SPECTROPHOTOMETRIC AND KINETIC STUDY OF MOLYBDENYL THIOCYANATE COMPLEXES IN METHANOL

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THESIS

ABSTRACT

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OF
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By

Christopher Chike Ezzeh

This thesis discusses the formation of molybdenyl thiocyanate complexes by the reaction of diammonium oxypentachloromolybdate(V) with the thiocyanate anion in methanol through the reaction

$$\mathrm{MoOCl_5^{=}} + \mathrm{n\ SCN^-} \longrightarrow \mathrm{MoOCl_{5-n}(SCN)_n} + \mathrm{nCl^-} \qquad (1)$$

In the visible region of the spectrum the reactant complex has two broad peaks at 712 mμ and 450 mμ and two well defined peaks at 257 mμ and 309 mμ in the ultraviolet region. On the addition of thiocyanate a new peak with a maximum at 460 mμ is formed. The peaks at 712 mμ and 309 mμ remain broad and diffuse but the peak at 257 mμ shows a very pronounced increase in absorbance with an increase in the thiocyanate ion concentration.

It was noted that mixing the original complex and thiocyanate resulted in the rapid formation of an absorbing species followed by a slower build-up of another species.

The continuous variation method showed that the species formed shortly after mixing is a 1:2 complex but that this soon gives way to a 1:4 species which is the principal absorbing complex at long times.

The presence of a 1:2 complex was also indicated by the determination of the association constants for the complexes. By using the method of Hume, association constants were obtained for the following presumed equilibria:

$$MoOCl_4MeOH^- + 2\ SCN^- \overset{K_1}{\rightleftarrows} MoOCl_2(MeOH)(SCN)_2^- + 2\ Cl^- \quad (2)$$

and

$$MoOCl_2(MeOH)(SCN)_2^- + 2\ SCN^- \overset{K_2}{\rightleftarrows} MoO(MeOH)(SCN)_4^- + 2\ Cl^- \quad (3)$$

K_1 and K_2 are $2.4 \pm 0.26 \times 10^2$ and $2.72 \pm 0.21 \times 10^4$. There was no evidence for the 1:5 complex at relatively low thiocyanate concentrations and it was assumed that the axial chloride anion in the original salt was replaced by a molecule of the solvent in solution.

A stopped-flow apparatus was used to determine the rate of formation of the complexes. This revealed, for ratios of molybdenum to thiocyanate less than 1:2, a very rapid build up in absorbance. The pseudo-first-order rate constant, obtained by a method similar to that used in treating the formation of the ferric thiocyanate complex (51, 52), was plotted against the ligand concentration. This plot gave a minimum in the region between the ratios of 1:2 and 1:3.

Studies with a rapid-scanning monochromater showed that during the first part of the reaction a very rapid formation of a complex (presumably 1:1) occurs followed by a slower build up in absorbance and a shift of the maximum to longer wavelengths. At higher concentrations the build up of the initial complex could not be followed and it was presumed that the 1:1 complex formed very rapidly, prior to the formation of the 1:2 complex.

Both the electron paramagnetic resonance spectrum and the optical spectrum indicated the absence of dimerization of molybdenum(V) in the thiocyanate system. The esr spectrum shows, at thiocyanate to molybdenum ratios of four to one and higher, nine hyperfine lines indicating an interaction with four nitrogen nuclei.

An overall reaction scheme compatible with these results is

$$\mathrm{MoOCl_5^{=} + MeOH \rightleftarrows MoOCl_4MeOH^{-} + Cl^{-}} \qquad (4)$$

$$\mathrm{MoOCl_4MeOH + SCN^{-} \xrightarrow{fast} MoOCl_3(SCN)(MeOH)^{-} + Cl^{-}} \qquad (5)$$

$$\mathrm{MoOCl_3(SCN)(MeOH)^{-} + SCN^{-} \overset{K}{\rightleftarrows} MoOCl_3(SCN)_2^{=}} \qquad (6)$$

$$\mathrm{MoOCl_3(SCN)_2^{=} \xrightarrow[rearrangement]{k} MoOCl_2(SCN)_2MeOH^{-} + Cl^{-}} \qquad (7)$$

$$\mathrm{MoOCl_2(SCN)_2MeOH^{-} + 2SCN \overset{slow}{\rightleftarrows} MoO(SCN)_4MeOH^{-} + 2Cl^{-}} \qquad (8)$$

$$MoO(SCN)_4MeOH^- + SCN^- \rightleftharpoons MoO(SCN)_5^= + MeOH \qquad (9)$$

Steps (6) and (7) are included to account for the ionic strength-dependence of overall rate as well as the concentration dependence of the apparent rate constant.

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A THESIS

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To my Parents

Mr. & Mrs. Johnson W. Ezzeh

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INTRODUCTION

The nature of the thiocyanates of molybdenum(V) cannot be easily explained. Different formulations have been proposed for these species depending on the media used. Previous workers have left unresolved several questions about the nature of the chemical reactions such as the stability and nature of the complexes, rate of ligand exchange and relation of exchange rate to the stability of the ligand in the complex, the extent of solvent association within the inner coordination sphere and the importance of the molybdenum—oxygen double bond in determining the kinetics of the substitutional processes.

In 60% acetone-water mixtures Perrin (1) reported that three species exist in equilibrium. These complexes, which have molybdenum to thiocyanate ratios of 1:1, 1:2, and 1:3, have different colors. The presumed 1:1 complex is colorless, the 1:2 complex, dominant at low thiocyanate concentration, is yellow, while the 1:3 complex is amber. Hiskey and Meloche (2) by using 4N hydrochloric acid in water reported the existence of a 1:3 complex. Babko (3) claimed that 1:5 and 1:3 complexes were formed and suggested that under appropriate conditions a colorless molybdenum thiocyanate anion and cation occur in solution, while Kolling (5) isolated a 1:5 complex from chloroform extracts. In addition to these, Wilson and McFarland (4) were able to extract molybdenum oxytetrathiocyanate from organic solvents. The complexity of these solutions is very evident from the above.

The present investigation was carried out by using methanol as the solvent in an attempt to determine the nature of the complexes formed in this medium and to study the kinetics of their formation. During the course of this investigation it became necessary to study the peak shape of the initial complexes formed at different thiocyanate concentrations for a given molybdenyl concentration. The kinetic study revealed that the interaction of molybdenum(V) and thiocyanate can be broken down into at least three steps. These are the rapid and sucessive formation of two light absorbing species of low thiocyanate-to-molybdenum ratios and the subsequent build-up of another absorbing species over long periods of time. In order to study the rapid formation of these species,stopped-flow-techniques were used. This thesis gives a description of the methods used and the results obtained and includes a proposed mechanism to explain the results.

Historical

Small amounts of molybdenum present as molybdate, can be detected by reduction with stannous chloride in the presence of an alkali thiocyanate. The red color formed by this reaction has been used in a number of colorimetric procedures. The earliest observation of this reaction was by Braun and Skey (6). The reaction has generally been carried out in approximately one molar acid and at high thiocyanate ion concentrations.

The nature of the red coloration has proved to be difficult to determine and has resulted in several conflicting descriptions. Some authors thought that molybdenum was in the +3 oxidation state (7,8) while others thought it was in the +5 state. Subsequently the complex has been formulated as $MoO(SCN)_3$, $MoO(OH)_2(SCN)_3$ and $MoO(SCN)_5^{=}$. Some of these complexes possess varying degrees of hydration depending on the conditions of their production. On the basis of simple analysis, Krauskopf and Schwartz (9) reported the extraction of $Mo(SCN)_3$ from ether. Much confusion existed about these complexes until 1928 when Wardlaw, et al (10) reinvestigated the problem and formulated the complex on the basis of Werner's Theory as $R_2[MoO_2(CNS)_3]$ or $R_2[MoO(SCN)_5]$ in which R is the univalent cation.

In 1940 Hiskey and Meloche (2) reviewed earlier formulations of these complexes. Their investigation attempted to throw more light on three issues:

$$MoOCl_4MeOH^- + 2\ SCN^- \overset{K_1}{\rightleftharpoons} MoOCl_2(MeOH)(SCN)_2^- + 2\ Cl^- \qquad (2)$$

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Steps (6) and (7) are included to account for the ionic strength-dependence of overall rate as well as the concentration dependence of the apparent rate constant.

(1) whether the complex formed in the usual analytical procedure was identical with that formed between molybdenum (V) and thiocyanate and whether molybdenum (III) formed a red complex,

(2) whether the pronounced color changes, which have been observed in molybdenum (V) solutions could be correlated with a previous observation of Hurd and Hiskey (11) that varying the acid concentration of such solutions resulted in a bleaching effect on the molybdenum thiocyanate complex, and

(3) whether an equilibrium study of the reaction between molybdenum (V) and the thiocyanate anion would give some information about the nature of the complexes.

Some of the results of their study have been confirmed by later workers.

A. Valence state of molybdenum in the complex.

Much work has been done on this subject over a long period of time. In the conventional analytical method for the estimation of molybdenum the molybdate solution in 2N HCl is reduced by use of such reducing agents as stannous chloride (12), the silver reductor (13) and metallic mercury (14). With stannous chloride as the reducing agent, Bergh and Haight (15) showed that Mo(V) is the product in 3N HCl and that an equimolar mixture of Mo(V) and Mo(III) is the product in 9N HCl (16). In 3N HCl the Mo(V) dimer is known to be inert and resistant to further reduction by the stannous ion (17, 18). Mo(V) in the monomeric thiocyanate complex is rapidly reduced at room temperature and results in the loss of absorbance at the characteristic wavelength where the red-colored species absorbs. This explains why as little as 50 percent of the theoretical absorbance is obtained when molybdate is determined as the thiocyanate complex after reduction by excess stannous chloride (19) since Mo(III) does not form any red-colored complex (2). Thus in the red-colored complex the valence state of molybdenum is +5 (3 and 16).

The interaction between molybdenum (V) and the thiocyanate anion.

