01	4.30
12.30	9.09	4.67
12.88	9.11	5.05

\* A least squares analysis of a plot of  $k_{\text{obs}}$  vs.  $(\text{OH})^-$  gives  
a  $k_{\text{OH}} = 4.17 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$

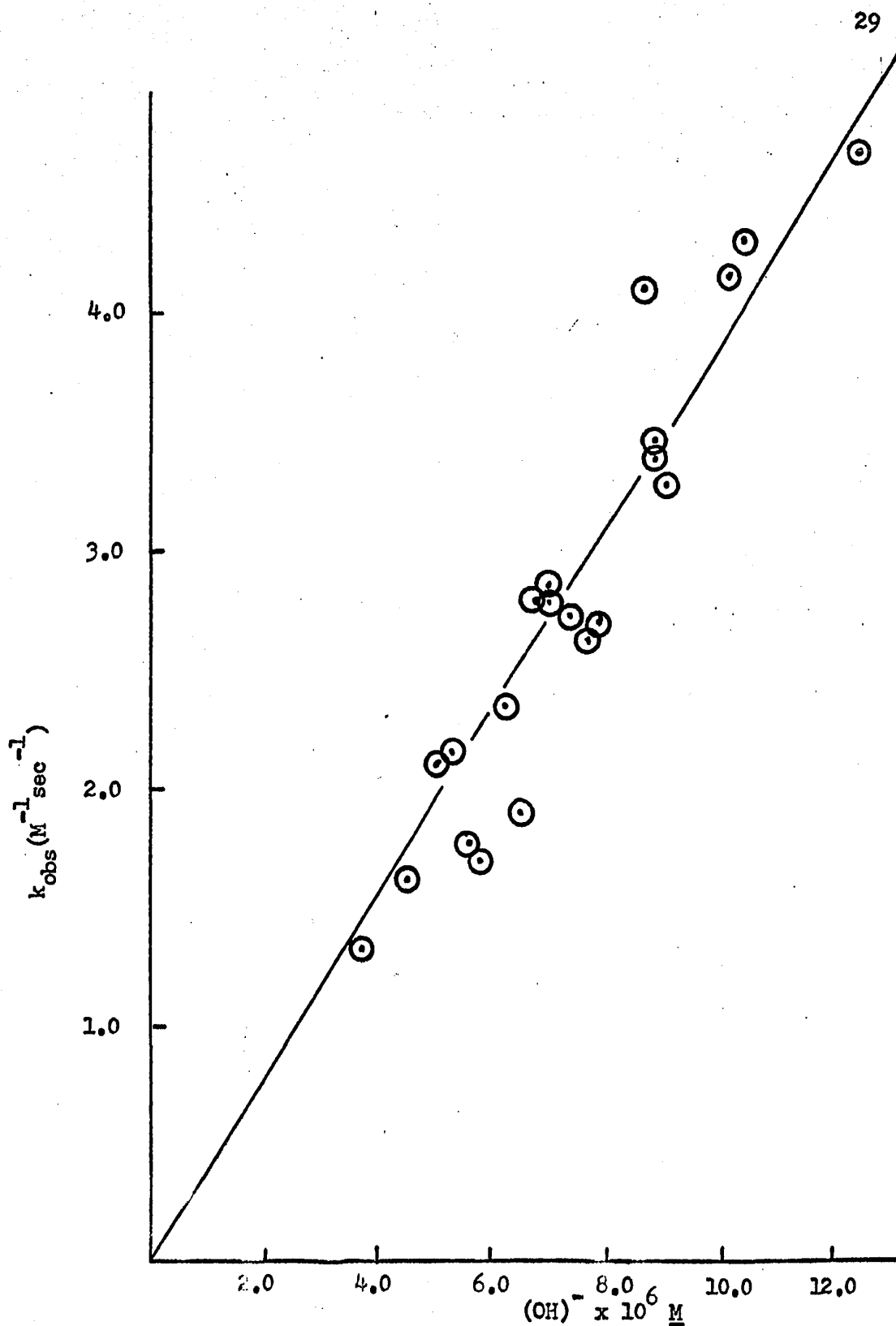


Fig. 1 Order of Reaction With Respect to  $(\text{OH})^-$  --  $k_{\text{obs}}$  vs.  $(\text{OH})^-$

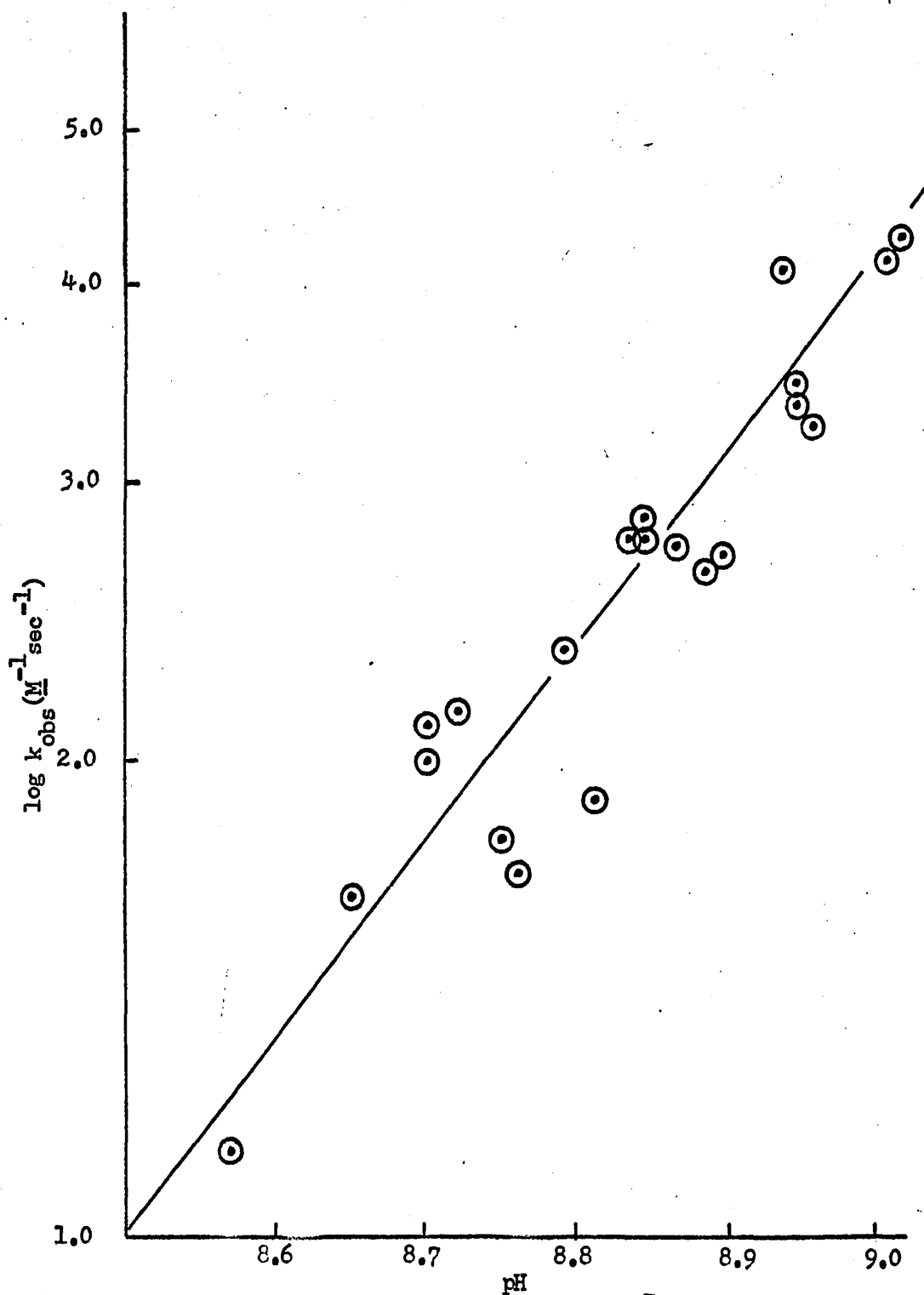


Fig. 2 Order of Reaction With Respect to  $(\text{OH})^-$  ---  $\log k_{\text{obs}}$  vs. pH

Table II

Order With Respect to Hydroxide Ion

Co(II) = $5.81 \times 10^{-4}$ M bipy = $11.62 \times 10^{-4}$ M		Air as Oxygent	0.5 M NaNO <sub>3</sub>	T = 26.9° C.
$(OH)^- \times 10^6$ M	Initial Slope (moles sec <sup>-1</sup> ) / $6.73 \times 10^{-4}$			
5.37	0.210			
7.59	0.260			
7.76	0.224			
7.94	0.208			
8.51	0.280			
10.47	0.314			
10.47	0.328			
10.47	0.310			
10.73	0.328			
10.72	0.366			
10.75	0.320			
12.30	0.344			
12.30	0.404			
12.59	0.350			
13.18	0.391			
13.49	0.344			
14.13	0.382			
14.79	0.412			
15.49	0.414			
15.59	0.367			
15.85	0.434			
15.85	0.444			
15.85	0.458			
17.78	0.504			
17.78	0.484			
19.95	0.575			

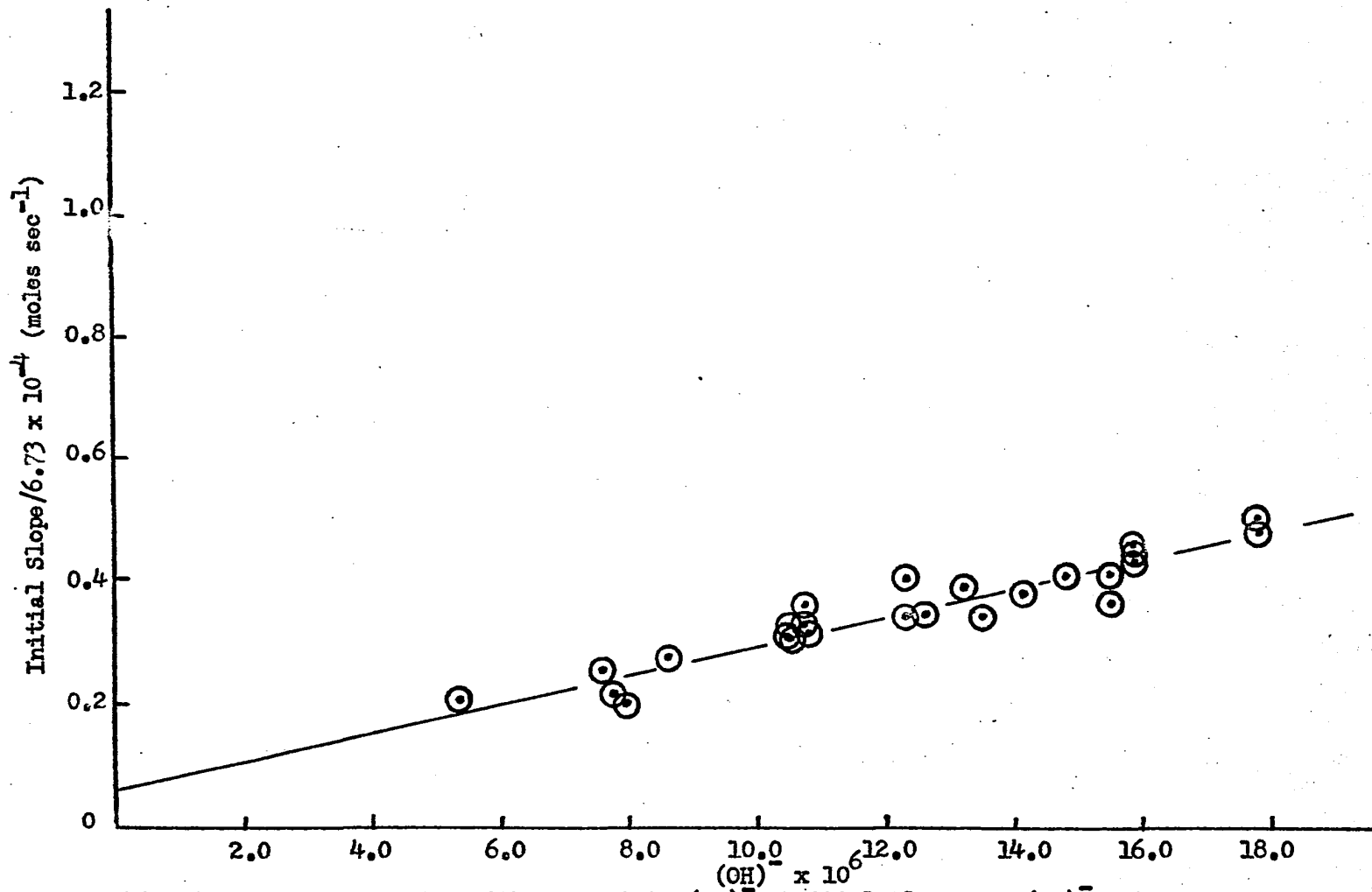


Fig. 3 Order of Reaction With Respect to (OH)<sup>-</sup>--Initial Slope vs. (OH)<sup>-</sup>--Air as Oxygent

Table III

## Order of Reaction With Respect to Hydroxide Ion

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Co(II) =  $3.77 \times 10^{-4}$  M    Pure O<sub>2</sub> as Oxygent    0.5 M NaNO<sub>3</sub>    T = 28.7° C.  
 bipy =  $7.54 \times 10^{-4}$  M

---

$(\text{OH})^- \times 10^6$ M	Initial Slope (moles sec <sup>-1</sup> ) / $6.73 \times 10^{-4}$
6.76	0.366
7.08	0.308
7.94	0.370
8.51	0.368
8.51	0.419
10.47	0.545
11.75	0.638
13.49	0.588
13.49	0.614
14.79	0.633
17.78	0.750
18.20	0.751
19.05	0.833
21.38	0.827
23.44	1.000

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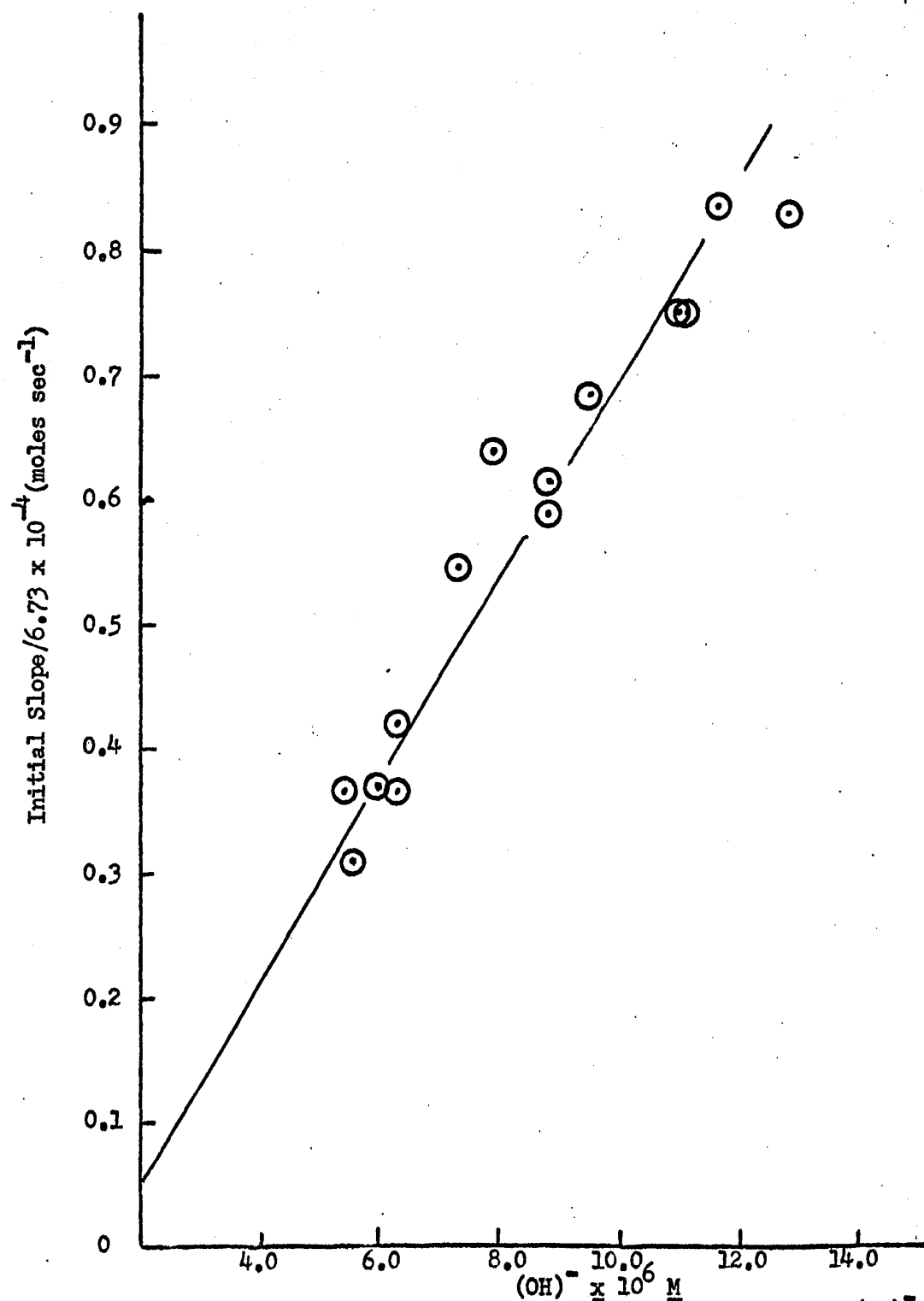


Fig. 4 Order of Reaction With Respect to  $(\text{OH})^-$  -- Initial Slope vs.  $(\text{OH})^-$   
Pure  $\text{O}_2$  as Oxygen

C. Order with Respect to the Complex

To ascertain the order of the reaction with respect to the complex, and indeed in order to discern whether the reaction being followed is the oxygenation reaction, several assumptions had to be made. Owing to the fact that the hydroxide ion and partial pressure of oxygen are kept constant over the entire path of the reaction, and since Co(II) and bipyridine undergo no apparent reaction at pH values close to 9 at normal temperatures, it appears safe to make the assumption that the reaction which is being followed is actually the oxygenation of Co(II) and its bipyridine complexes. The formation of the Co(II)-bipyridine complexes in basic solution is essentially instantaneous, so that initiating the reaction upon addition of the Co(II) to solutions of basic bipyridine should not introduce any error. As was stated before, Ritter's work illustrated that the oxygen absorption paralleled the pH changes. In addition, the color change from yellow to brown is analogous to both oxygen absorption and to the pH changes.