Earlier work on this subject was carried out in aqueous solutions at various acid concentrations. Interference due to the formation of a pink complex by thiocyanate ion, and the tendency of the color of the molybdenum complex to fade once formed made determination of the complexes formed uncertain. A characteristic phenomenon of acidified thiocyanate solutions is the formation of a pink-colored substance. The conditions for this formation are similar to those which prevail in the study of molybdenum thiocyanate complexes. To circumvent this difficulty, low acid concentrations were used by Hiskey and Melonche (2). Perrin (1) conducted his studies in a 60% acetone-water solution which forms a single phase system in which the complex is sufficiently stable to allow quantitative measurements to be made. Even in such a solution the possibility of forming the pink thiocyanate complex still existed. The present study has been carried out in dry methanol and in the absence of any mineral acid. No red coloration was observed when thiocyanate was dissolved in methanol.

The second difficulty encountered by previous investigators of this problem was the fading of the color which often occured after the maximum absorbance was attained. Hiskey (2) thought that this was due to the presence of an acid in the solution. Thus he noted that this fading was more rapid at high acid concentrations and slower at low acid concentrations. Wilson and McFarland (4) thought that the rapid fading was due to the reduction of Mo(V) to Mo(III). No satisfactory demonstration of the origin of this behavior has yet been made.

Ultraviolet and visible spectra of diammomum oxypentachloromolybdate (V) and molybdenum-thiocyanate complexes.

In most of the previous studies the molybdenum thiocyanate complex had been prepared by reducing molybdate in the presence of an alkali thiocyanate. Since we intended to study the kinetics of formation of this red complex without reduction it was necessary to begin with a molybdenum (V) compound. The complex found to be most suitable was the oxypentachloromolybdate (V) as the diammonium salt (59). Its spectrum has been studied extensively.

Until 1957 when C. K. Jørgensen (20) examined the visible and ultraviolet spectra of the $MoOCl_5^=$ anion, no band assignments had been made. Five absorption bands were found for this ion in 8M HCl as shown in Table I.

Table I

Absorption Bands of $[MoOCl_5^=]$

In Aqueous HCl (20) wavelength	ε	in dry Methanol (this work)
712 mμ (broad peak)	12	very broad diffuse and weak
445 mμ smooth peak	16	broad extends to U.V.
355 mμ sharp peak	500	not observed
310.5 mμ very sharp	-	sharp
250 mμ very sharp	-	sharp

In methanol as in aqueous solutions the complex ion $[MoOCl_5^=]$ shows two weak bands in the visible region. These [illegible] are ligand field bands assigned on the basis that the anion is essentially octahedral but with a strong asymmetry along the Z-axis resulting from the metal-oxygen bond (21). Ballhausen and Gray (22) explained this as a domination of the energy diagram through π-bonding between the metal and oxygen so that there is a considerable further splitting of both the E_g^2 and $^2T_{2g}$ states.

Two bands are observed in the ultraviolet region at 309 and 257 mμ. Figure I.Allen (21) assigned these to transitions involving transfer of an electron from a bonding π-orbital ($^{e}\pi$) which is largely associated with the oxygen atom, to either a non-bonding or an antibonding orbital which is essentially d in character.

To account for the entire spectrum, both visible and ultraviolet, Gray and Hare (23, 24) devised a molecular orbital scheme based on that suggested (22) for the vanadyl ion, $[VO]^{2+}$.

Comparison of the spectra in concentrated hydrochloric acid and in methanol solution shows that in methanol the band at 712 mμ is very weak, broad and diffuse while the band at 355 mμ is absent. The latter is a relatively weak electron transfer band and it appears strongly when molybdenum (III) is partially oxidized. In 6M hydrochloric acid molybdenum (V) gives a brown solution which absorbs at 720 and 445 mμ while the shoulder at 355 mμ is blurred out. This is also observed in 6M LiCl in methanol. Evidence has been presented (35) which indicates that this brown hydrolyses product contains at least two molybdenum atoms per complex. Although no shoulder appears at 355 mμ in highly concentrated solutions of molybdenum (V) in methanol, a brown solvolysis product was observed. It is possible that the paramagnetism of $[MoOCl_5^{=}]$ is changed to diamagnetism (25) as has been observed in dilute HCl solutions at high concentrations of molybdenum. This may also be due to the formation of oxygen

Figure I. Ultraviolet spectra of 0.003M $(NH_4)_2MoOCl_5$. Spectra run on Unicam S.P. 800 at room temperature

IA. $(NH_4)_2MoOCl_5$ in methanol

IB. $(NH_4)_2MoOCl_5$ in 6M HCl

IC. $(NH_4)_2MoOCl_5$ in 6M LiCl

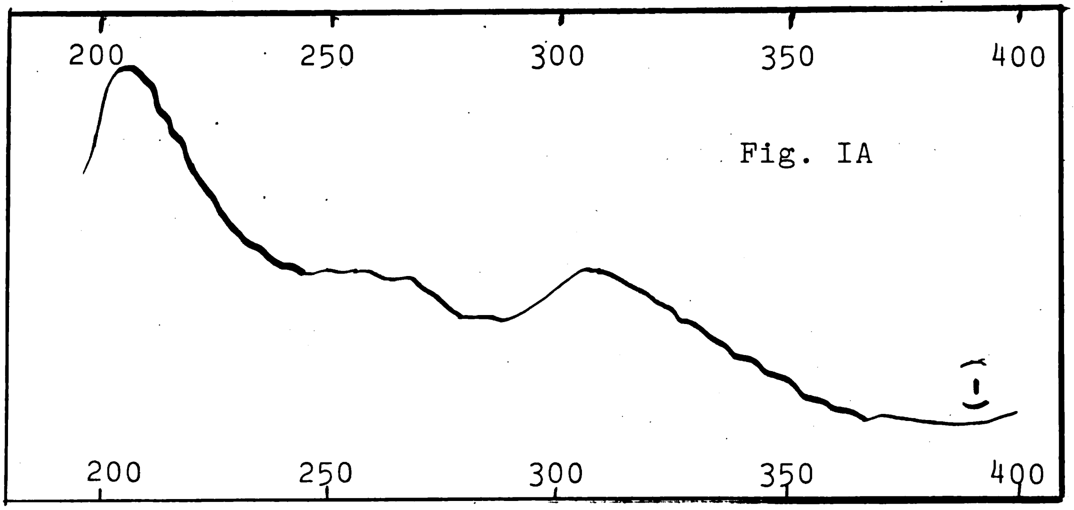


Fig. IA

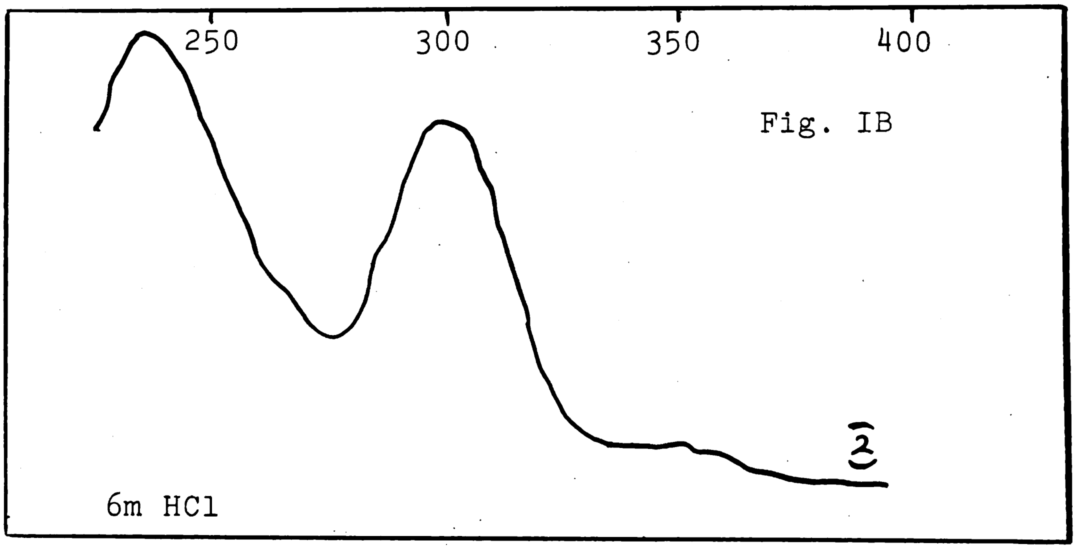


Fig. IB

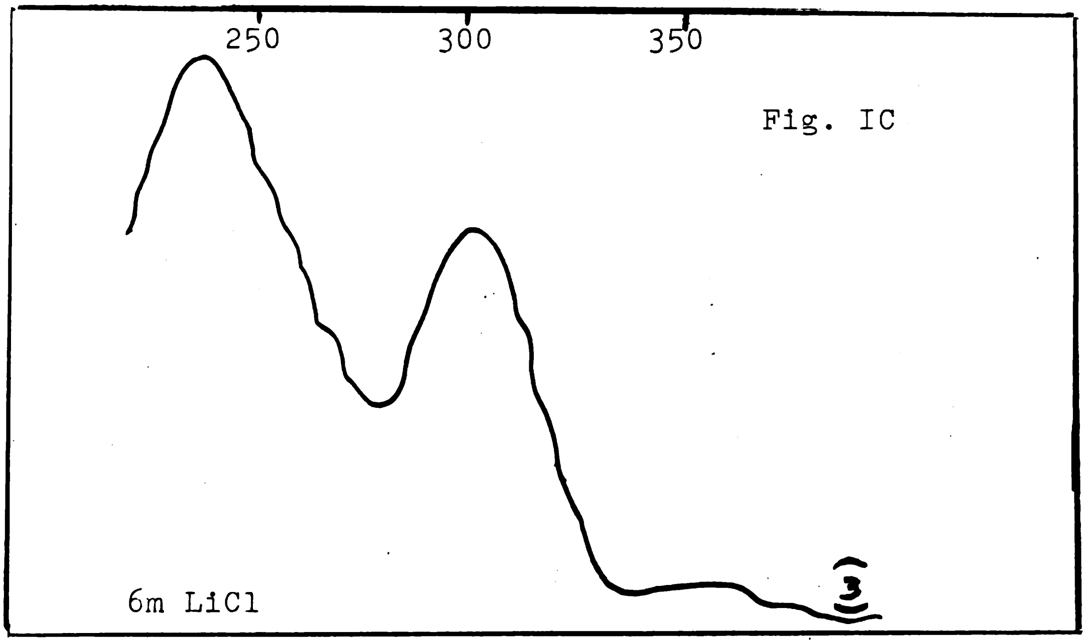


Fig. IC

bridges (26, 27, 28, 29) of the type encountered in $[Cl_5\text{-}Ru\text{-}O\text{-}RuCl_5]^{4-}$ and $[Cl_5ReOReCl_5]^{4-}$. The latter complex is in equilibrium (27) with the monomer $[ReCl_5(OH)]^{2-}$.