That the formation of the brown intermediate shows a second order dependence on the initial complex, is demonstrated by the fact that the plots of  $1/(A/2-X)$  versus  $t$  yield a straight line over 60% of the reaction. At lower pH values and subsequently slower rates, the deviation from the straight line plots is less over the entire range of the reaction, than at higher pH values and rates where a deviation from the straight line plots is noticeable after approximately one half life. Since the intermediate is also pH-stat active (removes hydroxide ions from solution), at the latter stages of the reaction, the slower change from brown intermediate to red product may be taking place at appreciable

velocities so that deviations from the second order rate curve may be noticed. Since the deviations are positive, this latter assumption seems to be borne out. That is, the value for  $1/(A/2-X)$  would increase more rapidly as more apparent  $x$  is formed--deviations resulting upon addition of the brown to red rate to the yellow to brown rate. The concentrations at time,  $t$ , are calculated from the volume of standard NaOH which is added during a pH-stat reaction.

D. Order with Respect to Oxygen

Finding the order of the reaction with respect to oxygen presented far greater problems for pH-stat monitoring of the reaction. Because of the inherent difficulties which a vacuum system accompanied by pH-stat apparatus would have, it was not possible to simply change the partial pressure of oxygen above the solution which would have been the most direct method of changing the oxygen "concentration" in solution. Yet by securing gaseous mixtures of oxygen and other inert gases (always nitrogen in this case), and saturating the solution with these gases, an apparent change of oxygen partial pressure could be attained, and pH-stat experiments could be made.

Reactions were run as was stated in the experimental section. However two different extensions of the experiments were employed, in attempting to find the order of the reaction with respect to oxygen. The first method was simply to measure the initial rates at different hydroxide ion concentrations as was done in previous experiments. This set of reactions was of course run with the same oxygenating agent and same initial Co(II) concentration throughout. A second collection of reactions was then undertaken at different hydroxide ion concentrations

and same initial complex concentration, but in this case, the oxygenating agent, itself, was changed; that is, compressed air would be substituted for pure oxygen. The curves could then be analyzed according to the method of initial slopes. The initial slopes were then plotted (as before) versus the hydroxide ion concentration, and, again, straight lines were obtained. The slopes of these latter plots would next be compared in order to obtain the rate dependence on oxygen. Since our reaction rate was directly proportional to hydroxide ion concentration, such a comparison could be made. That is;

$$\text{rate}_1 = k(\text{OH}^-)(\text{O}_2)_1^n \quad (1)$$

$$\text{rate}_2 = k(\text{OH}^-)(\text{O}_2)_2^n \quad (2)$$

Dividing equation (1) by (2) is obtained;

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{(\text{O}_2)_1^n}{(\text{O}_2)_2^n} \quad (3)$$

Taking the logarithm of both side of (3), and;

$$\log \frac{\text{rate}_1}{\text{rate}_2} = (n)\log(\text{O}_2)_1 - (n)\log(\text{O}_2)_2 \quad (4)$$

$$= (n)\log \frac{(\text{O}_2)_1}{(\text{O}_2)_2} \quad (5)$$

If pure oxygen is given the relative value of one, the relative value for air would be approximately 0.21, since that is the mole percent of oxygen in air.

Hence;

$$\log \frac{\text{rate}_1}{\text{rate}_2} = (n)\log(4.76) \quad (6)$$

Or;

$$n = \frac{\log \frac{\text{rate}_1}{\text{rate}_2}}{\log(4.76)} \quad (7)$$

An experiment of this type is tabulated in Tables IV and V, and illustrated in Figures 5 and 6. The slopes of the straight lines in Figures 5 and 6 are respectively 0.074 and 0.022 by least squares analyses. Relating the slopes of these curves with the same initial complex concentration, is calculated by equation (7) an order with respect to oxygen of 0.78.

The second method of experimentation was to run a series of experiments at the same pH (in all cases here the pH was equal to 9.26) and the same initial complex concentration each time. This relatively high pH value was necessary to obtain reproducible data over the range of oxygen mixtures. Different gaseous mixtures of oxygen and nitrogen would furnish different oxygen concentrations to the solution. Consequently, sequences of reactions would be completed, each at a different "partial pressure" of oxygen. The gaseous mixtures used were pure oxygen, compressed air, 65% oxygen-35% nitrogen, 35% oxygen-65% nitrogen. The pH-stat curves which were obtained were analyzed by calculating the second order rate constants as was done previously. This data is tabulated in Table 6. These observed rate constants were then plotted versus the oxygen "concentration", where again relative oxygen concentrations were used, setting pure oxygen equal to one. The data from Table 6 is illustrated in Figure 7. This yields a relatively straight line, with a zero intercept. This indicates the reaction dependence on oxygen is 1. The data for 100% oxygen lies

somewhat above the straight line drawn through the other three points. Because these reactions were carried out at a rather high pH value, the data which make up the point at 100% oxygen might consist of contributions from the hydroxide ion active brown to red reaction, which would tend to raise this point slightly.

Table IV

Order of Reaction With Respect to (O<sub>2</sub>)

Co(II) = $5.81 \times 10^{-4}$ M bipy = $11.62 \times 10^{-4}$ M		Pure Oxygen	0.5 M NaNO <sub>3</sub>	T = 26.9° C.
(OH) <sup>-</sup> x 10 <sup>6</sup> M	Initial Slope (moles sec <sup>-1</sup> ) / $6.73 \times 10^{-4}$			
3.71	0.329			
3.80	0.362			
4.47	0.434			
4.79	0.395			
5.01	0.487			
5.01	0.446			
5.25	0.532			
5.62	0.410			
5.75	0.440			
6.17	0.538			
6.46	0.455			
6.76	0.587			
6.92	0.621			
6.92	0.597			
7.59	0.614			
7.76	0.615			
8.71	0.750			
8.71	0.748			
8.91	0.846			
10.23	0.925			
12.30	0.925			
12.30	1.030			
13.80	1.110			
14.45	1.120			
15.14	1.100			
16.22	1.250			
17.78	1.460			

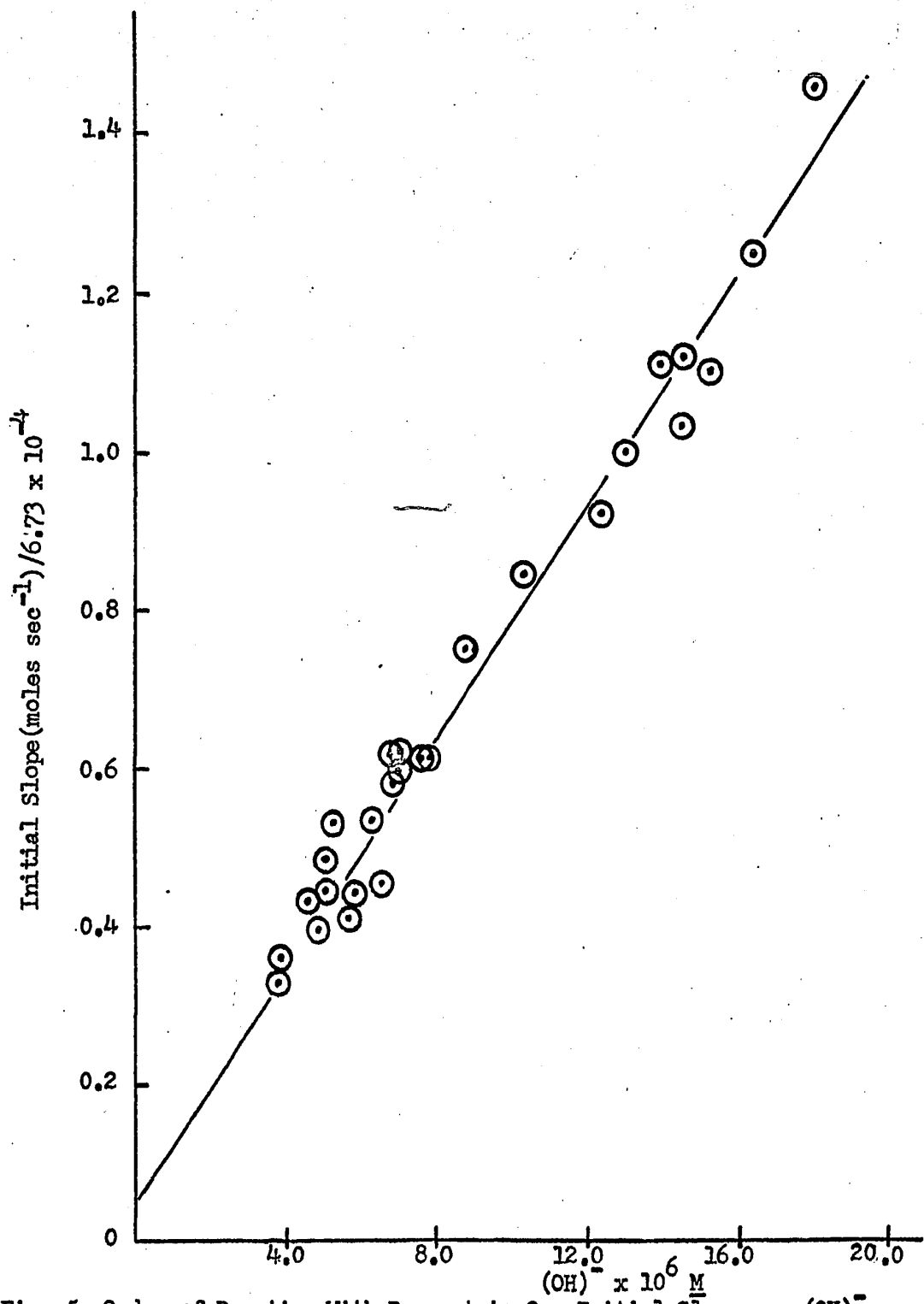


Fig. 5 Order of Reaction With Respect to O<sub>2</sub>---Initial Slope vs. (OH)<sup>-</sup>  
Pure O<sub>2</sub> as Oxygent

Table V

Order of Reaction With Respect to (O<sub>2</sub>)

Co(II) =  $5.81 \times 10^{-4} \underline{\underline{M}}$  Air as Oxygen  $0.5 \underline{\underline{M}}$  NaNO<sub>3</sub> T = 26.9° C.  
 bipy =  $11.62 \times 10^{-4} \underline{\underline{M}}$

$(\text{OH})^- \times 10^6 \underline{\underline{M}}$	Initial Slope(moles sec <sup>-1</sup> )/ $6.73 \times 10^{-4}$
5.37	0.210
7.59	0.260
7.76	0.224
7.94	0.208
8.51	0.280
10.47	0.314
10.47	0.328
10.47	0.310
10.72	0.328
10.72	0.366
11.75	0.320
12.30	0.344
12.30	0.405
12.59	0.350
13.19	0.391
13.49	0.344
14.13	0.382
14.79	0.412
15.49	0.414
15.49	0.367
15.85	0.434
15.85	0.444
15.85	0.458
17.78	0.504
17.78	0.484
19.95	0.575

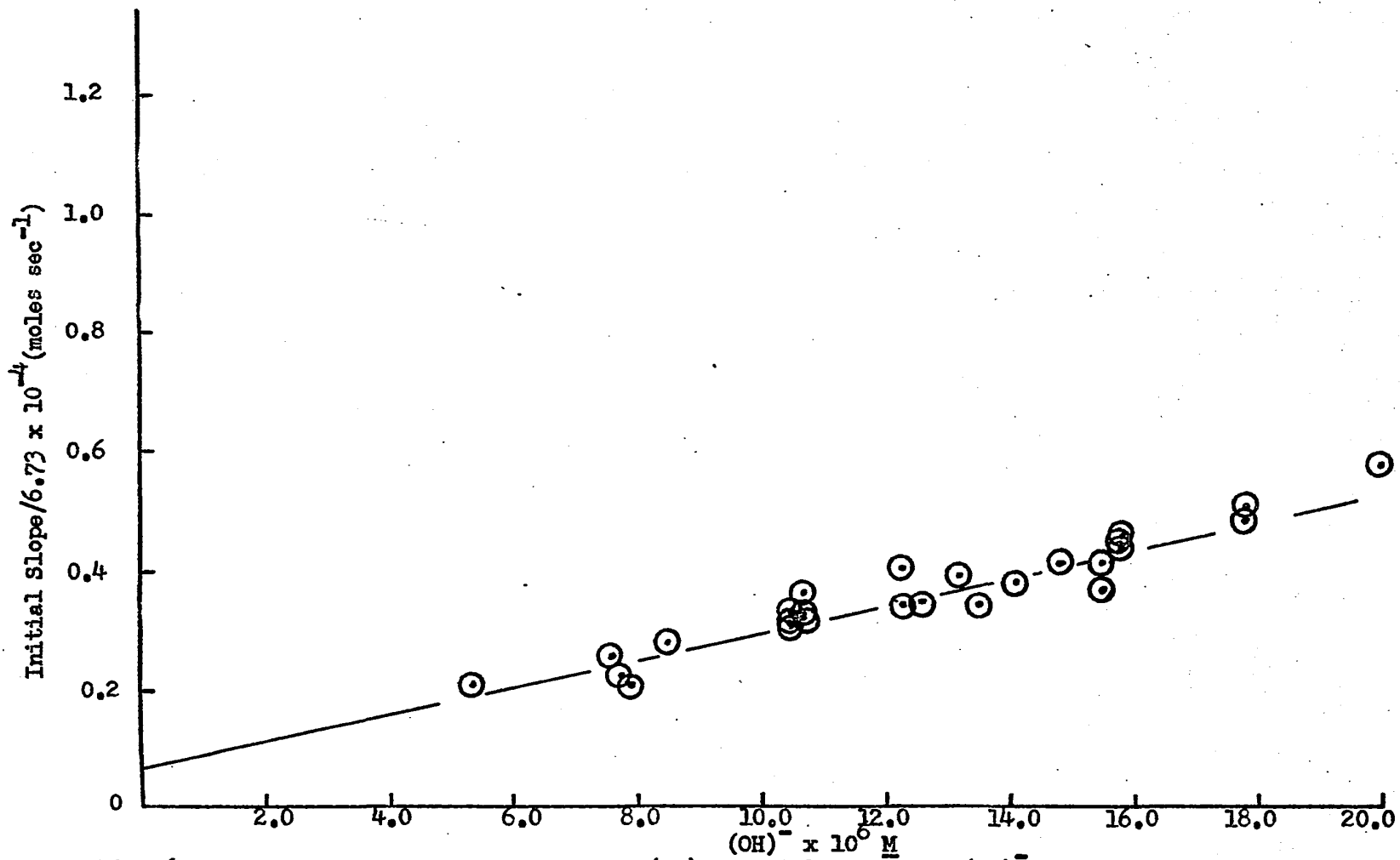
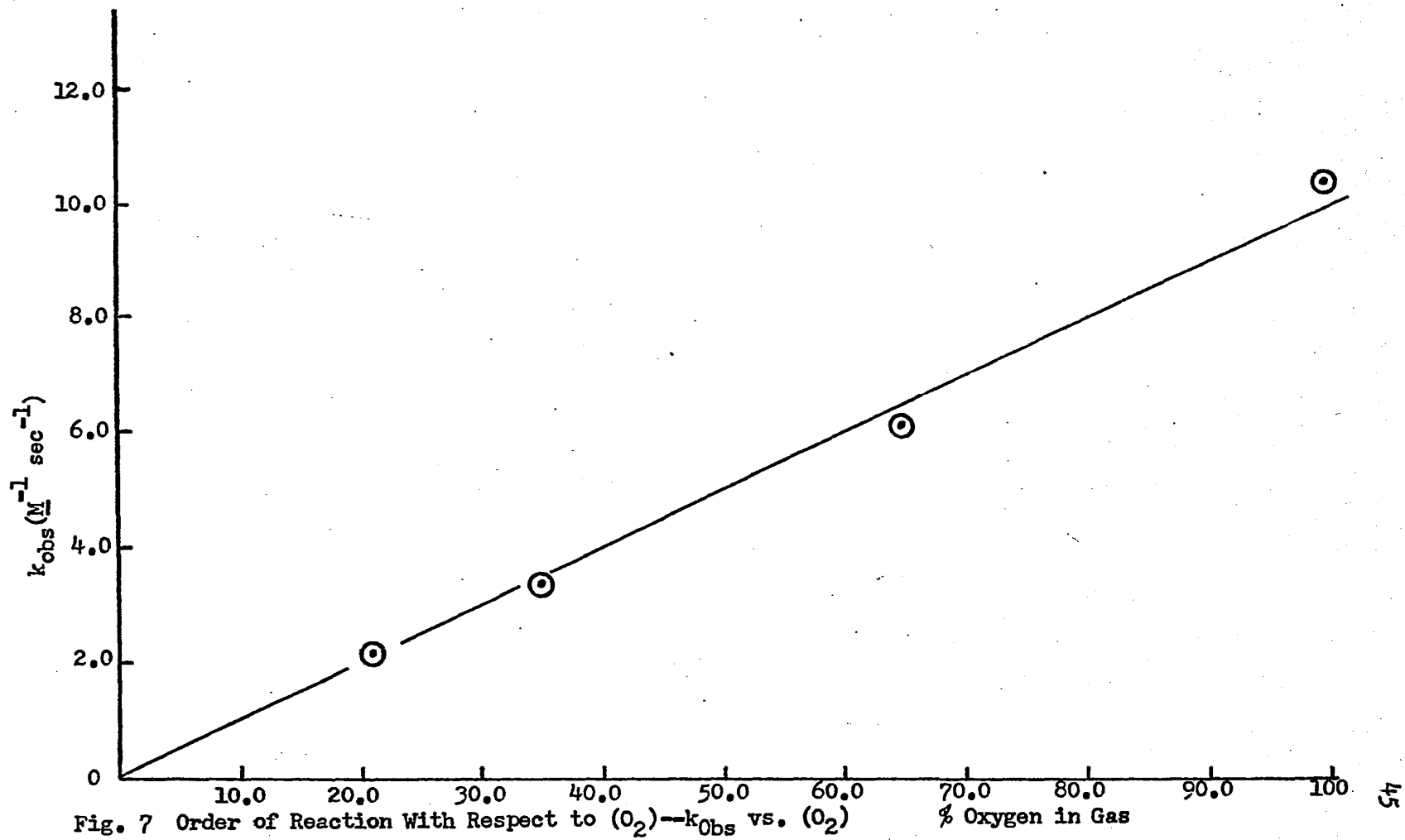


Fig. 6 Order of Reaction With Respect to  $(\text{O}_2)$ --Initial Slope vs.  $(\text{OH})^-$ --Air as Oxygent

Table VI  
Order of Reaction With Respect to (O<sub>2</sub>)

Co(II) =  $7.77 \times 10^{-4}$  M    0.5 M NaNO<sub>3</sub>    28.7° C.    pH = 9.26  
bipy =  $15.54 \times 10^{-4}$  M

k <sub>obs</sub> at different oxygen concentrations (M <sup>-1</sup> sec <sup>-1</sup> )			
21% O <sub>2</sub>	35% O <sub>2</sub>	65% O <sub>2</sub>	100% O <sub>2</sub>
2.25	3.19	6.42	9.17
2.40	3.77	5.30	9.75
2.02	3.00	7.17	10.90
2.40	3.32	7.42	11.20
2.20	3.77	5.30	11.75
2.11	3.37	5.70	8.33
2.12		6.35	10.97
-		5.60	11.60
n = 2.21	n̄ = 3.40	n̄ = 6.15	10.70
			n̄ = 10.48



### E. Temperature-Rate Studies of the Yellow to Brown Step

Temperature-rate experiments presented assorted problems to the pH-stat method. Because of the sensitivity of rate to small temperature changes, the problem arose of finding the correct conditions whereby controllable rates could be obtained over an approximate temperature range of  $30^{\circ}$  C. The concentration of Co(II) finally used was  $3.88 \times 10^{-4}$  M,  $7.76 \times 10^{-4}$  bipyridine,  $0.5$  M  $\text{NaNO}_3$ , and pure oxygen. The temperature spread ranged from  $28.7^{\circ}$  C. to  $46^{\circ}$  C. As was customary, pH-stat titration was the experimental method used to follow the reaction, and the data was analyzed both by "initial slopes" and by determining the second order rate constants. The basic problem of studying these reactions at different temperatures goes beyond the difficulty of measuring the rates at the higher temperatures, and is based on the fact that at different temperatures, different concentrations of oxygen are dissolved in water. For instance, at  $28^{\circ}$  C. the weight in grams dissolved in 100 grams of water is 0.003718. On the other hand, at  $50^{\circ}$  C., the weight of dissolved oxygen per 100 grams of water, is 0.002657 g (30). This is a decrease of almost 0.4 in oxygen concentration and certainly must be taken into account by applying a common factor to the slopes which are found, in order to take the relative concentrations of dissolved oxygen into effect.

By plotting the log "corrected" rate constant versus the reciprocal absolute temperature, the activation energy can be calculated since the slope of the resultant straight line is equal to the activation energy multiplied by  $-2.303(R)$ , where  $R$  is the gas constant in terms of calories. In Tables 7 and 8 are found the values for the slopes of

"initial slopes" and second order rate constants versus hydroxide ion concentration at different temperatures. Figures 8 and 9 contain the data tabulated in Tables 7 and 8. The activation energy of the yellow to brown step of the reaction is found to be  $9.08 \text{ Kcal mole}^{-1}$  using the method of initial slopes and  $11.9 \pm 2 \text{ Kcal mole}^{-1}$  utilizing the second order rate data. The values for the activation energy are surprisingly low and the agreement between the two values is quite amazing in view of the difficulties which low activation energies present to rate studies.

Table VII

## Temperature Rate Studies of Yellow to Brown Reaction

Co(II) = $3.77 \times 10^{-4}$ M bipy = $7.54 \times 10^{-4}$ M		
Pure Oxygen		
0.5 M NaNO <sub>3</sub>		
Temperature (°K.)	$10^3/T$	*Initial Slope (moles sec <sup>-1</sup> )/ $6.73 \times 10^{-4}$ (OH) <sup>-</sup>
301.7°	3.32	$3.96 \times 10^4$ (M <sup>-2</sup> sec <sup>-1</sup> )
309.0°	3.24	5.74
315.0°	3.18	6.34
321.0°	3.12	9.95

\* The Initial Slope points have been corrected to account for loss of oxygen concentration at higher temperatures.

Table VIII

## Temperature Rate Studies of Yellow to Brown Reaction

Co(II) = $3.77 \times 10^{-4}$ M bipy = $7.54 \times 10^{-4}$ M		
Pure Oxygen		
0.5 M NaNO <sub>3</sub>		
Temperature (°K.)	$10^3/T$	*k <sub>obs</sub> x $10^5$ M <sup>-2</sup> sec <sup>-1</sup> (OH) <sup>-1</sup>
301.7°	3.32	$5.14$ M <sup>-2</sup> sec <sup>-1</sup>
307.0°	3.26	6.76
313.0°	3.20	10.70
319.0°	3.14	16.50

\* The k<sub>obs</sub> points have been corrected to account for loss of oxygen concentration at higher temperatures.

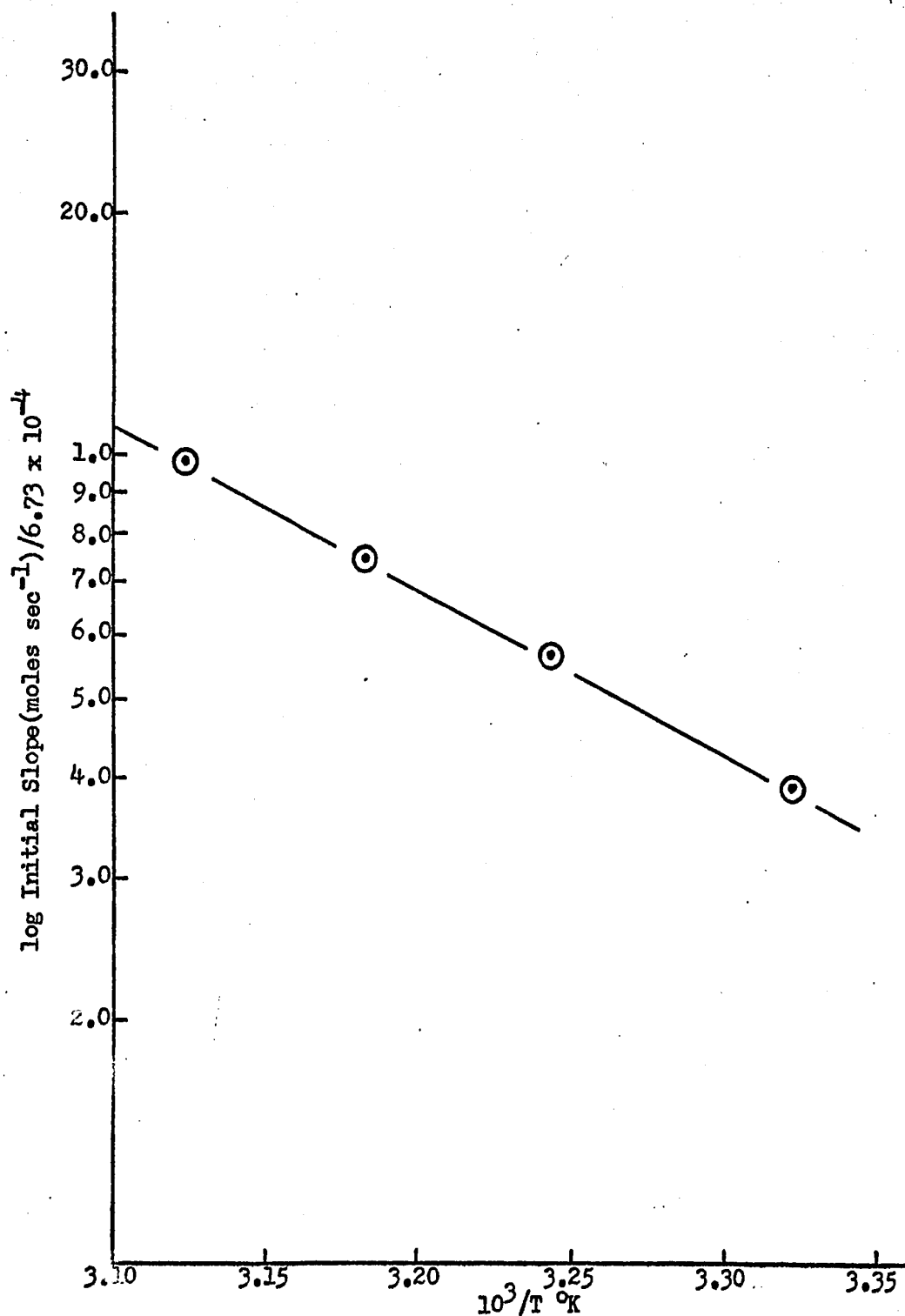


Fig. 8 Temperature-Rate Studies of Yellow to Brown Reaction  
 $\log \text{Initial Slope}/(\text{OH})^-$  vs.  $1/T$

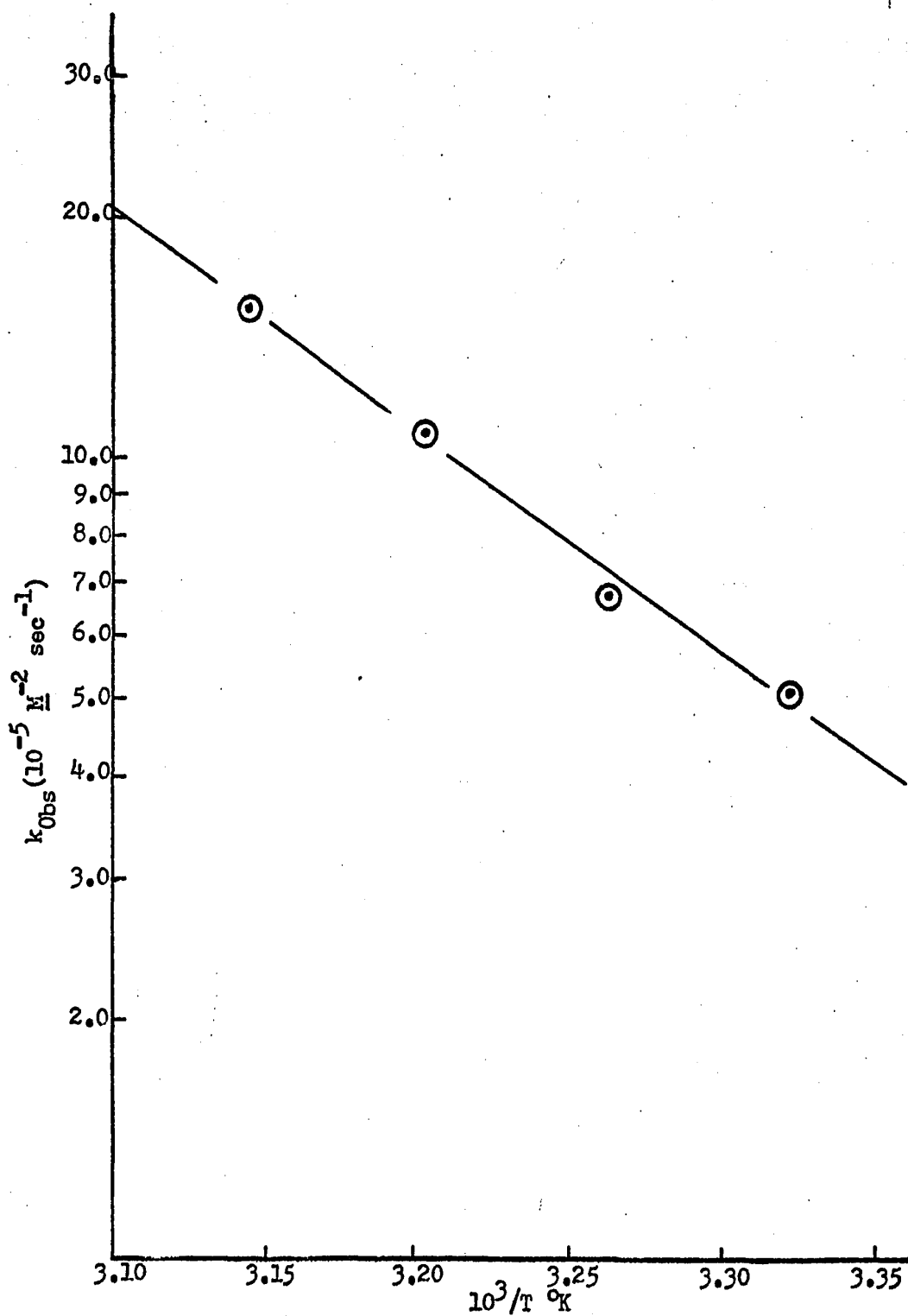


Fig. 9 Temperature-Rate Studies of Yellow to Brown Reaction  
 $\log k_{\text{obs}}/(\text{OH})^-$  vs.  $1/T$

#### F. Ionic Strength Studies

A further study involving the pH-stat technique, tested the influence which ionic strength would have on the reaction rate. The procedure for obtaining this information was the same as that described in the experimental section; keeping constant the initial complex and oxygen concentration but changing the pH for a series of runs. However, the ionic strength was adjusted by altering the concentration of  $\text{NaNO}_3$  in the solution. The same ionic strength would be maintained throughout a series of experiments. "Initial slope" analyses were made of all the reaction plots and straight lines were again obtained in the plots of initial slope versus the hydroxide ion concentration. The  $\text{NaNO}_3$  solutions which were used had concentrations of 0.50, 1.00, 2.00, and 4.00 M. The experiments at the different ionic strengths are tabulated in Tables 9, 10, 11, and 12, and are illustrated in Figures 10, 11, 12, and 13. It can be easily seen that an increase in the ionic strength (or increase in  $\text{Na}^+$  and  $\text{NO}_3^-$  ions) has a marked effect on the rate of reaction. The slopes of the lines in Figures 10 - 13 have been calculated by least squares analysis to be  $7.184 \times 10^4$ ,  $7.7 \times 10^4$ ,  $11.51 \times 10^4$ , and  $18.57 \text{ M}^{-1}$  respectively.

Table IX  
Ionic Strength Studies

$\text{Co(II)} = 5.81 \times 10^{-4} \text{ M}$ $\text{bipy} = 11.62 \times 10^{-4} \text{ M}$		26.9° C.	Pure Oxygen	0.5 M $\text{NaNO}_3$
$(\text{OH})^- \times 10^6 \text{ M}$	Initial Slope(moles $\text{sec}^{-1}$ )/ $6.73 \times 10^{-4}$			
3.71	0.329			
3.80	0.362			
4.47	0.434			
4.79	0.395			
5.01	0.487			
5.01	0.446			
5.25	0.532			
5.62	0.410			
5.75	0.440			
6.17	0.538			
6.46	0.455			
6.76	0.587			
6.92	0.621			
6.92	0.614			
7.59	0.597			
7.76	0.615			
8.71	0.750			
8.71	0.750			
8.91	0.748			
10.23	0.846			
12.30	0.925			
12.30	0.925			
14.45	1.030			
14.45	1.120			
13.80	1.110			
15.14	1.100			
16.22	1.250			
17.78	1.460			

Table X  
Ionic Strength Studies

Co(II) = $5.81 \times 10^{-4}$ M    26.9° C.    Pure Oxygen    1.0 M NaNO <sub>3</sub>			
bipy = $11.62 \times 10^{-4}$ M			
(OH) <sup>-</sup> x 10 <sup>6</sup> M	Initial Slope(moles sec <sup>-1</sup> )/ $6.73 \times 10^{-4}$		
3.80	0.567		
4.07	0.457		
4.79	0.622		
5.75	0.710		
6.61	0.706		
6.76	0.755		
7.94	0.784		
8.51	0.878		
10.72	1.070		
12.59	1.150		
14.13	1.320		
15.85	1.500		
19.50	1.700		

Table XI  
Ionic Strength Studies

Co(II) = $5.81 \times 10^{-4}$ M    26.9° C.    Pure Oxygen    2.0 M NaNO <sub>3</sub>			
bipy = $11.62 \times 10^{-4}$ M			
(OH) <sup>-</sup> x 10 <sup>6</sup> M	Initial Slope(moles sec <sup>-1</sup> )/ $6.73 \times 10^{-4}$		
4.27	0.556		
4.79	0.690		
5.50	0.750		
6.31	0.953		
6.76	0.907		
7.41	0.955		
7.94	1.110		
9.33	1.170		
10.23	1.350		
12.30	1.550		
12.59	1.630		
14.13	1.960		
14.79	1.800		
15.85	1.800		