Salts of the series $M[MoOCl_4]$ have been reported. These have the same spectra as the $M_2[MoOX_5]$ salts indicating that the anion $[MoOX_4]^-$ easily takes up X^- ion in solution.

The spectrum of $[MoOCl_4]^{-1}$ has two bands in the visible region but the position of the band at 712 mμ differs from that found for $[MoOCl_5]^{-2}$ anion. The other ligand field band at 450 mμ occurs at the same position both in the solid and in solution but differs very little from that found for $[MoOCl_5]^{-2}$ (23).

In the presence of a moderately concentrated solution of thiocyanate there are some pronounced changes in the spectrum. In the visible region the peak at 712 mμ remains broad and diffuse but a sharp peak having an absorption maximum near 460 mμ appears. This indicates that some new complexation has occurred in solution. At very high thiocyanate concentration a new peak starts to form at 510 mμ soon after mixing. This peak continues to build up and reaches a maximum eight minutes after mixing. The peak position then gradually shifts towards shorter wavelength reaching a maximum some 80 minutes later at 460 mμ. A possible explanation of this peak shift is disscussed later.

In the ultraviolet region the shoulder at 257 mμ becomes a well-defined peak showing a very high absorption while the peak at 309 mμ remains broad and shows no change in absorbance at very high thiocyanate concentrations. Since the peak at 460 mμ is well resolved and intense, the kinetic studies of this investigation were carried out by following the absorbance at this wavelength.

D. Dimerization of $[MoOCl_5]^=$ in Solution.

Molybdenum (V) in aqueous hydrochloric acid solutions has been studied spectrophotometrically. The conditions used by various workers have often been different and it is difficult to compare their results, particularly in connection with the phenomenon of polymerization.

It is generally agreed that in HCl solutions greater than 10M the major species is $[MoOCl_5]^=$. It is also possible that the species $[MoOCl_4]^-$ is present. Decreasing the acid strength produces reduced paramagnetism and enhanced absorbance without a change in the positions of maximum absorbance (25). These observations suggest the formation of a dimer, $[Mo_2O_3Cl_8]^{2-}$ or $[Mo_2O_3Cl_4]^{2+}$ (32). The nature of the diamagnetic species is not certain but has been formulated with two oxygen bridges (31) and as a tetramer (32). Spectrophotometric and conductometric studies indicated that the species $[MoOCl_3]$, $[MoOCl_4]^-$ and $[MoOCl_5]^=$ are formed in formic acid (33). It is thus to be expected that in methanol both $[MoOCl_5]^=$ and $[MoOCl_4]^-$ can form as well as polynuclear species.

Electron paramagnetic resonance (esr) studies of the thiocyanates of molybdenum (V) (59, 34) show the presence of four nitrogen atoms per complex.

The enhanced absorbance observed with increase in chloride ion concentration may be due to the formation of $MoOCl_5^{=}$ by the addition of chloride to $MoOCl_4^{-}$ rather than to the breaking up of the dimer to monomeric species. This explanation seems plausible since a plot of the log of the absorbance versus the log of the concentration of $MoOCl_5^{=}$ shown in Figure (8) gives a slope of unity indicating one molybdenum atom per complex. However it is possible that dimers are present which do not break up upon dilution.

Hydrolysis of diammonium oxypentachloromolybdate V.

James and Wardlaw (10) proposed a number of hydrolysis products for the salts of this series. More recently Jezowska-Trzebiatoska and Mikolaj (35) conducted a study with a magnetic susceptibility method on the hydrolysis products and possible species in equilibrium in solution. From their spectroscopic data they found that several hydrolytic products are formed (36) and that these have different spectroscopic properties. While the absorption spectra changed over the HCl concentration range of 3.5 to 5.5M, the stoichiometric coefficients of hydrogen and chloride ions remained invariant and indicated a change in the intramolecular arrangement of the primary product. On the basis of these data, and taking into consideration the analytical results of Jezowska-Trzebiatowska which confirmed that two HCl molecules and one NH_4Cl molecule are detached from one molecule of ammonium oxypentachloromolybdate (V), they suggested the following hydrolytic mechanism

$$2[MoOCl_5{}^{=}] + 2H_2O \rightleftharpoons 2[MoOCl_4(H_2O)]^- + 2\ Cl^- \qquad (1)$$

$$2[MoOCl_4(H_2O)]^- \rightleftharpoons [Mo_2(OH_2)O_2Cl_6]^{=} + 2H^+ + 2\ Cl^- \qquad (2)$$

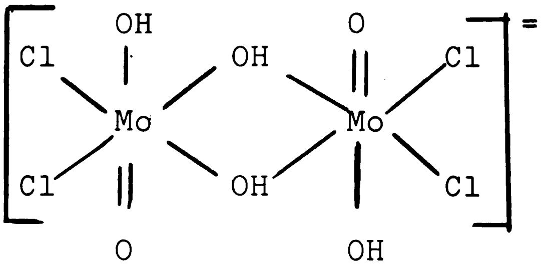
$$Mo_2(OH)_2O_2Cl_6]^{=} + 2H_2O \rightleftharpoons [Mo_2(OH_2)O_2Cl_4(OH)_2]^{=} + 2Cl^- \qquad (3)$$

$$[Mo_2(OH)_2O_2Cl_4(OH)_2]^{=} \rightleftharpoons [Mo_2O_4Cl_4(H_2O)_2]^- \qquad (4)$$

$$\begin{aligned} Mo_2O_4Cl_4(H_2O)_2]^- + 2H_2O \rightleftharpoons {} & (Mo_2O_4Cl_2(OH_2)(H_2O)_2]^{=} \\ & + 2H^+ + 2\ Cl^- \end{aligned} \qquad (5)$$

$$\begin{aligned} Mo_2O_4Cl_2(OH)_2(H_2O)_2]^{=} + 2H_2O \rightleftharpoons {} & [Mo_2O_4(OH)_2(H_2O)_4] \\ & + 2\ Cl^- \end{aligned} \qquad (6)$$

Thus two binuclear species are assumed to be in acid-base equilibrium and have the structures



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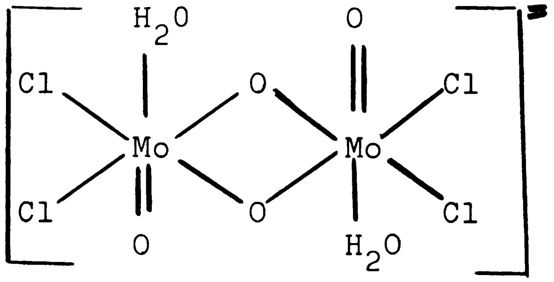


II

Magnetic susceptibility studies, absorption measurements and molecular orbital calculations have given evidence for the existence of these bimolecular complexes (37) in aqueous solutions. However it should be noted that most of these studies were carried out at very high molybdemum concentrations and it seems likely that at low concentrations ($<0.008M$) dimerization may not occur.

F. Evaluation of molybdenum to thiocyanate ratios in the complexes.

Earlier investigators used different methods to determine the ratios of molybdenum to thiocyanate in these complexes. Hiskey and Meloche (2) obtained the ratio 1:3 by considering the effect which a variation of the thiocyanate concentration has on the equilibrium constant for the reaction. From their results they concluded that only one complex exists in solution but they admitted that this ratio was not established with stoichiometric exactness from their data. Perrin (1) recognized, using 60% acetone-water mixtures, that the continuous variation method gave a rather diffuse absorbance maximum with a thiocyanate to molybdenum ratio between 2 and 3. He noted that at greater mole fractions of thiocyanate ion the absorption shifted to longer wavelengths but its position was not sufficiently sharp for accurate location. Thus in his determination of the association constants of the complex he assumed the ratios 2:1 and 3:1 in the development of his equations. Constant values for the association constants formed his basis for confirming the existence of these complexes.

Babko (3) had earlier obtained a ratio of 5:1 by use of different procedure based on the variation of absorbance of solutions with reactant concentrations. Thus there has not been agreement on this question. In the present investigation no prior assumption was made about the ratio of thiocyanate to molybdenum in these complexes.

III Experimental

Preparation and purification of materials.

Diammonium oxypentachloromolybdate (V) was prepared by electrolysis. Chilesotti (51) first showed that by electrolytic reduction of molybdenum trioxide dissolved in hydrochloric acid of appropriate concentration, a solution containing molybdenum (V) could be obtained if a platinized platinum cathode was used. This principle was utilized in the preparation of diammonium oxypentachloromolybdate (V).

Molybdenum trioxide (15g) was heated with 75 ml of concentrated hydrochloric acid until dissolved. The solution was evaporated to 37 ml, filtered and made up to 75 ml with the acid. It thus contained 20 percent molybdenum trioxide in 9N-HCl.

The solution was diluted with an equal volume of water and placed in the cathode compartment of a diaphragm cell. The anode compartment contained hydrochloric acid (5N). A polished platinum electrode served as the anode, while the cathode was of platinized platinum. A current of 2.5 amperes was employed and on reduction to the quinquevalent state, a reddish-brown cathodic solution was obtained. This solution was concentrated to 50 ml under diminished pressure, a 30 ml sample of ammonium chloride (9g, 5M) solution was admitted and the mixture heated for one minute. On saturating with hydrogen chloride gas and cooling, emerald green crystals separated. These were recrystallised by dissolving in a minimum volume of water at 80° and saturating with hydrogen chloride gas until it had cooled to 25°. The crystals were washed with hydrochloric acid and dried in a vacuum over solid potassium hydroxide. The methanol (ACS certified) was dried over Drierite and distilled prior to use.

Since a solution of $(NH_4)_2MoOCl_5$ in methanol shows a decrease in absorbance on standing for long periods, fresh solutions of this reagent were prepared five minutes before use. Appropriate amounts of $(NH_4)_2MoOCl_5$ were accurately weighed and dissolved in calculated volumes of methanol.

The thiocyanate solutions were also prepared just before use. Ammonium thiocyanate was dried in an oven at 100°C then allowed to cool in a desiccator. The calculated amount was weighed out and made up to volume in a volumetric flask.

In cases which required constant ionic strengths calculated amounts of lithium perchlorate were added to the solutions. Reagent grade lithium perchlorate was dried in an oven and allowed to cool in a desiccator. This salt was chosen because the perchlorate ion has little tendency towards complex ion formation.

B. The stopped-flow apparatus.

Hartridge and Roughton (43) introduced a method for studying reactions with half-lives as short as a few milliseconds. The method involves forcing two reactants into a special mixing chamber and determining the composition of the mixture after suddenly stopping the fluid. More detailed descriptions of this type of apparatus can be found in the references (44, 45, 46, 47, 48, 49, 50). Since it was found that air had no effect on the reaction, it was not necessary to use a closed system.

The apparatus consisted of two glass syringes from which the reactants can be forced into a mixing chamber. These syringes were also connected to reactant reservoirs with a two-way stopcock. All of these components were mounted on a framework of properly cut aluminum plates bolted together and attached to a metal table. The other parts of the apparatus are: a lever mechanism for pushing the syringes; a light source (tungsten lamp); a monochromator and appropriate lenses; and a photomultiplier. Rapid mixing of the reactants was accomplished by pushing the plungers manually. The reactants were forced up into the mixing chamber and then into the observation tube and through a Teflon solenoid valve which stopped the flow when a microswitch was tripped. This switch also triggered an oscilloscope which monitored the photomultiplier current.

The mixing chamber was constructed of Pyrex. Four jets of internal diameter 1.0 mm were arranged tangentially to the bore of the observation tube which was 1.9 mm in internal diameter.

The reactions were followed by measuring the changes in light absorption as a function of time. Light from the tungsten lamp passed through the monochromator and was focussed on the center of the observation tube. After passing through the reacting mixture the light was focussed onto a photomultiplier tube. The response was amplified and displayed on the screen of the oscilloscope. The trace so obtained was photographed and analysed. Figures 18 a, b show typical traces obtained in this way.

The rapid-scanning monochromater used in several experiments has been described elsewhere (58). These experiments were performed with the help of Mr. Earl Hansen. esr measurements were made on a Varian X-Band Spectrometer by Mr. Vincent Nicely.

IV Results and Discussion

A. Association constants for the complexes.

A number of workers have attempted to determine the association constants for the various species existing in solution. Perrin did the pioneer work on this and obtained various values for these constants on the basis of the following mechanism (using Perrin's notations):

$$Mo(V) + CNS^- \rightleftharpoons Mo(V)(CNS) \qquad \log K_1 = 1.7 \pm 0.22$$

$$Mo(V)(CNS) + CNS^- \rightleftharpoons Mo(V)(CNS)_2 \qquad \log K_2 = 3.54 - 3.08$$

$$Mo(V)(CNS)_2 + CNS^- \rightleftharpoons Mo(V)(CNS)_3 \qquad \log K_3 = 3.54 - 2.68$$

His method involved separating the absorbance into its contributions from the different species by assuming no absorption from the 1:1 complex.

In the present investigation the method due to Newman and Hume (40) was employed. To determine the association constant for the highest complex, Equation 18 of the Appendix is plotted as $\log \frac{Ao - A}{A}$ against $\log X_t^m$.

Values were assumed for m such that the slope was unity. From the plot, Fig. (2A), K_n was found to be $2.72 \pm 0.21 \times 10^4$. The value of m which gives the proper slope is two. This value represents the number of ligand groups added to the lower complex to give the higher complex. Thus this mechanism can be pictured as

$$[MoO(SCN)_{n-2}Cl_{n-3}]^= + 2(SCN^-) \rightleftharpoons MoO(SCN)_nCl_{5-n}]^= + 2\ Cl \qquad (1)$$

For equation 18 to hold the concentration of the ligand has to be much greater than that of molybdanum.

However in order to determine the association constant of the lowest complex the experiment was carried out with the concentration of the ligand comparable to that of the molybdenum. A new set of equations was developed for this case and a plot of equation 23 (see Appendix) as

$$\log \frac{A - A_o' \frac{Mt}{Mo}}{A_o'' \frac{Mt}{X_o} - A} \quad \text{versus} \quad \log [X_t - 2 \frac{A - A_o' \frac{Mt}{Mo}}{\frac{A_o''}{X_o} - \frac{A_o'}{Mo}}$$

gave a straight line of slope 2 and an intercept log K = 2.38. The slope obtained agrees with that expected and establishes the mechanism as

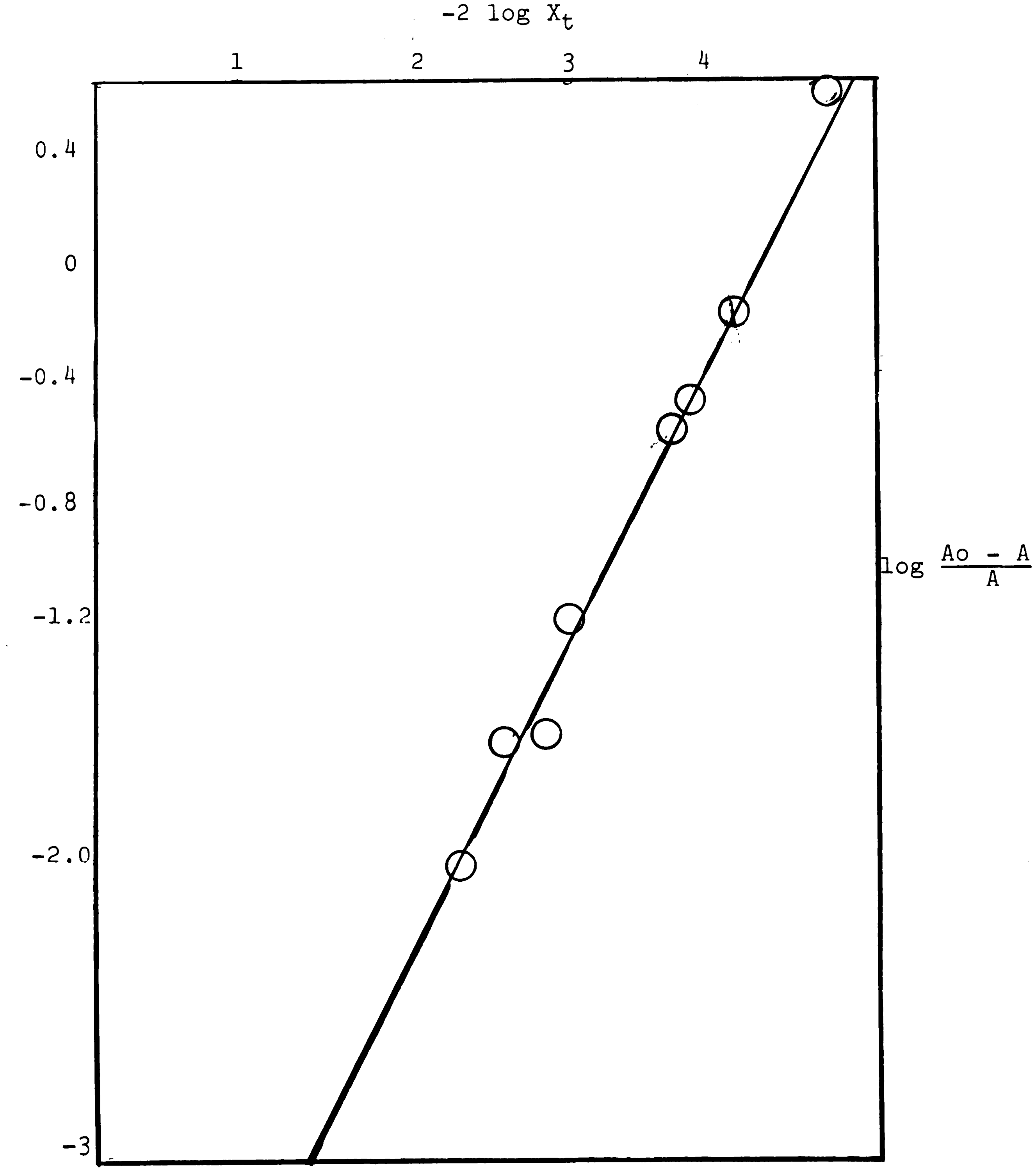
$$[MoO(SCN)_2Cl_3]^{=} \rightleftharpoons [MoOCl_5]^{=} + 2(SCN^-) \qquad (2)$$

or

$$[MoOCl_2(SCN)_2MeOH]^- \rightleftharpoons [MoOCl_4MeOH]^- + 2(SCN^-) \qquad (3)$$

The values of n in equation 1 above remains to be evaluated. The ratios of the thiocyanate to molybdenum in the different species were determined by continuous variation method.

In this determination two distinct colors were observed. The first is yellow and forms at low molybdenum to thiocyanate ratios soon after mixing. The other, which is amber, forms at higher molybdenum to thiocyanate ratios and takes a long time to attain maximum absorbance. In view of this, the continuous variation method was carried out in two stages, namely; one minute after mixing, and 195 minutes later. Various ratios ranging from 1:1 to 1:8 were chosen.



log K = 4.36

Fig. 2

Determination of the highest complex with 2 species, one absorbing.