Table XII  
Ionic Strength Studies

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Co(II) = $5.81 \times 10^{-4}$ <u>M</u>	26.9° C.	Pure Oxygen	4.0 <u>M</u> NaNO <sub>3</sub>
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(OH) <sup>-</sup> x 10 <sup>6</sup> <u>M</u>	Initial Slope (moles sec <sup>-1</sup> )/6.73 x 10 <sup>-4</sup>
2.34	0.819
2.40	0.867
2.57	0.935
2.82	0.959
3.09	1.100
3.24	1.140
3.55	1.210
4.57	1.540
4.57	1.330
4.90	1.430
5.75	1.650
6.03	1.730
6.17	1.820
8.51	2.120
10.00	2.140

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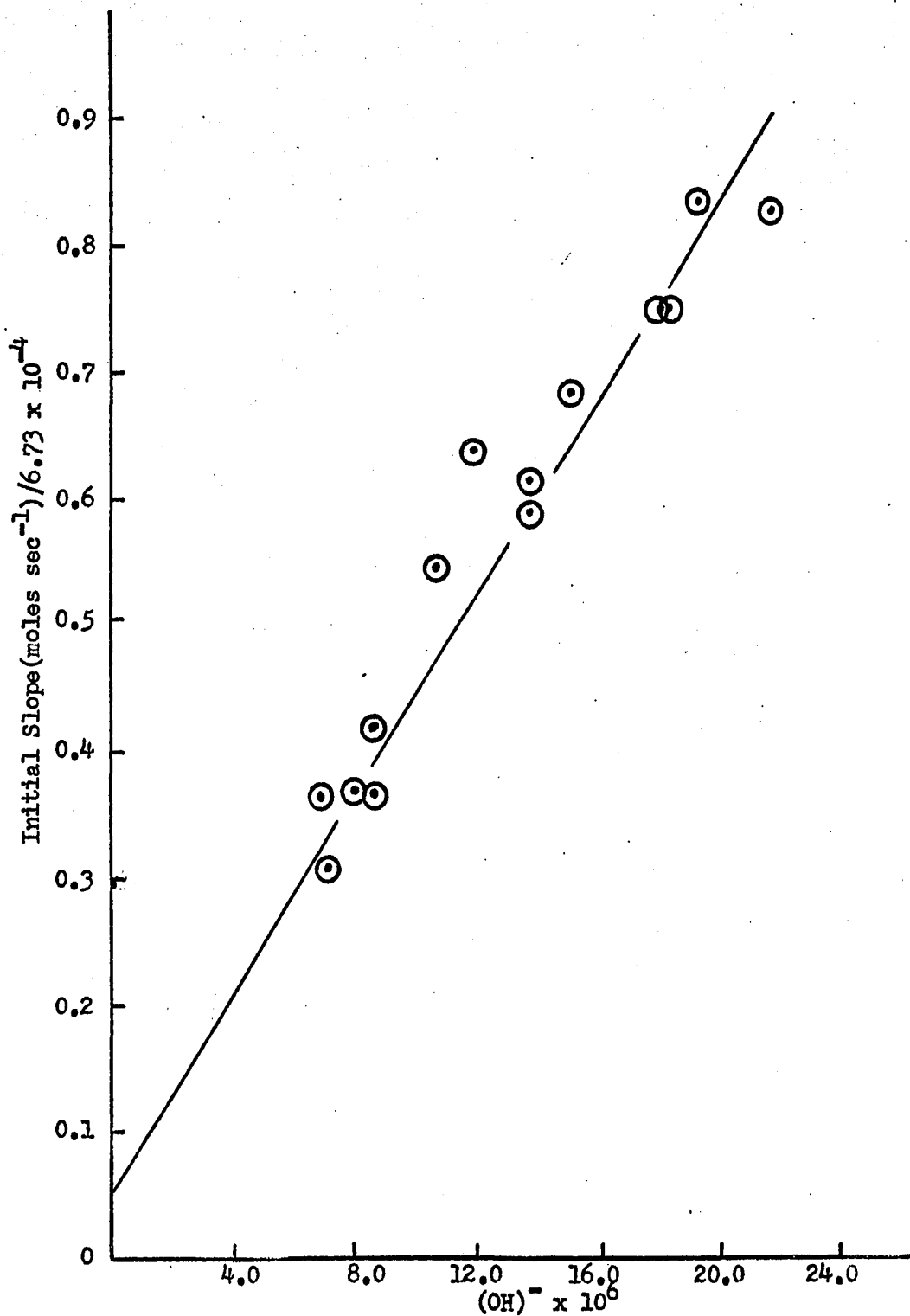


Fig. 10 Ionic Strength Effect on Reaction ( $\mu = 0.5 \text{ M}$ )

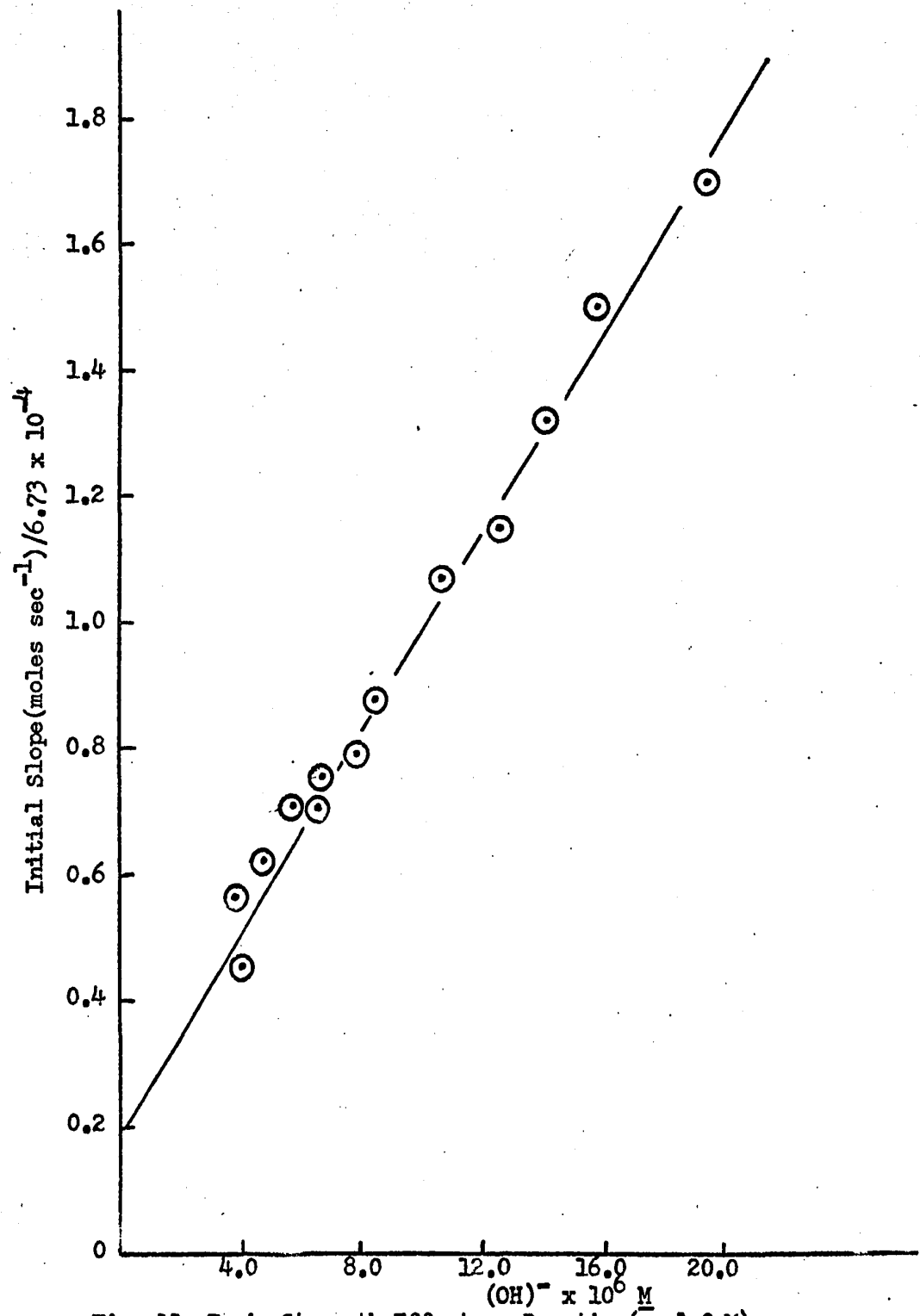


Fig. 11 Ionic Strength Effect on Reaction ( $\mu = 1.0 \text{ M}$ )

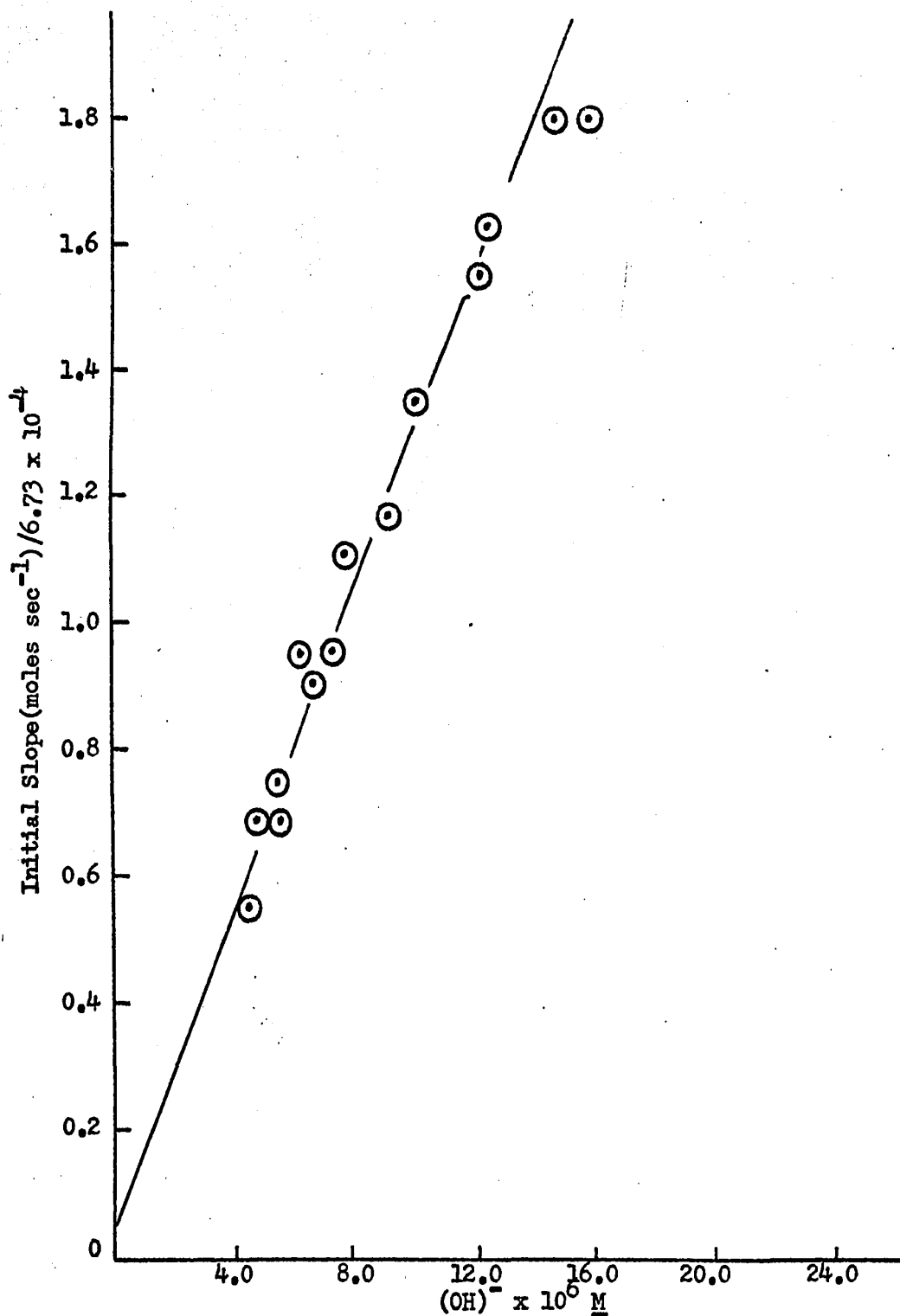


Fig. 12 Ionic Strength Effect on Reaction ( $\mu = 2.0 \text{ M}$ )

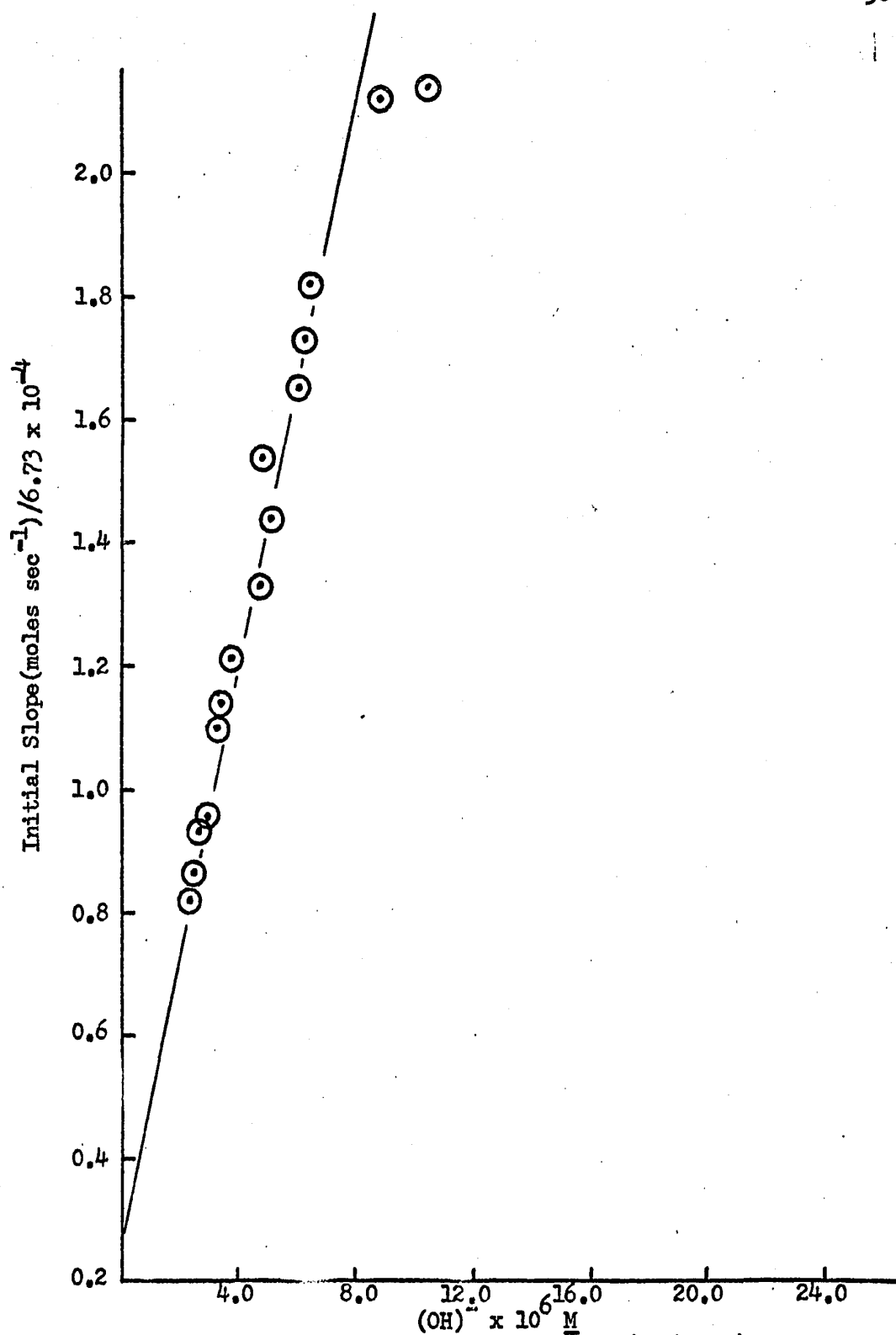


Fig. 13 Ionic Strength Effect on Reaction ( $\mu = 4.0 \text{ M}$ )

### G. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were used to determine the number of unpaired electrons in the various reaction species, as well as the magnetic susceptibility of the final red product. In addition, they were utilized to ascertain at which stage of the reaction, yellow to brown, or brown to red, the susceptibility of the reactant solution was lost. This, then, could be related to the oxidation of Co(II), which would contain three unpaired electrons to Co(III), which would probably contain zero unpaired electrons.

To calibrate the sample tubes which were used to measure the susceptibilities of the solids,  $\text{Hg}(\text{Co}(\text{CNS})_4)$  (25) was used as a standard. This yielded a tube constant equal to;

$$K = \frac{4984 \times 10^{-6}}{T + 10} \cdot \frac{\text{weight of salt}}{\Delta \text{ weight of salt}}$$

where K is the tube constant and weight of salt is the change in weight of the sample + tube in and out of the field minus the change in weight of the empty tube in and out of the magnetic field (32).

The calibration of the solution susceptibility tubes was attained by employing concentrated  $\text{NiCl}_2$  as the calibrant, which according to Nettleton yields a tube constant, K is equal to;

$$K = \frac{(10,030 (y/100) - 0.72 (1-y/100))}{T} 10^{-6} \frac{\text{wt of solution}}{\Delta \text{ wt of solution}} ;$$

where y is the weight per cent of NI(II) in the solution (26).

The final red species at  $26.6^\circ \text{C}$ . was found to be diamagnetic and to have a gram susceptibility of  $X_g = -0.08777 \times 10^{-6}$ .

The diaquo compound,  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_3$  also possessed diamag-

netic properties with a gram susceptibility of  $X_g = -0.059754 \times 10^{-6}$  at  $26.6^\circ \text{C}$ .

The gram susceptibility was calculated with the following equation;

$$X_g = K \frac{\Delta \text{ wt of sample}}{\text{sample weight}} ;$$

where K is the tube constant from above (32).