Table 2

Data for the Determination of the Association constant for the Highest Complex

$2 \log X_t$	$\log \frac{A_o - A}{A}$
4.83	+0.57576
3.066	-1.5965
4.3186	-0.17386
4.0686	-0.4559
2.43	-2.0386
3.782	-0.5597
3.1804	-1.1818
2.694	-1.5965

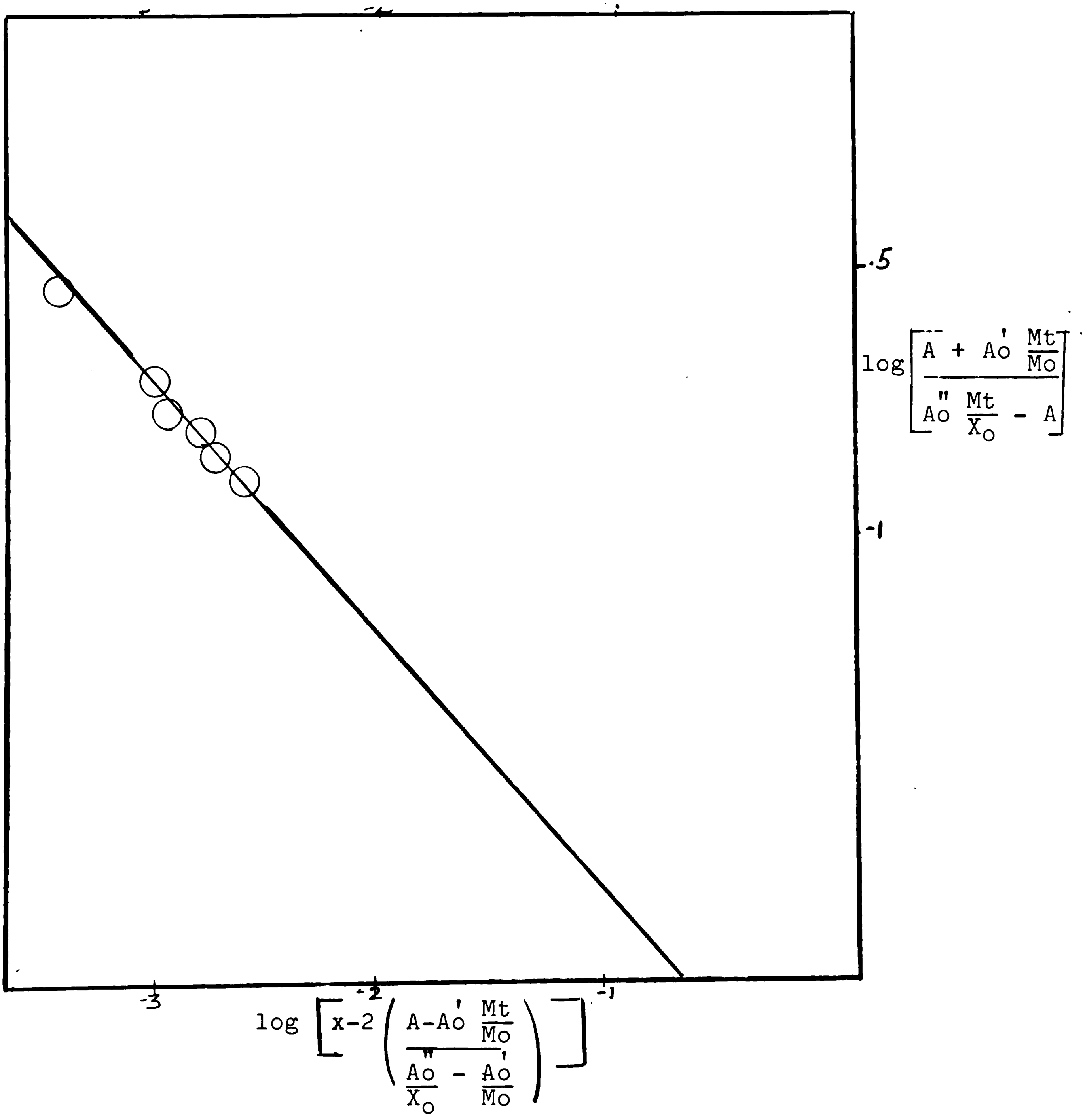


Fig. 3

Determination of the association constant for the lowest complex with 2 species both absorbing.

Table 3

Data for the Determination of the association constant for the lowest complex

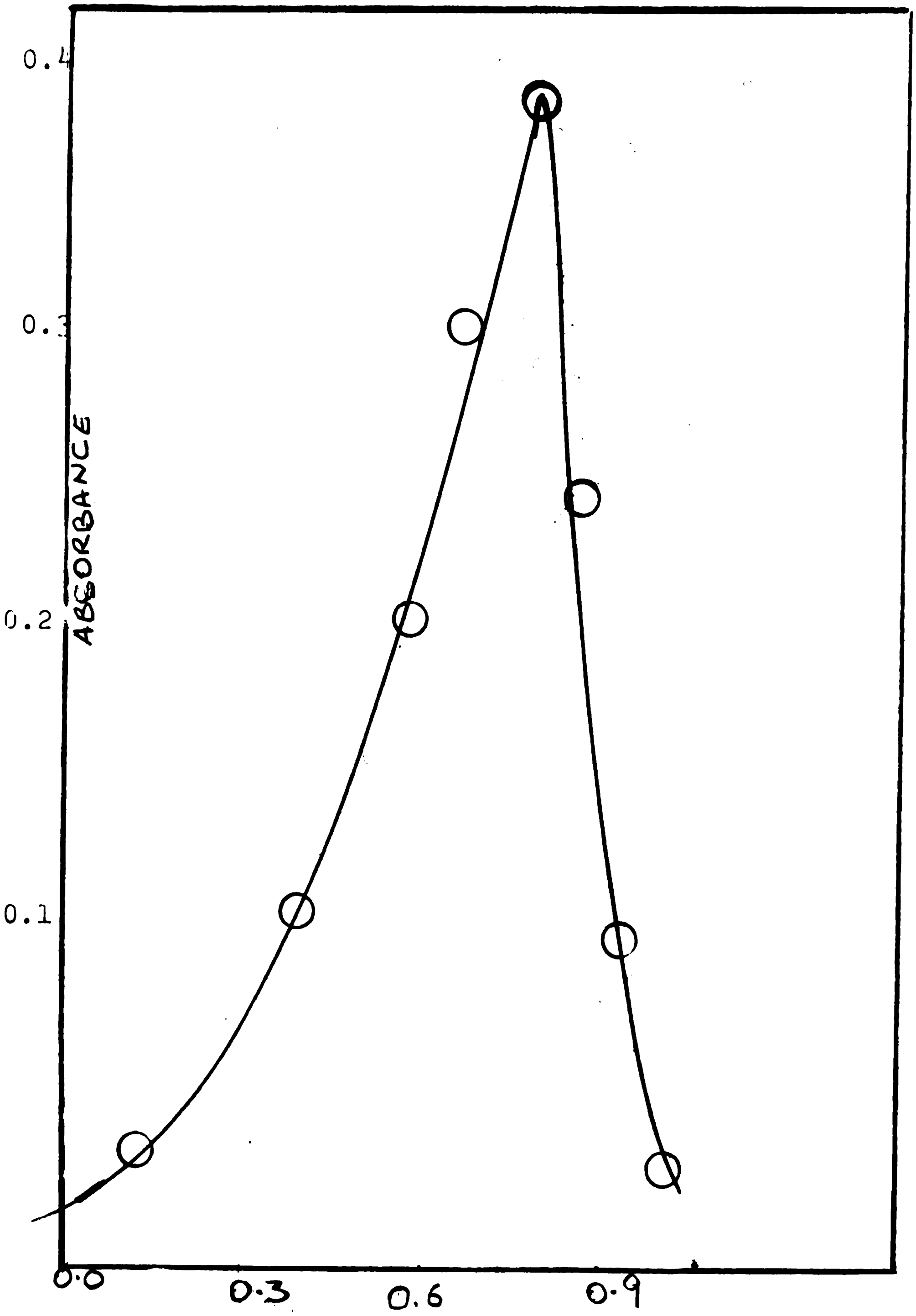
$\lambda = 460$

$\log \dfrac{A + A_o' \frac{M_t}{M_o}}{A_o'' \frac{M_t}{X_o} - A}$	$2 \log\left[X - 2 \dfrac{A - A_o' \frac{M_t}{M_o}}{\frac{A_o''}{X_o} - \frac{A_o'}{M_o}}\right]$
-0.6456	-1.9735
0.47893	3.438
0.7503	2.61
0.645	2.66
0.6914	2.941
0.7158	2.92
0.653	3.053
0.6063	3.075

Fig. 3 shows that one minute after mixing the highest absorbance was recorded for the mixture whose molybdenum to thiocyanate ratio is 1:2. This suggests that the species probably formed during this time interval is the 1:2 complex. This confirms the results of the determination of the association constant for the lowest species which indicated that this species contains two ligand groups per atom of molybdenum.

After a long time interval, as shown in Fig. 4 , the highest absorbance occurs for the 1:4 ratio. It follows from this that the complex which has the highest absorbance is the 1:4 complex, whose formation constant is 2.72 x 0.21 ± 10^4. Since the highest complex contains four thiocyanate groups per molecule the value of n in equation 1 above is four. Thus the two important complexes existing in solution and which are in equilibrium after a considerable time are the 1:2 and 1:4 complexes.

From the structure of the complex, it was expected that five ligand groups would be present in the highest complex. In fact, Babko (3) claimed that such a complex exists in methanol and absorbs at 500 mμ and reaches its maximum absorbance in eight minutes. The spectra shown in Figure 5 were obtained by use of a concentration of molybdenum of 0.0025M while that of thiocyanate was 0.3M. It is seen that soon after mixing the build-up starts around 505 mμ and reaches a maximum in eight minutes. Once this maximum had been attained, the peak position gradually shifted towards shorter wavelength. The maximum absorbance was reached after 83 minutes at a wavelength of 460 mμ.



Mole Fraction of [SCN]

Fig. 4

Continuous Variation Plot at Time One Minute after Mixing.

If the initial build up was due to the formation of the 1:5 complex, it follows that this species changes with time to some other complex absorbing in the region of the 1:4 complex.