The magnetic susceptibility of the  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  ion itself has not been measured but there exists measurements for the tris-bipyridine  $\text{Co}(\text{II})$  ion which gives susceptibilities analogous to a magnetic moment of 4.86 EM (32). This indicates that the tris complex is spin free, has three unpaired electrons, plus a strong orbital contribution to the magnetic moment. The spin only moment for spin-free  $\text{Co}(\text{II})$  complexes would be equal to 3.88 EM. (However, the observed moment is generally greater than 4.5 EM.) Since the tris-bipyridine species of  $\text{Co}(\text{II})$  is still spin-free, the bis-bipyridine species, containing one less bipyridine, would also be expected to be spin-free and to contain three unpaired electrons. The bis compound itself was not isolated, but a solution of 2 moles of bipyridine per one mole of  $\text{Co}(\text{II})$  was measured for its magnetic susceptibility. By assuming that the solution consisted entirely of the bis-compound, a gram susceptibility of at least  $13 \times 10^{-6}$  could be calculated for the solution at  $26.6^\circ \text{C}$ . This would correspond to a magnetic moment of over 4.00 EM which is consistent with some values for  $\text{Co}(\text{II})$  spin-free moments.

An experiment of importance here indicated that the acid solution obtained by mixing two moles of bipyridine plus one mole of  $\text{Co}(\text{II})$  --the whole solution being saturated with oxygen free nitrogen--yield-

ed a paramagnetic solution with a susceptibility of  $14 \times 10^{-6}$ . However, upon making the solution slightly basic, the paramagnetic property is slowly decreased as the brown compound forms. That is, within several hours, the previously yellow solution changes to the brown intermediate, and with this change there is an accompanying decrease of paramagnetism, the susceptibility approaching that of water itself only after several days when the formation of the red species is complete. A solution which has been well protected from oxygen loses this susceptibility quite slowly, but if the solution is subjected to air or if hydrogen peroxide is injected into the solution, the change to the brown solution is more rapid and the parallel decrease of paramagnetism is more rapid as well.

#### H. Conductivity Measurements

The results of the conductivity experiments are discussed below. Standardized 0.02 M KCl solutions were used to calculate the cell constant. At 25° C., the temperature at which these measurements were taken, a 0.02 M KCl solution has a specific conductance,  $k=0.00277 \text{ ohms}^{-1}$  (33). Since  $k$  by definition is equal to  $1/r$ ,  $r$  being the resistance in ohms/cubic centimeter of solution,  $k$  will equal  $q/R$ ,  $q$  being the cell constant and  $R$  the actual resistance which is measured on the conductivity bridge. The calculated cell constant in this experiment is 0.435.

By dissolving 0.0980 g of the final red compound in 100 ml of de-ionized water (which has a specific conductance of  $1.27 \times 10^{-6}$ ), and measuring the resistance of the resultant solution, the average measured resistance was found to be 2370 ohms. Since  $k=q/R$ , the calculated specific conductance for the solution of the red compound is 0.0001836

$\text{ohm}^{-1}$ . If it is assumed that the molecular weight of the dried red product is approximately 980, the molar concentration of the solution is  $0.001 \text{ M}$ . With this assumed concentration of  $0.001 \text{ M}$ , a molar conductance, which is equal to  $1000(k)/\text{molarity}$ , was calculated to be  $183.6 \text{ ohm}^{-1} - \text{mole}^{-1}$ .

Literature values for coordination compounds with 1:1 ions and at  $0.001 \text{ M}$  concentrations have a molar conductance of  $96-115 \text{ ohm}^{-1}$  (34). For 2:1 ions the molar conductance is  $225-270 \text{ ohm}^{-1}$ , and for 3:1 ions the molar conductance is between  $380$  and  $432 \text{ ohm}^{-1}$  (34). Thus, if the molar concentration of the red compound is, indeed,  $0.001 \text{ M}$ , its molar conductance lies between the values given for 1:1 complexes and the 2:1 complexes. If the molecular weight of the red complex is actually less than 980, then the value which we obtained for the molar conductance is actually too high and the molar conductance would be less than  $183.6 \text{ ohm}^{-1}$ . By dissolving  $0.0480 \text{ g}$  of red complex in  $100 \text{ ml H}_2\text{O}$  (where the formula weight of a dihydroxy monomer final oxidation product is 480), a molar conductance of  $106 \text{ M}^{-1} \text{ ohm}^{-1}$  is obtained. On the other hand, if a dimer is actually present, the molar conductance is somewhat low for a 2:1 ion; yet the size of the ion may be the reason for the lower conductance since the mobility of the complex would be hindered. In order to consist of 3 particles, the dimer would have to contain both a peroxy bridge and a hydroxide ion on each Co atom. The Co is presumed to be in the (III) oxidation state.

#### I. Decay of the Brown Intermediate to the Final Red Species

The decay of the brown intermediate to the final red species was followed using spectrophotometric methods in the visible spectral re-

gion. Although, for this reaction, no sharp absorption peaks are observed in this region, it was believed to be possible to monitor the reaction in this manner, as Tanford, Kirk, and Chantooni (17) had followed the decay of the brown oxygenated species of Co(II) and glycylglycine. An assumption had to be made that all of the original Co(II) had reacted with oxygen and hydroxide ion to form the reaction intermediate, the brown compound, and that the brown compound was the dominant species in solution. Besides, the brown intermediate possesses a very strong charge-transfer type band in this region, with an extinction coefficient approaching 4000, assuming that the oxygenated species is composed of a dimer utilizing two Co atoms. At this same wavelength, 450 mu, the  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  has an extinction coefficient of approximately 26, while the product of the decay has an extinction coefficient at this wavelength of less than 50. Hence, even if there was a sufficient amount of interfering ions in the solution (and there is no reason to believe that such a condition exists), the overwhelming value for the extinction coefficient of the brown species should more than compensate for absorption by any interfering ion.

As was described above in the experimental section, the pH-stat apparatus was used to keep the pH constant over the course of the reaction. Molecular oxygen was bubbled through the solution throughout the reaction. The solution was thermostatted in an oil bath at  $50^\circ$ , and at specified intervals, solution was removed and the absorbance read on the Spectronic 20 spectrophotometer. The Spectronic 20 was frequently adjusted with distilled water to the 100% transmittance point, and the readings were all taken at 450 mu.

The infinity point absorbance reading was obtained by sealing a vessel containing the solution and leaving it at the same temperature until absorbance readings yielded a constant value. A small amount of flocculent precipitate was evident in the "infinity reading" tube. In all runs,  $3.88 \times 10^{-4}$  M solutions of Co(II) were used in conjunction with a  $7.76 \times 10^{-4}$  M concentration of bipyridine. To maintain constant ionic strength over the course of the reaction, 0.5 M solutions of  $\text{NaNO}_3$  were employed. All in all, the reactions were run in the same manner as were all the pH-stat reactions, except that the absorbance readings were taken.

The decay of the brown species followed pseudo first order decay schemes which resulted from plotting values of  $\log(A_t - A_\infty)$  versus time,  $t$ . Straight lines were observed over at least seventy-five percent of the reaction. This indicated a first order decay rate of the brown complex. The observed rate constant obtained at  $50^\circ$  and pH equal to 9.10 was  $k_{\text{Brown}} = 1.41 \times 10^{-2} \text{ min}^{-1}$ .

Since the decay of the brown complex appeared to depend also on the hydroxide ion concentration, a series of reactions were followed at various initial pH values (held constant throughout for a given reaction). The observed rate constants,  $k_{\text{Brown}}$ , were next plotted versus the hydroxide ion concentration, with the results tabulated in Table 13 and shown in Figure 14. This yields the information that the decay of the brown species is directly dependent on the hydroxide ion concentration, but also undergoes a hydroxide ion independent decay. The slope of Figure 14 presents a  $k_{\text{OH}}$  equal to  $3.77 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ , as calculated by least squares analysis of the line. The non-zero inter-

cept, the hydroxide ion independent decay constant is equal to  $9.85 \times 10^{-3} \text{ min}^{-1}$ .

Finally, temperature-rate studies were made, keeping the pH constant in each case and over all runs. Reactions were undertaken at temperatures of 35.5, 50.0, 60.0, and 70.0° C. The conclusions for these experiments are provided in Table 14 and Figure 15. The plot of  $\log k_{\text{Brown}}$  versus  $1/T$  gave a value of  $19.05 \pm 3.0 \text{ Kcal mole}^{-1}$ .

Table XIII

Dependence of Brown to Red Step on  $(\text{OH})^-$ 

$\text{Co(II)} = 3.77 \times 10^{-4} \text{ M}$ $\text{bipy} = 7.54 \times 10^{-4} \text{ M}$		0.5 M $\text{NaNO}_3$	50° C.
* $k_{\text{brown}} \times 10^2 \text{ min}^{-1}$	$(\text{OH})^- \times 10^6 \text{ M}$		
1.15	6.31		
1.57	10.00		
1.69	12.59		
1.41	12.59		
1.58	15.85		
1.60	19.95		
1.79	19.95		
2.27	31.62		
2.52	39.81		
2.93	50.12		

\* The  $k_{\text{brown}}$  is the first order decay constant of the brown intermediate.

\*\* Least squares analysis of the straight line yields a slope of  $3.77 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ .

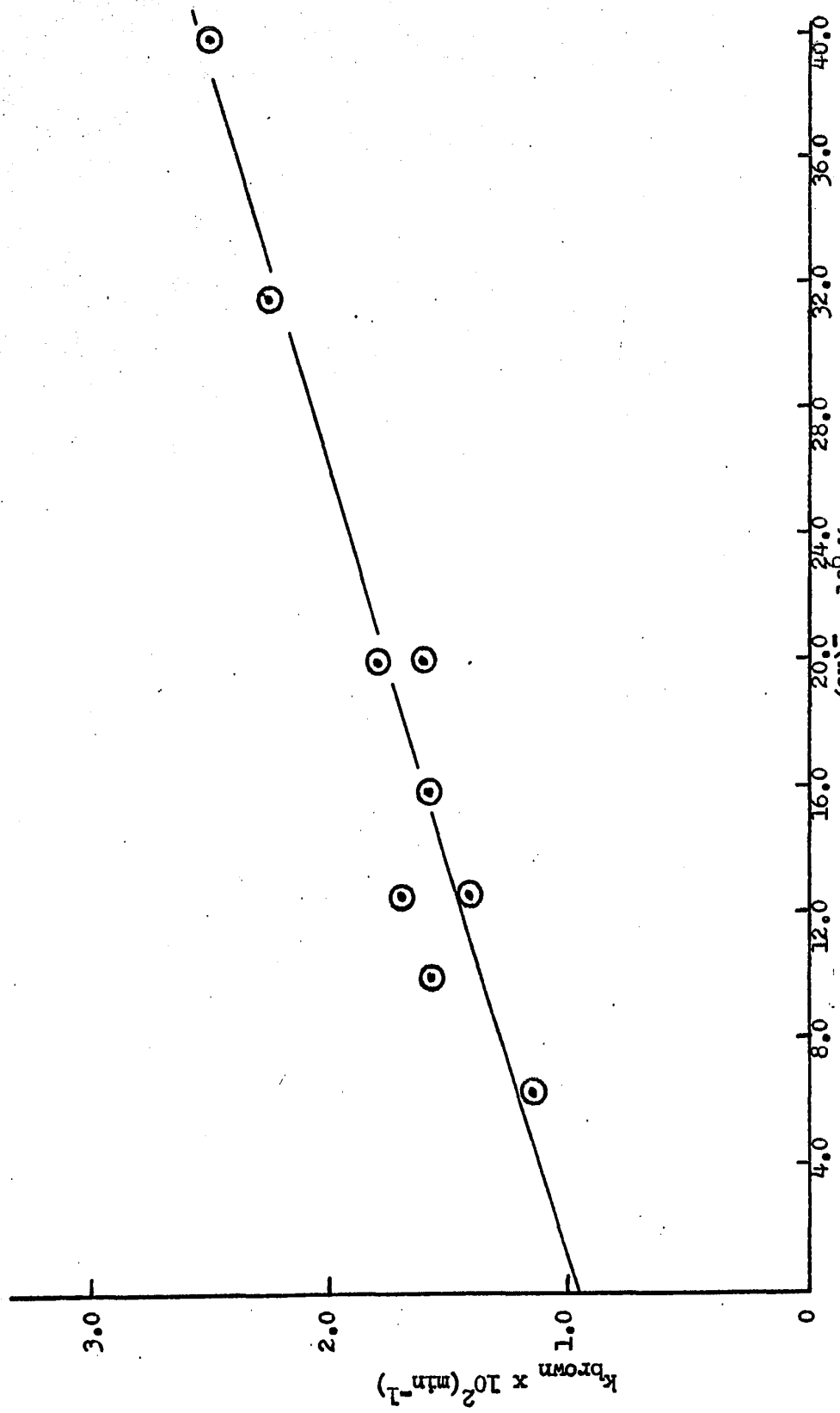


Fig. 14 Dependence of Brown to Red Reaction on  $(\text{OH})^-$

Table XIV

## Temperature-Rate Studies of Brown to Red Step

Co(II) = $3.77 \times 10^{-4}$ M    0.5 M NaNO <sub>3</sub> pH = 9.50 bipy = $7.54 \times 10^{-4}$ M		
T(°K.)	$10^3/T$	* $k_{\text{brown}} \times 10^3 \text{ min}^{-1}$
343.0°	2.92	84.1
333.0°	3.02	32.5
323.0°	3.09	22.7
308.5°	3.24	3.7

\* The  $k_{\text{brown}}$  values are the average of several runs at that temperature.

\*\* The plot of  $\log k_{\text{brown}}$  vs.  $1/T$  gives an activation energy of  $19.05 \pm 3.0$  Kcal mole<sup>-1</sup>.

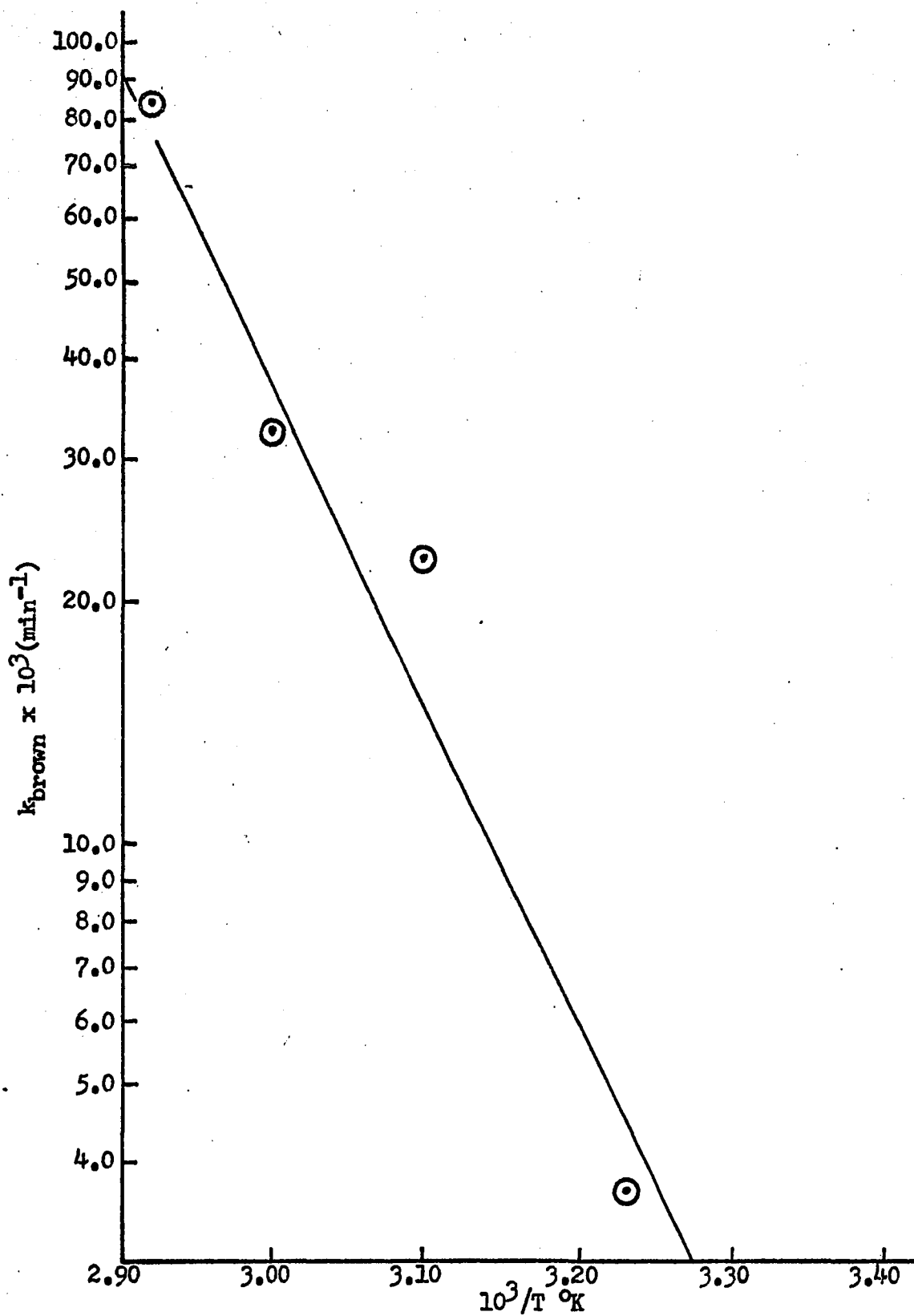


Fig. 15 Temperature-Rate Studies of Red to Brown Reaction

### J. Quantitative Drying of the Red Complex

In order to further clarify the formulation of the final oxidation product, it was necessary to undertake quantitative drying experiments on freshly prepared red crystals. These crystals were prepared as already described in the experimental section. The only difference in these cases was further purification by recrystallization from hot distilled water. The air dried crystals were next pulverized in a mortar and pestle to a fine powder. This powdered form exhibited no hygroscopic properties. The crystals were carefully transferred to weighed one ml beakers, and weighed to obtain the undried crystal weight. The beakers were next placed in a vacuum desiccator over concentrated sulfuric acid for 12 hours. They were then weighed again and the loss in weight recorded. This desiccator-dried product quickly picked up moisture from the atmosphere. The crystalline powder was then heated in a drying pistol, both at 50° C. and 80° C., each for 24 hours; the quantitative loss in weight being recorded after each respective drying. The following table illustrates % weight lost by desiccation and heating, and indicates the amount of crystalline water in the undried crystal. It should be noticed that at least 95% of the water is lost upon the first desiccation and further drastic heating does not alter the loss in weight appreciably.