B. Evidence against Dimer Formation

It was found that for a given molybdenum concentration, the absorbance increased as the concentration of added thiocyanate increased. However the absorbance upon dilution obeys Beer's law and yields a straight line as long as the concentration of thiocyanate is not much larger than that of molybdenum. When the concentration of the thiocyanate is much larger than that of molybdenum the absorbance reaches a maximum indicating that the highest complex species has been formed. Figure 6A shows the Beer's law plot for thiocyanate concentrations in the region of 10^{-3}M while Figure 6B is the plot for higher thiocyanate concentrations. Beer's law plots for various solutions containing 1:4 ratios of molybdenum to thiocyanate can be seen in Figure 7. Soon after mixing, the law does not hold but after 1 1/2 hours a straight line results.

To determine whether there was dimerization of molybdenum (V) as many workers have suggested for aqueous systems, a log-log plot of absorbance _versus_ total concentration was made. Figure 8 shows the straight line that results. The slope of one indicates that there is but one molybdenum atom per molecule of the complex. This result which seems to indicate the absence of

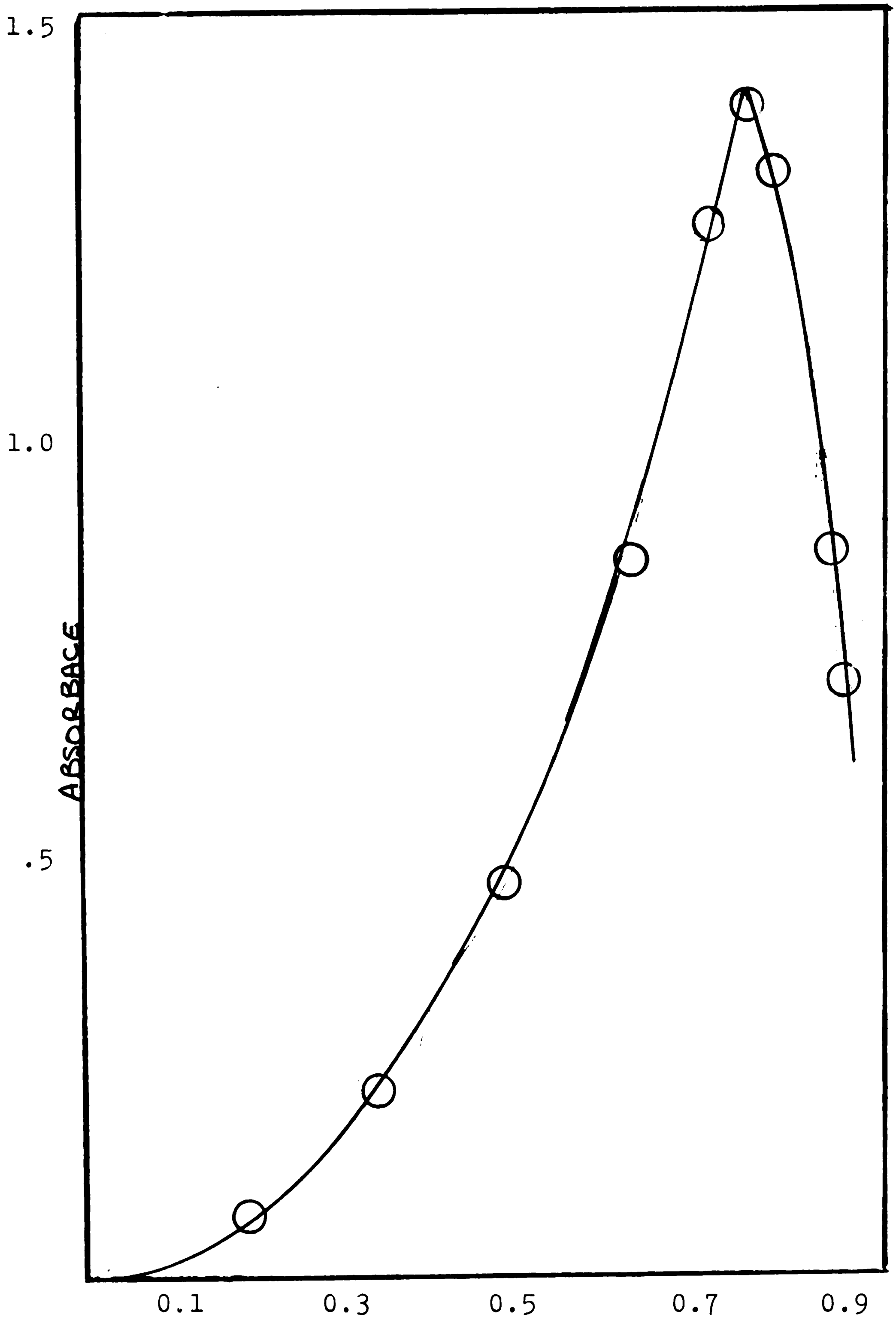


Fig. 5

Continuous variation plot at time = 195 min. after mixing.

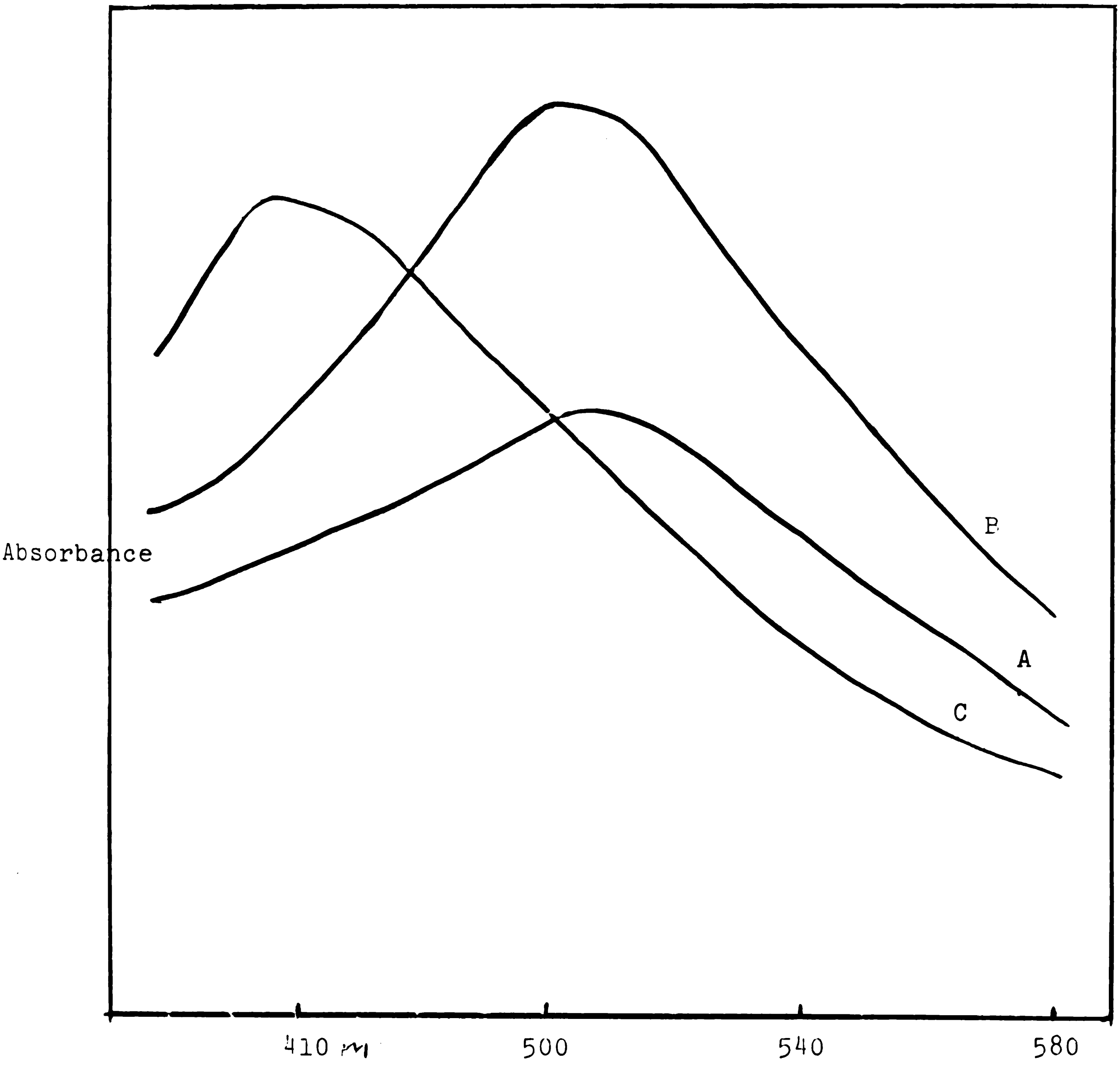


Fig. 6

Shift in wavelength with time at high thiocyanate concentration.

Curve A Time = 1 Min.

Curve B Time = 8 Min (Max. absorbance reached at λ = 505mμ

Curve C Time = 83 Min. Peak shifted to λ = 460mμ dimers, may not be conclusive since it is possible that non-dissociating dimers might have formed.

Electron paramagnetic resonance measurements throw more light on this problem. As in earlier work on this complex (59) nitrogen hyperfine interaction was observed on the central line arising from the interaction of molybdenum isotopes for which I=0,with the paramagnetic electron. These hyperfine structures, shown in Figure (9) consist of nine equally spaced lines having an intensity distribution which shows interaction of the paramagnetic electron with four equivalent nitrogen nuclei. This also gives strong evidence that the thiocyanate bonds through the nitrogen rather than through sulfur.

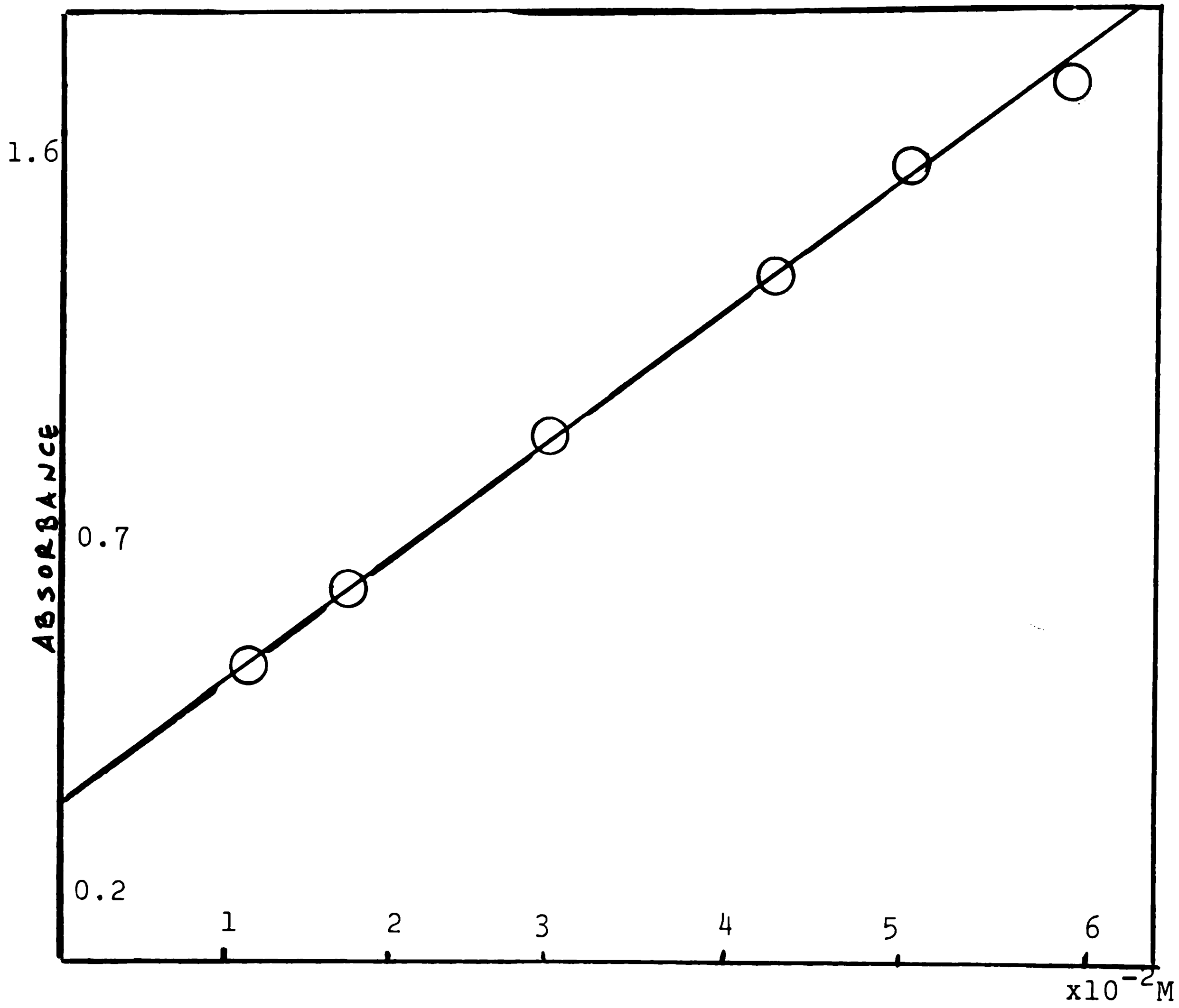


Fig. 7

Beer's law plot for the complex at
moderate concentrations

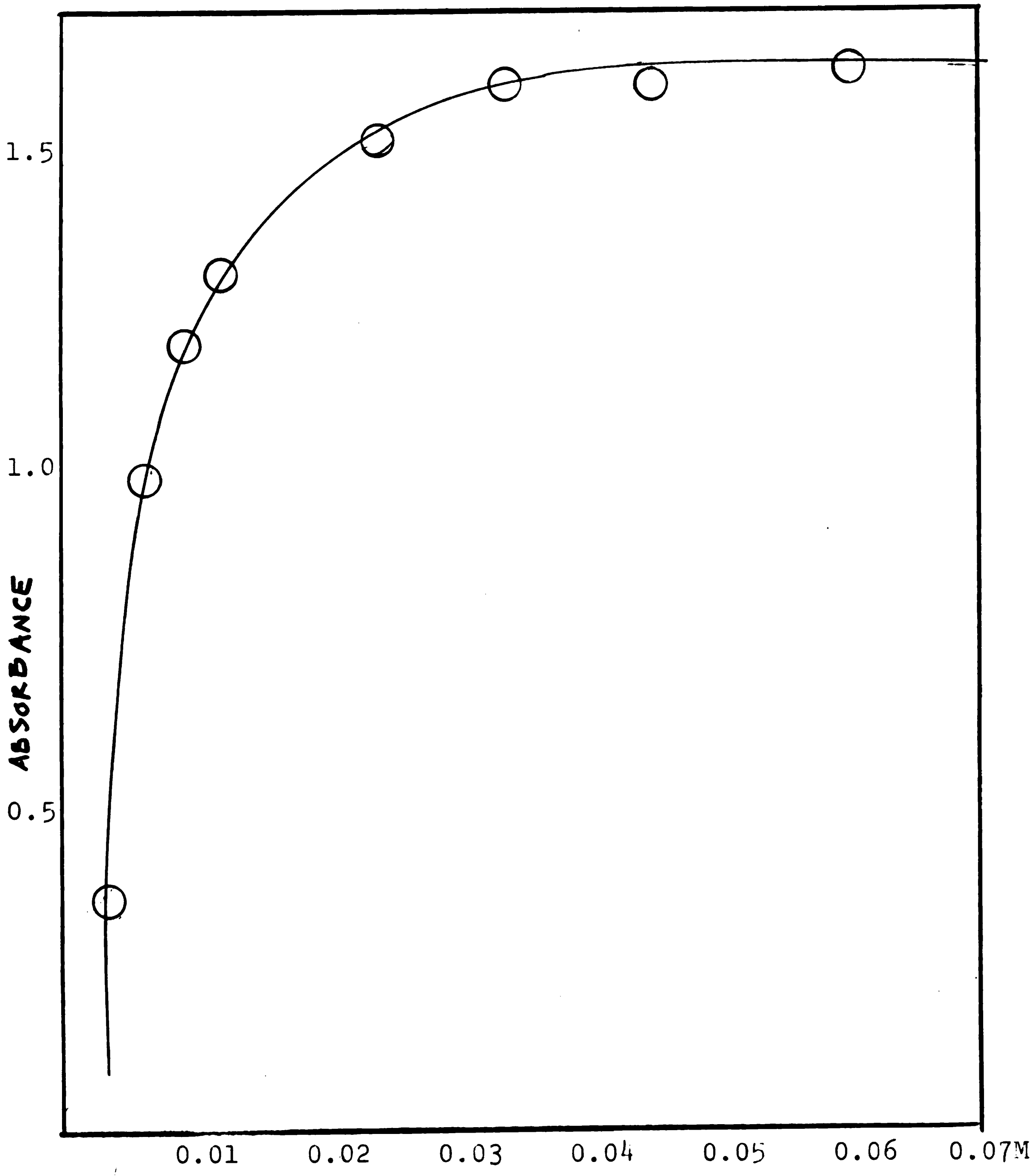
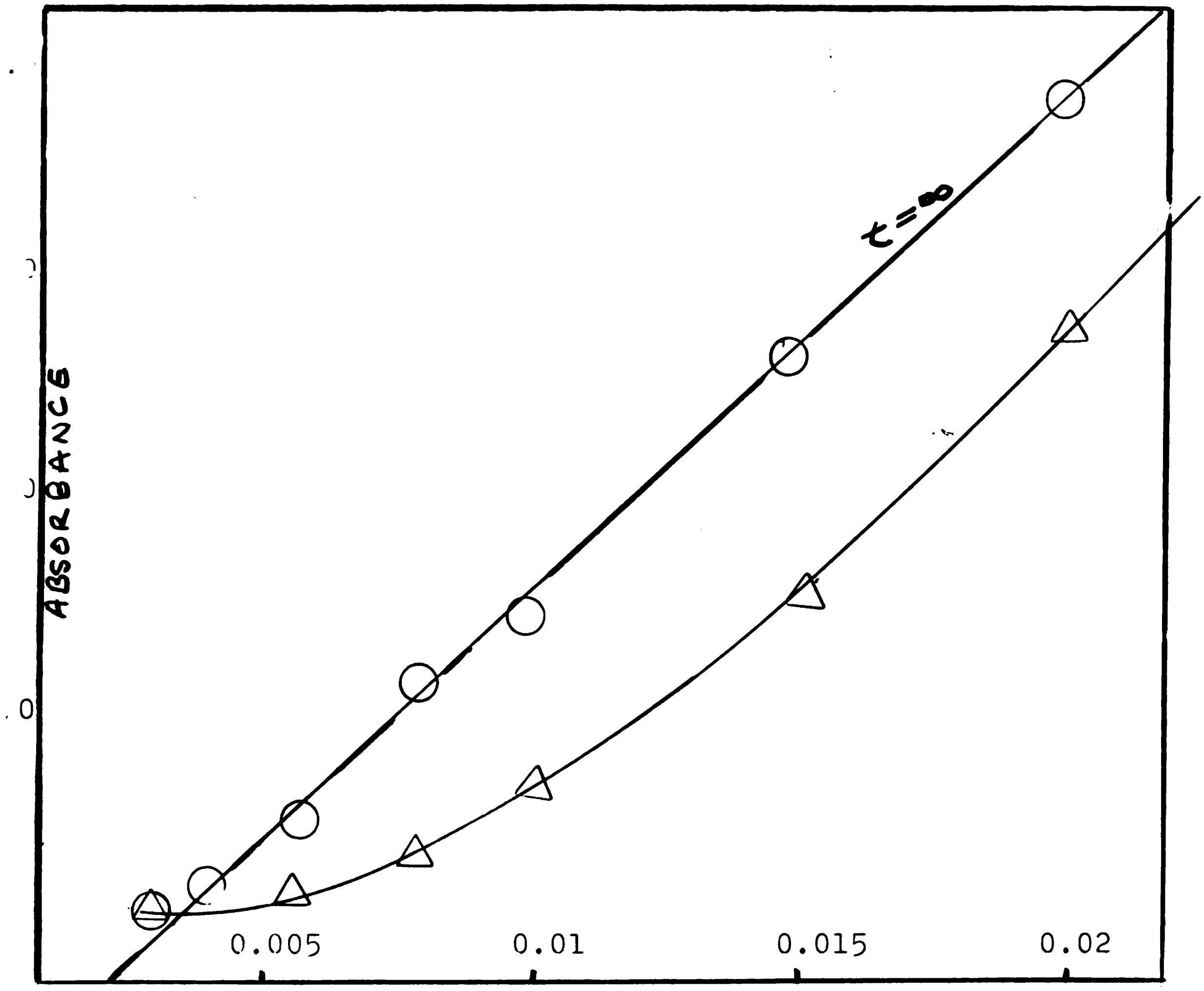