Ritter has done some preliminary x-ray studies on the undried, lustrous red crystal and has determined that the material appears to be a single substance, and that the crystal surface is altered upon x-ray bombardment. He also determined that there are 1120 molecular weight units per unit cell; or,  $n(M)=1120$ , where  $n$  is equal to the

number of molecules per unit cell and  $M$  is the molecular weight (35). These values should be regarded with reservations, however, due to the facts that the cell dimensions were not reported and the general difficulty in this type of determination. Below are the results of the drying experiments:

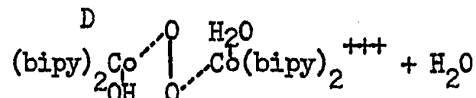
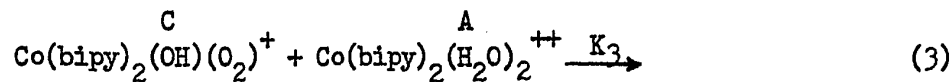
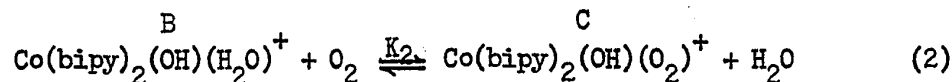
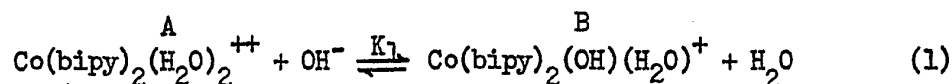
Desiccator Drying	#1	#2	#3	#4	#5
% weight lost	14.4	14.3	14.5	14.1	14.5
Drying pistol (50°)					
% weight lost	14.4	14.3	14.1	13.9	13.9
Drying pistol (80°)					
% weight lost	14.5	14.5	14.3	14.3	14.5

The per cent weight lost in each case is the total weight lost from the original air-dried sample.

## IV DISCUSSION

A. The Yellow to Brown Reaction

The reactions of basic solutions of cobaltous ions and 2,2'-bipyridine proceed through two distinctive phases; The first being a fast reaction involving a color change from yellow to intense brown, which has been found to be both first order in hydroxide ion and oxygen partial pressure and second order in complex concentration; and the second phase being a slow first order, base catalyzed decay of the brown intermediate to a final red species. A mechanism which will describe these kinetics is illustrated below.



Equation (3) is postulated as the rate determining step for the fast yellow to brown reaction. The two equilibria steps are quickly established in this mechanism. From equation (1),

$$K_1 = \frac{(\text{B})}{(\text{A})(\text{OH})^-} \quad (4)$$

Equation (2) yields;

$$K_2 = \frac{(\text{C})}{(\text{B})(\text{O}_2)} \quad (5)$$

Combining equations (4) and (5), equation (6) is arrived at;

$$(\text{C}) = K_1 K_2 (\text{O}_2) (\text{A})(\text{OH})^- \quad (6)$$

The rate determining step is (3), thus;

$$d(D)/dt = k_3(C)(A) \quad (7)$$

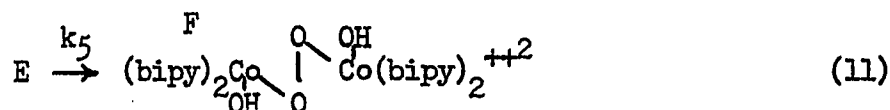
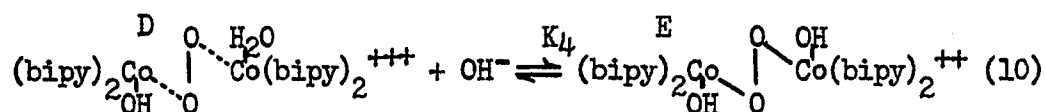
Substituting (6) into (7) gives the overall rate equation for the yellow to brown step;

$$d(D)/dt = k_3 K_1 K_2 (A)^2 (OH^-) (O_2) \quad (8)$$

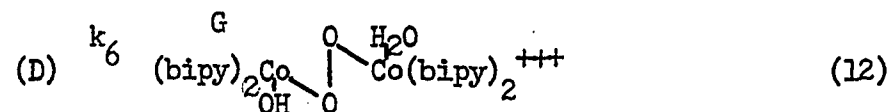
By applying steady state approximations to B and C and making several further approximations, one can also arrive at equation (8) (See Appendix). The slower brown to red phase consists of two simultaneous first order decays of (D), one hydroxide ion catalyzed and one hydroxide ion independent. Thus;

$$-d(D)/dt = k_6(D) + k_5(D)(OH^-) \quad (9)$$

A mechanism which is consistent with this follows;



Equation (11) is rate determining and is the oxidation of Co(II) to Co(III), with the resultant reduction of  $O_2$  to the peroxide ion. The base independent reaction is simply the oxidation of Co(II) to Co(III) without the prior deprotonation of the remaining water molecule;



The oxygen bridges in both (11) and (12) are true peroxide ( $O_2^{--}$ ) and the cobalt atoms are now in the (III) oxidation state. The product of (12) is red at this time and the slow deprotonation of this to the final dihydroxy species cannot thus be monitored spectrophotometrically.

The fast yellow to brown step will be discussed first. The postu-

lated mechanism states that  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  is the reactive species in solutions in which oxygenation reactions occur. This was shown in the pH-stat rate studies in which solutions containing a bipyridine/Co(II) ratio of 2, reacted faster than solutions with bipyridine/Co(II) ratios of 2/5, 3/5, 1, 3, and 4. This confirmed the results of Silvestroni who showed in his work that the amount of oxygen absorbed by Co(II) bipyridine solutions was directly proportional to the ratio of bipyridine to Co(II) in the solution, increasing as the ratio approached two, after which his plot of bipyridine/Co(II) versus  $i_d$  (diffusion current) only slowly increased to the ratio of 2.5 after which it decreased sharply (22).

Cabani (23) also measured the respective diffusion currents as a function of hydroxide ion and bipyridine/Co(II) ratio. He stated that the maximum absorption of oxygen takes place with a bipyridine/Co(II) ratio of 2.5.

Ritter (24) also measured the effect of the bipyridine/Co(II) ratio in solution by measuring the rate of oxygen absorption of basic solutions of Co(II) and bipyridine. Again, similar to Silvestroni and Cabani, Ritter established the maximum oxygen absorbance rate with solutions containing a bipyridine/Co(II) ratio of two.

In as much as Co(II) generally is six-coordinated, any substitution reaction of  $\text{Co}(\text{bipy})_3^{++}$  involves the dissociation of one bipyridine in some manner from the tris compound. The color changes for oxygenation and oxidation of yellow to brown to red were originally observed in solutions containing the  $\text{Co}(\text{bipy})_3^{++}$  ion. For the oxygenation reaction to take place in this solution there must be some

$\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  present, the diaquo ion resulting from the aquation by substitution of a coordinated bipyridine. That is,  $\text{Co}(\text{bipy})_3^{++}$  must first of all dissociate to  $\text{Co}(\text{bipy})_2^{++}$  and bipyridine. The two positions vacated by bipyridine are quickly filled by water molecules. The exchange between  $\text{Co}(\text{phen})_3^{++}$  - phen (which would be expected to be similar to  $\text{Co}(\text{bipy})_3^{++}$  - bipy exchange) has been measured by Ellis and Wilkins (29), who found a rate constant equal to  $1.4 \times 10^{16} \exp(-20,600/RT) \text{ min}^{-1}$ . This is striking lability in comparison to slow exchanging Co(III) compounds. Even at  $11^\circ \text{C}$ ., the half life for the exchange of  $\text{Co}(\text{phen})_3^{++}$  with phenanthroline is 31 seconds. West (36) reported that the half life for exchange between  $\text{Co}(\text{phen})_3^{++}$  and  $\text{Co}(\text{phen})_2^{++}$  and phenanthroline was less than 28 seconds at  $15^\circ \text{C}$ . Qualitative evidence for the lability of  $\text{Co}(\text{phen})_3^{++}$  has been gathered by Ellis and Wilkins (29). Solutions of  $\text{Co}(\text{phen})_3^{++}$  (yellow) become dark red in color after only a few minutes with Fe(II) is added to the solution. This signals the appearance of the intensely red Fe(II)-phenanthroline complex. Additionally,  $\text{Co}(\text{phen})_3^{++}$  catalyzes the exchange of  $\text{Co}(\text{phen})_3^{+++}$  with phenanthroline. The  $\text{Co}(\text{bipy})_3^{++}$  ligand exchange or dissociation would be expected to be quite similar to the exchange rate for  $\text{Co}(\text{phen})_3^{++}$  with phenanthroline. It is well known that reactions of metal complexes containing either of these two bidentates are quite similar. The suggested mechanism states that there must be two very fast equilibria set up, both of these equilibria involving substitution on a Co(II) complex. Since the  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  species is itself unreactive (no reaction occurs in acid solution), but reactions are evident in solutions with pH values greater than 7,

$\text{Co}(\text{bipy})_2(\text{H}_2\text{O})(\text{OH})^+$  is postulated as the reactive species. Reactions are initiated immediately in basic solutions indicating a rapid reaction with base followed by the rapid oxygenation.

The rates of substitution reactions of Co(II) complexes, in contrast to substitution reactions for Co(III) complexes, are rapid at ordinary temperatures. Basolo and Pearson (37) have discussed the energies of activation which might be expected for substitution reactions, as they undergo different mechanisms and pass through different transition states. In their discussion they relate the loss of crystal field stabilization energy, which results from the complex going from an octahedral to a transition state of different coordination number (in this case from octahedral to square pyramidal), to the lability of the cation involved. A loss of crystal field stabilization energy would result in a slower substitution reaction (higher energy of activation), while little or no loss of crystal field stabilization energy during an octahedral-square pyramidal transition would result in higher lability. The crystal field stabilization energy for Co(II) spin-free complexes, of which the Co(II)-bipyridine complexes are members, would have no loss of crystal field stabilization energy on going from an octahedral to a square-pyramidal state. These reactions, as was shown in this research, are fast. An additional example of extreme Co(II)-bipyridine lability and aquation was demonstrated in this research by dissolving pink  $\text{Co}(\text{bipy})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  in water--the resulting yellow color illustrates the rapid formation of  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$ . The evidence for the reactivity of Co(II) complexes is great, and the possibility for the rapid equilibria suggested in (1) and (2) is brought forth on this basis.

Base hydrolysis of octahedral complexes is usually relatively fast however, even for such inert complexes as those of Co(III). For instance Pearson and Basolo (38) showed that the acid hydrolysis rate constants at 25° C. of the following compounds,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$ ,  $\text{Co}(\text{en})_2\text{Cl}_2^+$ ,  $\text{Co}(\text{trien})\text{Cl}_2^+$ , and  $\text{Co}(\text{en})_2\text{Br}_2^+$ , were  $1.7 \times 10^{-6}$ ,  $2.5 \times 10^{-4}$ ,  $1.5 \times 10^{-4}$ , and  $1.4 \times 10^{-4} \text{ sec}^{-1}$  respectively. For the same compounds the respective base hydrolysis rate constants at 25° C. were  $8.5 \times 10^{-1}$ ,  $1 \times 10^3$ ,  $2 \times 10^5$ , and  $1.2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ . This special reactivity of the hydroxide ion with Co(III) complexes has been a special enigma for coordination chemists for several years now. The Northwestern school (Basolo and Pearson) have supported the conjugate base mechanism (as originally conceived of by Garrick (39)) as the reason for the special base reactivity. This mechanism depends on the existence of an acidic proton on one of the ligands, and the specific labilizing effect which the resulting conjugate base has on the rest of the ion (37). On the other hand, Tobe of the University School (London) favors a Grottaus chain transfer for the unusual reactivity of base. In this mechanism the cation is seen surrounded by a cage of water molecules. When one ligand exits, hydroxide ion, the attacking ion, does not have to be exactly in an advantageous position for substitution. But, due to Grottaus chain transfer, the hydroxide ion may be pictured as being "delocalized" around the entire cation, and upon loss of a ligand will always be in a favorable position for the substitution (40).

In the Co(II)-bipyridine-oxygen reaction the fast yellow to brown step is governed by a rate constant of the order of  $1 \text{ M}^{-1} \text{ sec}^{-1}$ . The fact that rate constants for base hydrolysis are of the order of

$10^3 - 10^6 \text{ M}^{-1} \text{ sec}$ , even for the relatively unreactive Co(III) complexes indicates that a reaction with  $(\text{OH})^-$  ion cannot be a rate determining step in the mechanism. Figure 1 does show that a small increase in  $(\text{OH})^-$  concentration causes a great increase in rate. Attempts were made to obtain the hydrolysis constants of the  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  ion by titrating solutions, which contained the dissolved  $(\text{Co}(\text{bipy})_2\text{Cl}_2 \cdot \text{H}_2\text{O})$ , with NaOH, but the immediate reaction of the hydroxy complex with oxygen plus the precipitation of an unknown substance made these attempts unsuccessful. Trials were carried out both in air and in a stream of oxygen-free nitrogen.

In this research it was found that the pale yellow  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  solutions start turning brown immediately after making the solution basic. This implies a fast reaction not only with base, but with oxygen as well, as the developing brown color has been attributed to oxygen carriers. Additionally, the oxygen is reversibly absorbed as was verified in this experiment. Silvestroni (22) in 1960 had recognized in his study that oxygen could be reversibly absorbed by solutions of Co(II) and bipyridine at neutral or slightly acid pH values. He noted the similarity of this oxygen absorption to those reactions which Hearon in 1949 (12), Tanford in 1954 (17), Silvestroni in 1958 (18), and Caglioti in 1960 (19), had observed on reactions of Co(II) and its complexes with histidine and glycylglycine, which also reversibly absorb oxygen in neutral aqueous solution. In the Co(II)-histidine and Co(II)-glycylglycine solutions, the color of the oxygen carrying intermediate is brown, as is the color of the oxygen carrier in the Co(II)-bipyridine case. It is this brown color which is generated in all three cases

and it is this same brown color which disappears upon bubbling oxygen-free nitrogen through the solution or by lowering the pH of the solution to one. The degree of reversibility is determined by the length of time the solution is subjected to oxygen and by the pH of the solution. At pH = 7 or less, Cabani (23) was able to return the brown oxygen-carrying complex to its original yellow color (qualitatively) by heating the brown solution to 80° C. Ritter (24) found by reducing the pressure above the solution, one could successfully decrease the brown color and remove oxygen, while addition of nitric acid to the solution had the same effect. The author was able to confirm the reversals using nitrogen and nitric acid. At the pH values used in this study (8.25-9.30), however, the complete reversibility was not possible and no amount of nitrogen flushing could return the original yellow color. The ease of removal of reversible oxygen at pH values less than seven coupled with the rapid development of the brown color, indicates the possibility of a fast equilibrium of oxygen with  $\text{Co}(\text{bipy})_2(\text{OH})(\text{H}_2\text{O})^+$ .

Although several metal ion complexes will absorb oxygen, most do not absorb it reversibly. With those compounds which irreversibly absorb oxygen, the metal ion is ultimately oxidized to a higher oxidation state. Coordination compounds which absorb oxygen may go through a binuclear-peroxy bridged intermediate or may go through a monomeric intermediate. Frey's original peroxy compound (1), the u-peroxo decamine dicobalt (III) complex is a cobalt complex which does not absorb oxygen reversibly, but which goes through a peroxy bridged intermediate. At the opposite end of the spectrum are the  $\text{Co}(\text{II})$ -(BSAD) chelates (6) which will absorb oxygen reversibly while in solution or

even in the solid state.

Iron(II) complexes are known to absorb oxygen, but except for naturally occurring chelates, generally do not reversibly sorb the gas. The Fe(II)-dihistidine complex (41) takes up oxygen but leads only to the oxidation of Fe(II) to Fe(III) with no oxygen carrying properties and no peroxide in the final oxidation product. The Fe(II) chelates of EDTA and 2, picolylamine-N,N' diacetate (41) will reversibly sorb oxygen but this is followed by rapid oxidation of Fe(II) to Fe(III). In the same manner, the Fe(II)-nitrilotriacetate(NTA) complex reacts. The Fe(II) dimethylglyoxime is claimed to be a true synthetic oxygen carrier, as pointed out by Drake and Williams (42). It reversibly absorbs oxygen in aqueous-dioxane solutions containing such bases as pyridine,  $\text{NH}_3$ , histidine, and imidazole. Nitrogen bubbling was used to reverse the oxygenation. This complex absorbed either one or two oxygen molecules per Fe(II). Of course the biologically important Fe(II) complexes containing porphyrin and its derivatives need not be mentioned as the important Fe(II) oxygen carriers. Fallab (41) made the observation that changing the arrangement and type of ligand around Fe(II), the reaction rate of oxidation can vary over eight orders of magnitude.

Other metal ion complexes which absorb molecular oxygen are those of Cr(II) (43), vanadium (44), and the unusual Ir(I) complex of Vaska (45)--  $\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_3$ .

That reversible oxygenation may take place in synthetic Co(II) chelates has been well documented. These have been mentioned generally in the Introduction. Most of the research which has been done on these type of complexes postulate the existence of a peroxide group bridging

the two Co(II) ions. However, in general, most studies are reluctant to postulate the existence of a peroxide group in the final oxidation product. Bekaroglu and Fallab (7) in their examination of the oxygenation of  $\text{Co}(\text{trien})^{++}$ , postulate  $(\text{trien})\text{Co}-\text{O}_2-\text{Co}(\text{trien})^{++}$  as the reversible oxygenation product, with this intermediate subsequently being easily oxidized to  $\text{Co}(\text{trien})^{+++}$ , which they claim as the final oxidation product. The irreversible oxidation step was determined mainly by additional basic particles which were in the solution. Thus, in acetate buffer solution, the irreversible oxidation was quite fast (the product being  $\text{Co}(\text{trien})\text{ac}^{++}$ ), while in pyridine buffer the oxidation was restrained. Bekaroglu observed the same properties with solutions of Co(II) and en and dien. However, as excess polyamine iminodiacetates, NTA, or EDTA are added to these solutions, the oxygen carrying properties are lost. Adding en to solutions of Co(II)-iminodiacetates initiates oxygen carrying properties, with the ultimate oxidation product being a mixed complex. Additionally, excess oxalate, malonate, or glycinate added to oxygen carrying solutions cause a loss of transporting power. Reducing the concentration of oxalate, however, in such a solution, reintroduces oxygen carrying properties and the final red-brown oxidation product  $(\text{Co}(\text{dien})(\text{C}_2\text{O}_4)^+)$  has been isolated and characterized. On these observations Bekaroglu and Fallab surmised that at least three metal-ligand bonds must be of the metal-nitrogen type for the Co(II) chelates to exhibit oxygen transport, and that oxygenation was impossible if all six coordination sites are filled (with ligands other than solvent). The author found in this research that  $\text{Co}(\text{bipy})_3^{++}$  would not absorb oxygen while basic solutions of  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{++}$  will

sorb the gas. This is in line with the evidence that there must be 3 metal-nitrogen bonds and that when all 6 coordination positions are filled, no oxygen absorption takes place.

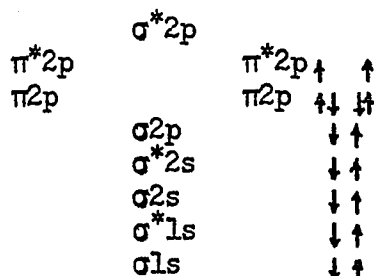
Again, as mentioned in the Introduction, oxygen transport is additionally obtained with the histidine and glycylglycine complexes of Co(II).

Finally, oxygen carriers of Co(II) are found with 3-azapentylene-1,5-diamine (APDA) (7) and with 3,6-diazaoctylene-1,8-diamine (DODA) (7).

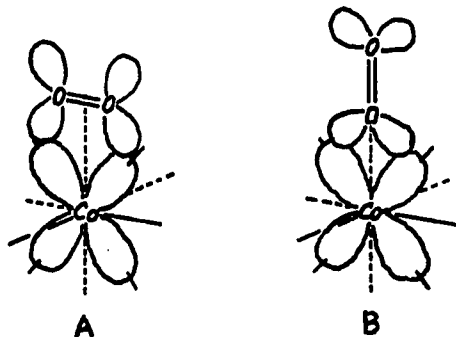
The existence of the oxygen bridged binuclear intermediate appears fairly well established, and in all cases cited, the intermediate possesses a strongly absorbing, charge transfer type brown coloration. This strong band obscures all other bands which might be in the region from 500 to 300  $\mu$ . Tanford (17) stated an extinction coefficient of 4000 per Co atom at 350  $\mu$  for the  $(\text{Co}(\text{GG})_2(\text{OH}))_2\text{O}_2^-$  complex, while in the present work an extinction coefficient of approximately 4000 per Co atom at 450  $\mu$  was found for the brown compound. Sano and Tanabe (13) even isolated the brown intermediate for the Co(II)(bisthistidine) ( $\text{O}_2$ ) complex. This isolation product corresponded to the following formulation; tetrakis histidine u-peroxo di-cobalt(II).

The arrangement and bonding of the peroxy bridging group in these cobalt complexes has been the subject of several papers, including one x-ray determination. The two possibilities for bonding of Co(II) and oxygen are with the oxygen-oxygen axis parallel to the Co-Co axis or with the oxygen molecular axis perpendicular to the Co-Co axis. In terms of simple molecular orbital theory (after Mulliken and Lennard-

Jones) (46), an oxygen molecule can be described with the following sim-  
molecular orbitals.



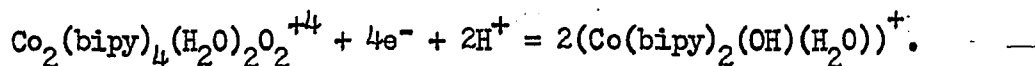
The molecule contains 16 electrons, which fill up the lower orbitals, leaving single unpaired electrons in the  $\pi^*2p$  orbitals. The somewhat loosely bound  $\pi 2p$  electrons are situated between the two oxygen atoms, both above and below the O-O axis, and in front and behind the axis-- these electrons possess bonding character. The antibonding 2p orbitals, also situated in the plane of the paper and perpendicular to the plane of the paper, each contain one unpaired electron. Hence, it may be seen that the oxygen molecule possesses both donor as well as acceptor properties. The two most favorable Co-O<sub>2</sub> bonding possibilities follow; (41)



A has possibilities for strong  $\sigma$  donation plus strong  $d\pi-p\pi$  interaction. B would be expected to be a weak  $\sigma$  donor, enhanced by  $d\pi-p\pi$  back donation. One can see the possibility for ultimate donation of an electron from the metal  $d_e$  to an oxygen  $\pi^*2p$ . Vlcek (8), using a more sophisticated molecular orbital approach, arrived at the same con-

clusions as Fallab; that the more stable configuration would be the one with the O-O axis perpendicular to the Co-Co axis. Fallab shows that a very compact binuclear center is attained in this arrangement. Models for the  $\text{Co} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \end{array} \text{Co}$  were constructed during this research and showed the compactness of the molecule as a whole, with the Co-O<sub>2</sub>-Co center being quite small and sterically hindered by the bipyridines. The x-ray determination of a Co-peroxy bridged complex has been done by Vannerberg (9), which established a O-O axis perpendicular to the Co-Co axis perpendicular to the Co-Co axis (this involved, however, Co(III) centers while in the oxygen carriers, Co(II) centers are involved).

Cabani (23), in his polarographic study on the Co(II)-bipyridine system found direct evidence for a binuclear intermediate and postulated  $\text{Co}_2(\text{bipy})_4(\text{H}_2\text{O})_2\text{O}_2^{++++}$ . He found that the number of electrons exchanged at the reduction electrode was four, and stated that the following reaction took place at this electrode;



That the cathodic diffusion current increases slightly, with each cycle of oxygenation and deoxygenation, indicates that the intermediate includes cobalt in the (II) oxidation state and that the irreversible process at this pH (neutral or pH less than 7) is the oxidation of Co(II) to Co(III) (commensurate with the increase of the cathodic diffusion current). Cabani measured the polarographic wave of Co(II)-bipyridine alone in acidic solution, and the resulting polarogram consisted of only one wave, an anodic wave which he assigned as the oxidation of  $\text{Co}(\text{bipy})_3^{++}$  to  $\text{Co}(\text{bipy})_3^{+++}$ . Upon making a solution of Co(II) and bipyridine basic and exposing to oxygen, a redox wave soon develops



unoccupied  $\pi$  orbitals. Pearson has attributed a certain extra stability to complexes containing similar ligands. The extra stability of the binuclear complex of  $(\text{bipy})_2\text{Co} \begin{array}{c} \text{OH} \\ | \\ \text{O} \\ | \\ \text{H}_2\text{O} \end{array} \text{Co}(\text{bipy})_2^{+3}$  could in this sense be attributed to the fact that all the positions but two (which hold  $\text{OH}^-$  and  $\text{H}_2\text{O}$ ) are filled by "soft" bases. It is significant that of the second and third transition series, only Ir, as  $\text{Ir}(\text{O}_2)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Cl}$ , is known as an actual oxygen carrier (45). In this molecule, Pearson would classify  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{P}(\text{C}_6\text{H}_5)_3$  as being soft bases with only  $\text{Cl}^-$  being "hard" in this case. Likewise, simple hydrated ions such as  $\text{Fe}^{++}$  and  $\text{Co}^{++}$  do not bind oxygen molecules but upon coordinating to "soft" bases such as bipyridine or phthalocyanine or porphyrin, the metal ion is rendered "soft" and can then form stable adducts with molecular oxygen.

The dimerization step (3) is the rate determining step of the yellow to brown reaction. This involves the collision of two rather large cations, which owing to simple electrostatic repulsion of two positively charged particles would not be expected to be rapid, even though  $\text{Co}(\text{II})$  substitution reactions are generally fast. The pseudo second order rate constant for this reaction, depending on the pH, at  $28^\circ \text{C}$ ., is of the order of  $1 \text{ M}^{-1} \text{ sec}^{-1}$ . This second order dependence on the complex coupled with the stoichiometry of the yellow to brown reaction (2 complex: 1 oxygen molecule: 1 hydroxide ion) do indicate a binuclear intermediate. The existence of the oxygen bridged  $\text{Co}(\text{II})$  complexes has been well documented above. Especially notable are the suggested dimers which are postulated for the analogous reactions of  $\text{Co}(\text{II})$ -histidine and  $\text{Co}(\text{II})$ -glycylglycine. All possess a strong charge transfer band in the ultra violet (13), (17), (18), (19). Under the conditions of this research,

pH values of 8.25-9.30, complete reversibility of oxygen is not attained and the "equilibrium" of (3) is far to the right.

All octahedral complexes of Co(III) are known to be diamagnetic (with the exception of  $\text{Co}(\text{F})_6^{-3}$ ) and the fact that the paramagnetism of the original yellow compound is only partially lost as the change from yellow to brown is made is indicative of the survival of the Co(II) oxidation state as the yellow to brown change is made. The acidic solution of 1 atom of Co(II) per 2 molecules of bipyridine has a gram susceptibility of  $13.636 \times 10^{-6}$ , which is equivalent to three unpaired electrons plus an orbital contribution. Immediately after making the oxygen saturated solution basic (and with a ten minute wait for preparation and stabilization of the Gouy tube), the susceptibility has decreased to  $6-8 \times 10^{-6}$ . With passing time, several days, the paramagnetic susceptibility approaches that of the diamagnetic solvent itself. Because the yellow to brown phase is reasonably fast and certainly should be complete within several hours (much sooner if high pH is maintained), it is anticipated that if the oxidation of Co(II) to Co(III) has already occurred, the paramagnetism would be completely lost by this time. That some paramagnetism is lost in going from yellow to brown is evincive that some mixing of Co(II) unpaired electrons with the oxygen free electrons is transpiring. The unpaired electron in the Co(II)  $d_{xz}$  has the right symmetry to mix with the oxygen  $\pi^*2p$  electron, conceivably causing the reduction in paramagnetism. The final red product, (F), is diamagnetic, as is its acid hydrolysis product--  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_3$ . Because of the postulated structure for the intermediate, there is also the possibility that there is some metal-

metal interaction. Since the oxygen molecule bridged intermediate would contain a total of 8 unpaired electrons, and since the paramagnetism of the brown intermediate is much lower than this, extensive mixing of orbitals must be occurring as was stated above. In addition to metal-oxygen-metal interaction, the close approach of the cobalt atoms would possibly allow mixing of metal-metal orbitals, especially the  $d_{z^2}$  orbitals.

There is some magnetic evidence that oxygen bridged binuclear compounds have a paramagnetism less than what is expected if there would be no interaction. The strongest example of this is in the  $K_4(Re_2OCl_{10})$  complex. Rhenium(IV) has a  $5d^3$  configuration electronic structure but this compound was found to be diamagnetic (48). In addition,  $(Cr_2OH(NH_3)_{10})Cl_5$ ,  $(Cr_2OH(NH_3)_9H_2O)Cl_5$  and  $(Cr_2OH(NH_3)_9OH)Cl_4$  all have magnetic moments equivalent to one unpaired electron per Cr(III) while Cr(III) compounds generally have magnetic moments equivalent to 3 unpaired electrons (49) and (50).

By increasing the ionic strength with added  $NaNO_3$  (to 1.0, 2.0, and 4.0 M), the pH active yellow to brown reaction rate can be enhanced. An increase of the ionic strength could be an influence on the different equilibria in the system. If, instead of the second coordination shell containing solvent exclusively,  $NO_3^-$  filled some of the positions (via ion pairing to the cation), the reverse reaction in (1) will be hindered. In addition, an increase of  $Na^+$  and  $NO_3^-$  ions would exert a "caging" effect on the hydroxide ion and on the complex (both being charged) but not to as great an extent on oxygen (being uncharged). This would tend to prevent some of the rate reducing re-

actions which are possible--such as formation of  $\text{Co}(\text{bipy})_2(\text{OH})_2$ . The oxygen molecule reactions would be relatively increased. Although the Debye-Huckel theory would not strictly apply at these high ionic strengths, the prediction remains that reactions between like charged particles would be speeded up by increasing the ionic strength. The rate determining step (3) is just such a reaction between like charged particles. Figures 10-13 show that the rate can be increased by increasing the ionic strength.

Baker, Basolo, and Neuman (51) found an inert ion effect on the rate of electron transfer in solutions of tris-phenanthroline  $\text{Co}(\text{II})$ , tris-phenanthroline  $\text{Co}(\text{III})$ . The transfer rate at  $0^\circ \text{C}$ . ( $4 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$ ) is 2-3 times greater for  $\text{KNO}_3$  solutions than for  $\text{KCl}$  solutions. Baker assumes the formation of ion pairs between  $\text{Co}(\text{phen})_3^{+3}$  and  $\text{Cl}^-$ . Molecular models illustrate that  $\text{Cl}^-$  may occupy a position quite close to the metal ion, between the planes of the phenanthroline rings. For there is no free energy change during the electron exchange the  $\text{Cl}^-$  must transfer from  $\text{Co}(\text{III})$  to  $\text{Co}(\text{II})$ . Because this necessitates moving several Angstroms, it is possibly energetically unfavorable and the reaction is slowed. The  $\text{NO}_3^-$  also forms ion pairs but not as strongly. During the electron exchange  $\text{NO}_3^-$  would not have as far to move and the reaction would be more favorable than the one with  $\text{Cl}^-$ .

The low activation energy found for the  $\text{Co}(\text{bipy})_2^{++}$  oxygen reaction is 9-12 Kcal mole<sup>-1</sup> and is consistent with the presumed stability of the oxygen adduct. Due to the paucity of rate-temperature data for oxygenation of  $\text{Co}(\text{II})$  complexes, no activation energy comparisons can be drawn.

### B. The Brown to Red Reaction

The brown to red phase of the reaction is much slower than the yellow to brown step, and was followed by monitoring spectrophotometrically the decay of the intensely colored brown complex to the red (See Figure 14). The brown complex decayed by simultaneous simple first order decay and a hydroxide ion dependent pseudo first order decay. These reactions have been attributed to the irreversible oxidation of Co(II) to Co(III).

In order to look at the oxidation of the bridged complex, it is important to inspect the d electron configuration for the complexed Co(II) ion. Magnetic measurements attest to the fact that the  $\text{Co}(\text{bipy})_3^{++}$  has three unpaired electrons. Even though bipyridine is a strong field ligand; it cannot force the spin paired complex of Co(II), even with three bipyridine ligands per cobalt. Water, hydroxide ion, and oxygen, all being low crystal field ligands, would not be expected to yield spin paired complexes either, when they are derivatives of  $\text{Co}(\text{bipy})_2^{++}$ . The binuclear Co(II) complex (D), would accordingly be envisioned as having this d electron configuration on the Co(II);  $d_e(5) d_\gamma(2)$ --three unpaired electrons. The final red oxidation product is diamagnetic and is postulated therefore to be in the III oxidation state. Co(III) complexes are all diamagnetic (except the hexafluoride) and their 6 d electrons would all be paired in the  $d_e$  orbitals. In order for oxidation to the (III) state, the Co(II) ion must undergo major rearrangements, both of its electronic state and of its bond lengths with its coordinated ligands. The electronic rearrangement involves the prior translocation of electrons from  $d_e(5) d_\gamma(2)$  to

$d_e(6) d_{\gamma}(1)$ , before the electron can be transferred. Moreover, the Co(II)-ligand bonds must shorten to the lengths required for the final complex. The electron which undergoes the transfer must occupy either the  $d_{z^2}$  or the  $d_{x^2-y^2}$  orbital, both of which have unfavorable symmetry properties for transfer of an electron to the  $\pi^*2p$  orbital of the oxygen molecule. All in all the rearrangement energy for the electron transfer should be high. The final red compound, in contrast to the intensely colored brown intermediate, is a weakly absorbing complex. The Co(III) ions, being in a stable d-electron configuration, would not be expected to engage in further electron transfer with the bridging oxygen.

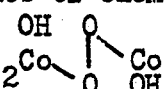
The  $(OH^-)$  ion dependent decay of the brown comprises another pre-equilibrium before the final oxidation of Co(II) to Co(III). This equilibrium is assumed to be far to the left as it is dependent on the  $(OH^-)$  concentration and on the oxidation of Co(II) to Co(III), the slow rate determining step. The oxidation step which follows would proceed as has been described above. The activation energy for the brown to red step has been found to be  $19 \text{ Kcal mole}^{-1}$ . The activation energy, considering the rearrangements which must be undergone, is expected to be high. It may be compared to the analogous oxidation of the  $(\text{trien})\text{Co} \begin{array}{c} \text{O} \\ | \\ \text{O} \end{array} \text{Co}(\text{trien})^{+4}$ , which has an activation energy of  $20 \text{ Kcal mole}^{-1}$  (10).

Finally, the ligands would also have an extreme effect on the oxidation process. Fallab (41) showed that the second order rate constant of the reaction of the Fe(II)-ethylenediaminediacetate(EDDA) chelate with molecular oxygen is  $2.8 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ . This is  $10^5$

times faster than the reaction of the hydrated ferrous ion with molecular oxygen. By replacing the two ethyleneamino groups by 2-picolyamine-N-N, diacetate, the oxidation rate is lowered to  $0.6 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$ . On the other hand with the Fe(II)-NTA chelate, the oxidation rate is increased to  $1.5 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$ . Furthermore, the Fe(II)-EDTA complex is oxidized with a rate constant equal to  $5.4 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$ . It appears that carboxyl groups have a positive effect on the oxidation rate while the replacement of an ethyleneamino group by the aromatic picoline nitrogen has a retarding effect on the oxidation. Fallab explains the ligand influence in this manner. With carboxyl groups trans to a bound oxygen molecule, the donating ability of a full acetate oxygen  $p\pi$  orbital deforms an accepting  $d_e$  orbital on the iron. This deformation facilitates the overlap of the  $d_e$  metal orbital with the  $\pi$  antibonding orbital of the oppositely bound oxygen molecule, and ultimately expedites the electron exchange. The aromatic nitrogen ligand works in the opposite direction. The aromatic delocalized orbitals of the picoline chelate may have the right symmetry to mix with a metal  $d_e$  orbital and the drain of electrons may be away from the oppositely bound oxygen molecule. Since bipyridine has aromatic character also, it can act in the same fashion as the picoline chelate. This stabilizing effect plus the extreme rearrangements of the Co(II) ion could explain the slowness of the oxidation.

The postulated red oxidation product, (F), has been analyzed several times for carbon, hydrogen, nitrogen, oxygen, and cobalt, and somewhat erratic results have been obtained. This is surprising in lieu of the facts that large, well formed crystals are obtained, which

can be recrystallized easily from hot distilled water. Several examples of elemental analysis are found below. For

(bipy)<sub>2</sub>Co  several analyses yield;

	%C	%H	%N	%O	%Co
Found:	50.4	3.75	14.3	-	13.2
	50.4	3.47	14.7	-	10.0
	50.4	3.84	14.9	19.9	-
	50.6	3.71	14.8	20.0	-
	50.9	3.56	14.1	19.5	11.9
	50.8	3.68	14.3	19.6	11.7
Calcd:	50.1	3.99	14.6	19.2	12.3

The hydroxide ions in this compound are surrounded by parts of the organic ligands and are well shielded by these ligands. Attempts to titrate this dimer with HNO<sub>3</sub> yielded no equivalence points. On the other hand, by heating the dimer at 65° C. for 24 hours in 1 M HNO<sub>3</sub>, the binuclear complex can be converted to Co(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>. Ritter (24) isolated and purified this diaquo compound, and titrated with NaOH. He found equivalence points at 296 and 594, while the calculated equivalence points are 297 and 594. Assuming that the titration with base of Co(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>+3</sup> yields Co(bipy)<sub>2</sub>(OH)<sub>2</sub><sup>+</sup>, the fact that Ritter immediately back titrated with HNO<sub>3</sub> and could receive a titration curve with the same inflection points signifies that the hydroxy groups in Co(bipy)<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> are active and easily titrated. This activity of the hydroxo group in Co(III) complexes was shown in 1950 by Basolo (52) who upon dissolving Co(en)<sub>2</sub>OH(H<sub>2</sub>O)<sup>++</sup> in 0.1 M HBr, and immediately taking the spectra, found the absorption spectra equivalent to that of Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>+3</sup>. Basolo (53) reports that Werner made these compounds:

$\text{Co}(\text{NH}_3)_4\text{NO}_2(\text{OH})^+$ ,  $\text{Co}(\text{NH}_3)_5\text{OH}^{++}$ ,  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})^{+2}$ , *cis*- $\text{Co}(\text{en}_2)\text{H}_2\text{O}(\text{OH})^{++}$  and *trans*- $\text{Co}(\text{en}_2)(\text{H}_2\text{O})(\text{OH})^{++}$ . The first three will liberate  $\text{NH}_3$  from cold  $\text{NH}_4^+$  solutions and precipitate  $\text{AgO}$  from  $\text{AgNO}_3$ , and all will absorb  $\text{CO}_2$  and react basic to litmus.

The diaquo compound is also red and has a visible spectra quite similar to that of the dimer (dimer has a peak at 495 mu with an extinction coefficient of 49/Co while the diaquo complex has a peak at 491 mu, with an extinction coefficient of 39/Co). By adding 2 millimoles of  $\text{NaOH}$  to 1 millimole of diaquo (at pH - 13.5) and refrigerating, the dimer (proven spectrally) could be filtered off several days later. The pH of the solution had fallen to eight.

Silvestroni (22) claimed he could receive the final oxidation product by prolonged contact of base and  $\text{Co}(\text{bipy})_3^{+++}$ .

Silvestroni (18) also stated that he could obtain the final oxidation product of  $\text{Co}(\text{II})$  and glycylglycine in the absence of oxygen, by the coulometric oxidation of  $\text{Co}(\text{II})$ -glycylglycine solutions. No analysis or further proof of the identity of this oxidation product was given, which could also be said of Silvestroni's product above. These experimental claims, however, cannot be discounted and, indeed, present evidence that the red oxidized species (by analogy) obtained from  $\text{Co}(\text{II})$ -bipyridine solutions could be the simple monmeric dihydroxy species-- $\text{Co}(\text{bipy})_2(\text{OH})_2(\text{NO}_3)$ . The fact remains, nonetheless, that the red oxidation product cannot be titrated at room temperature with acid. As stated above, Ritter could back titrate the  $\text{Co}(\text{bipy})_2(\text{OH})_2^+$  obtained from titration with base of  $\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_2^{+++}$ , which indicates the final product is not the simple monomer.

Moreover, the solubility properties of (F) are important here. The dimer is fairly insoluble in water at room temperatures (0.9 g/100 ml H<sub>2</sub>O, where the diaquo is extremely soluble and difficult to isolate from solution. If (F) is a monomer, its solubility properties would be expected to be similar to those of the diaquo compound. This difference in solubility implies the likelihood that there is some major structural variation between the final species and its hydrolysis product.

Ritter (24) also did a molecular weight determination of the final red complex using the isothermal distillation method. He found the average molecular weight of the particles in solution to be  $291 \pm 16$ . This would be consistent with the dimer (MW=960) but not with the monomer (MW=485).

Molecular models reveal that the dimer is a very compact molecule. In this structure the hydroxide groups are "buried", which would lend credence to the inactivity of the two hydroxy groups, or the peroxide linkage, in attempts to titrate with either acid or base. There is also the potentiality of hydrogen bonding between the hydroxide groups and the peroxy bridge.

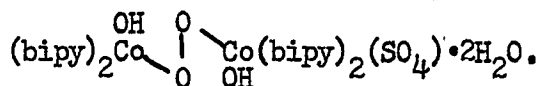
Conductimetric data in aqueous solution offers no real assistance to the final resolution of the question of whether the red crystals are a monomer or a dimer. Assuming a formula weight of 960, a 0.001 M solution of dimer has a molar conductance of  $186 \text{ ohm}^{-1} \text{ mole}^{-1}$ . This is somewhat low for the conductance expected from the literature values given; 2:1 complex-- $225\text{-}270 \text{ ohm}^{-1} \text{ mole}^{-1}$  (34). Due to the size of the cation, the mobility might be expected to be low and hence the

molar conductance lower than the literature values. Conversely, a 0.001 M solution (formula weight of 480) of "monomer" yields a molar conductance of  $106 \text{ ohm}^{-1} \text{ mole}^{-1}$ . This value falls directly in the middle of the range for the literature conductance values for 1:1 complexes ( $96\text{-}115 \text{ ohm}^{-1} \text{ mole}^{-1}$ ) (34).

Supplementary data which might be utilized in elucidating the formulation of the red oxidation product have been gathered. Ritter (35), in a highly questionably preliminary x-ray study, ascertained that each unit cell of the red crystal contained 1122 molecular weight units or  $n(\text{MW}) = 1122$ , where  $n$  is the number of molecules per unit cell. This determination was done on air-dried red crystals. As mentioned in the experimental section, lustrous, large well formed crystals can be isolated from evaporating the brown solutions. These crystals are stable in "Hawaii" air for several months. Quantitative drying of the air dried crystals produce a 14.5% loss in weight (95% of which is lost by simply placing above  $\text{H}_2\text{SO}_4$ ). Assuming a molecular weight of 960 for the dried crystals, a 14.5% increase in weight would boost the molecular weight of the vacuum dried crystals up to 1120, very close to the value which Ritter found for the molecular weight units per unit cell. A monomer molecule (dried),  $\text{Co}(\text{bipy})_2(\text{OH})_2(\text{NO}_3) \cdot \text{H}_2\text{O}$ , has a molecular weight of 470. If its weight is increased by 14.5%, its formula weight would be approximately 565. Two molecules of the monomer per unit cell would also fulfill Ritter's findings.

The dimer has also been made with the anions, sulfate or chloride.

A formula which fits the sulfate elemental analysis is;



Calculated: Co, 12.51; C, 51.1; H, 4.08; N, 11.92; O, 17.00.

Found: Co, 12.25; C, 51.1; H, 3.92; N, 12.38; O, 17.00.

An analogous structure for the chloride but with 8 H<sub>2</sub>O gives these calculated percentage values.

Calculated: Co, 11.78; C, 47.4; H, 4.17; N, 11.05; O, 18.92; Cl, 6.97.

Found: Co, 11.00; C, 48.52; H, 4.37; N, 11.24; O, 18.84; Cl, 6.14.

The solubility of the nitrate and the sulfate are similar, but the chloride is much more soluble, and difficult to isolate as a crystalline product.

On the bases of solubility differences between the red oxidation species and its acid hydrolysis product, and the difficulties in titrating the oxidation product, the dimer form is chosen as the actual oxidation product.

In conclusion, the kinetics of the Co(II)-bipyridine complex and its reaction with oxygen have been studied in basic aqueous solution. This system had been examined previously by Silvestroni and Cabani, both of whom concentrated only on the reversible oxygenation of Co(bipy)<sub>2</sub><sup>++</sup>. Additionally, Ritter studied this system and isolated the final oxidation species and its acid hydrolysis product (titrating the latter compound).

The present research actually studied the kinetics of the formation of the brown intermediate and the final red species. A kinetic study in basic solution had not previously been done in any of the Co(II)-oxygenation reactions. This research has also contributed to the sparse magnetic data on this type of compound. The magnetic measurements taken during the course of the experiment are especially important. The final

oxidation product has also been studied extensively, something which has not been done previously.

A further study on this system would have to include an x-ray determination of the final oxidation product. This is the only unique manner of elucidating the structure of this product. Short of this, the determination of the dipole moment would be helpful. The monomer dihydroxy compound would be expected to have a larger dipole moment than the dimer dihydroxy compound. Finally, an oxygen-18 experiment would be advantageous in the elucidation of the mechanism. If the above proposed mechanism is correct, oxygen-18 should be found in the final red oxidation product.

## APPENDIX

Using steady state approximations to arrive at equation (8):

$$dB/dt = k_1(A)(OH) - k_{-1}(B) - k_2(B)(O_2) + k_{-2}(C) \quad (1)$$

$$dC/dt = k_2(B)(O_2) - k_{-2}(C) - k_3(C)(A) \quad (2)$$

Apply steady state approximations to  $dB/dt$  and  $dC/dt$  and add equations (1) and (2). Also assume equilibrium between B and C. That is;

$$K_2 = (C)/(B)(O_2) \quad (3)$$

The addition of (1) and (2) gives:

$$0 = k_1(A)(OH) - k_{-1}(B) - k_3(C)(A) \quad (4)$$

Substituting (3) into (4) gives:

$$k_1(A)(OH) = k_3(C)(A) + k_{-1}(C)/(O_2)(K_2) \quad (5)$$

Solving for C gives:

$$C = \frac{k_1(A)(OH)}{k_3 + k_{-1}/(O_2)(K_2)} \quad (6)$$

Since

$$dD/dt = k_3(A)(C), \quad (7)$$

substituting (6) into (7) gives:

$$\frac{dD/dt = k_1 k_3 (A)^2 (OH)}{k_3(A) + k_{-1}/(O_2)K_2} \quad (8)$$

If  $k_{-1}/(O_2)K_2$  is much greater than  $k_3(A)$ , we receive equation (8) as stated in the discussion.

## BIBLIOGRAPHY

- (1) E. Fremy, Ann. chim. et phys., 35, 257 (1852).
- (2) A. Werner, Ann., 375, 1 (1910).
- (3) L. H. Vogt, H. Falgenbaum, and S. Wiberly, Chem. Revs., 63, 269 (1963).
- (4) B. Pfeiffer, E. Breith, E. Lubbe, and T. Tsumaki, Ann. Chem. Liebigs, 503, 84 (1933).
- (5) T. Tsumaki, Bull. Chem. Soc. Japan, 13, 252 (1938).
- (6) M. Calvin, and C. H. Barkeley, J. Am. Chem. Soc., 68, 2267 (1946).
- (7) O. Bekaroglu, and S. Fallab, Helv. Chim. Acta, 46, 2120 (1963).
- (8) A. Vlcek, Trans. Faraday Soc., 56, 1137 (1960).
- (9) C. Brosset, and N. Vannerberg, Nature, 190, 714 (1961).
- (10) B. Erdem, and S. Fallab, Chimia, 19, 463 (1965).
- (11) D. Burk, J. Hearon, L. Caroline, and A. Schade, J. Biol. Chem., 165, 723 (1946).
- (12) J. Greenstein, and M. Winitz, "Chemistry of the Amino Acids," John Wiley and Sons, New York (1961) pp. 635-637.
- (13) Y. Sano, and H. Tanabe, J. Inorg. Nucl. Chem., 25, 11 (1963).
- (14) R. Leberman, and B. Rabin, Trans. Faraday Soc., 55, 1660 (1959).
- (15) A. Earnshaw, and C. Larkworthy, Nature, 192, 1068 (1961).
- (16) J. Gilbert, N. Otey, and V. Price, J. Biol. Chem., 173, 571 (1948).
- (17) C. Tanford, D. Kirk, and M. Chantooni, J. Am. Chem. Soc., 76, 5325 (1954).
- (18) P. Silvestroni, and G. Chantooni, Ricerca Sci., 28, 1211 (1958).
- (19) P. Silvestroni, V. Caglioti, and C. Furlani, J. Inorg. Nucl. Chem., 13, 95 (1960).
- (20) G. Waand, and B. Martin, J. Inorg. Nucl. Chem., 13, 95 (1960).
- (21) A. Vlcek, Z. phys. chem. (Sonderheft), 208, 143 (1958).
- (22) P. Silvestroni, and L. Ceciarelli, Ricerca sci., 30, 1760 (1960).

- (23) S. Cabani, Gazz. chim. Ital., 90, 1410 (1960).
- (24) J. Ritter, Master's Thesis (1963), Univ. of Hawaii.
- (25) B. Figgis, and R. Nyholm, J. Chem. Soc., 4190 (1958).
- (26) H. Nettleton, and S. Sugden, Proc. Roy. Soc. (London), A173, 313 (1939).
- (27) C. Foulk, H. Moyer, and W. MacNevin, "Quantitative Chemical Analysis," McGraw-Hill, New York (1952) p. 433.
- (28) A. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York (1939) p. 549.
- (29) P. Ellis, and R. G. Wilkins, J. Chem. Soc., 299 (1959).
- (30) Lang, N., "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio (1952) p. 1083.
- (31) H. Irving, and D. Mellor, J. Chem. Soc., 5222 (1962).
- (32) B. Figgis, and J. Lewis, "Technique of Inorganic Chemistry, Vol IV" (Jonassen, H. and Weissberger, A., Editors), John Wiley and Sons, New York (1965) p. 216.
- (33) S. Maron, and C. Prutton, "Principles of Physical Chemistry," The Mac Millan Co., New York (1958) p. 450.
- (34) M. Jones, "Elementary Coordination Chemistry," Prentice Hall, New York (1964) pp. 254-255.
- (35) J. Ritter, (Private Communication).
- (36) J. West, J. Chem. Soc., 578 (1954).
- (37) F. Basolo, and R. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York (1958) pp. 96, 269.
- (38) R. Pearson, R. Meeker, and F. Basolo, J. Am. Chem. Soc., 78, 709 (1956).
- (39) F. J. Garrick, Nature, 139, 507 (1937).
- (40) S. Chan, and M. Tobe, J. Chem. Soc., 4531 (1962).
- (41) S. Fallab, Chimia, 16, 189 (1962).
- (42) J. Drake, and R. Williams, Nature, 182, 1084 (1958).
- (43) T. Joyner, and W. Wilmarth, J. Am. Chem. Soc., 83, 576 (1961).
- (44) J. Swinehart, Inorg. Chem., 4, 1089 (1965).

- (45) L. Vaska, Science, 140, 809 (1963).
- (46) C. Coulson, "Valence," Oxford Press, London (1961 p. 103).
- (47) R. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).
- (48) B. Zezowska, and S. Wajda, Bull. Acad. Polon. Sci., 2, 249 (1954),  
6, 217 (1958), 9, 57 (1961).
- (49) K. Wilmarth, and H. Graff, J. Am. Chem. Soc., 78, 2683 (1956).
- (50) A. Earnshaw, and J. Lewis, J. Chem. Soc., 369 (1961).
- (51) B. Baker, F. Basolo, and H. Neumann, J. Am. Chem. Soc., 63, 37  
(1959).
- (52) F. Basolo, J. Am. Chem. Soc., 72, 4393 (1950).
- (53) F. Basolo, "The chemistry of the Coordination Compounds," (J. C.  
Bailar, Editor), Reinhold Publishing Corp., New York (1956)  
p. 425.