Fig. 8

Beer's law plot for the complex at high thiocyanate concentrations



Concentration of the complex

Fig. 9

Beers law plot for 1:4 complex
at infinite time and time zero

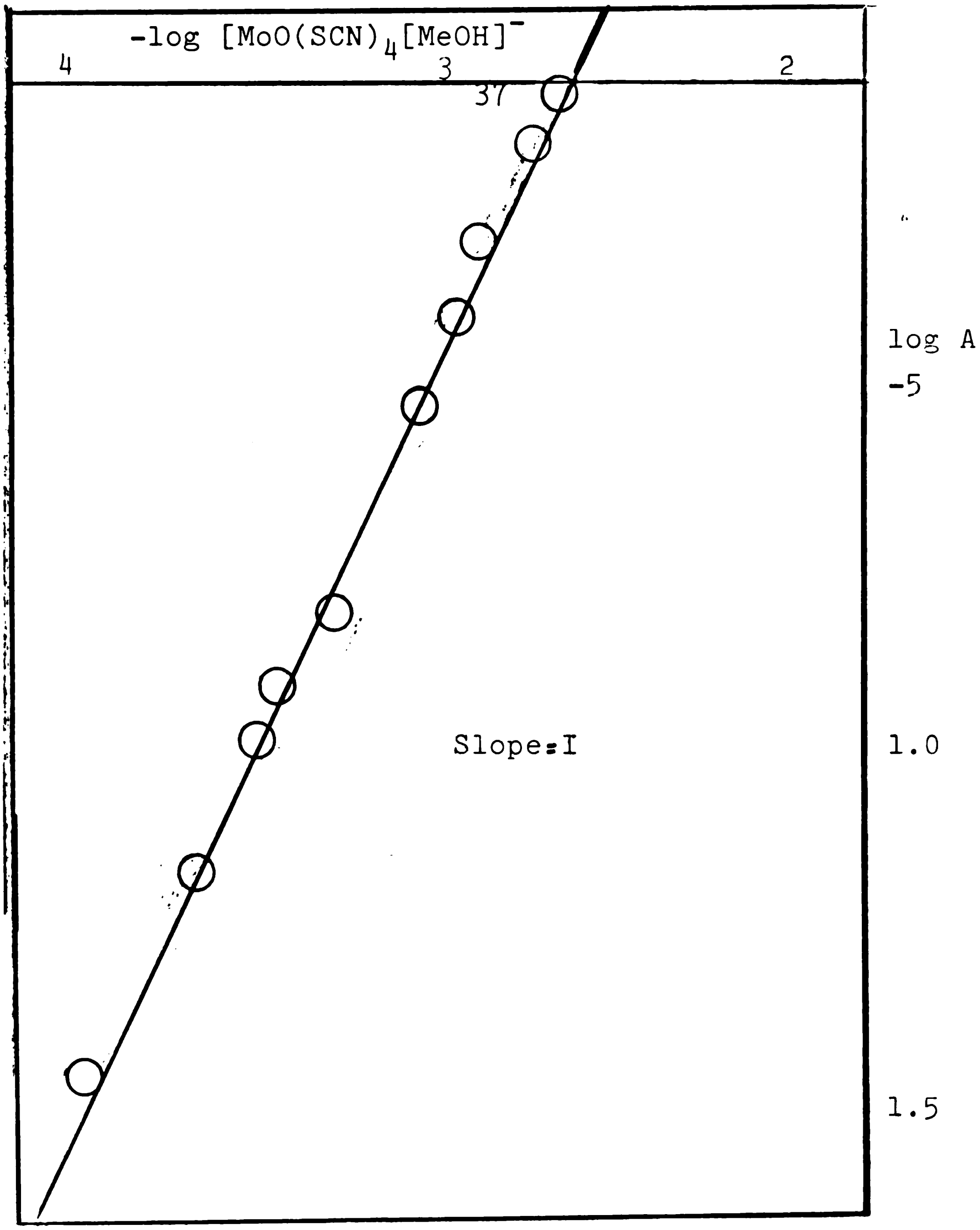


Fig. 8

Log plot of Beer's law for the complex at moderate concentrations of thiocyanate.

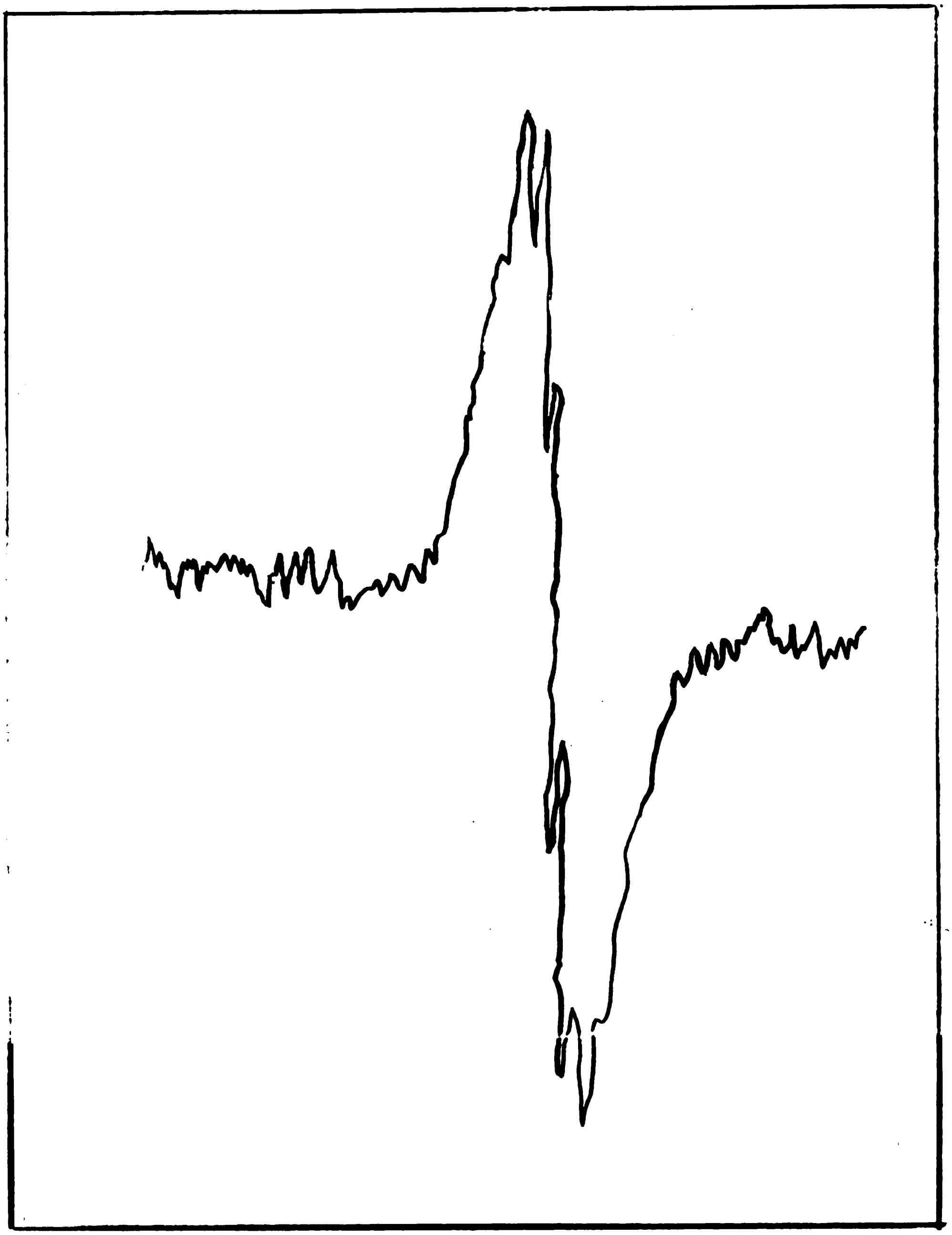


Fig. 11

Frozen glass epr spectrum of complex
at high ligand concentration.

If dimers were present initially or formed by reaction in the concentration range studied it would be expected that there would be a change in the esr spectrum with time. No significant change with time was observed and it is reasonable to conclude that in the concentration range studied there was either no dimerization or that the degree of association of these dimers did not change with time. In most investigations on the dimerization of molybdenum(V)the lowest concentration used was about 0.01 molar. Among the latest works are those of I.N. Marov and co-workers (60) who used esr methods to establish the presence of dimers in concentrations greater than 0.01 Molar. R. Colton and G. G. Rose (61), also working at high concentrations, concluded that the diamagnetic species $[Mo_2O_3Cl_8]^{-2}$ containing an oxo bridge, was present.

The presence of only four nitrogen nuclei in the esr measurements is noteworthy. Five nitrogen atoms were expected as indicated earlier. Neither the continuous variation method nor the esr investigation has shown any evidence in support of the 1:5 complex. However, it is misleading to state that splitting due to four nitrogen nuclei establishes the presence of a 1:4 complex. It is probable that the fifth nitrogen, axial to the oxygen atom, is not esr sensitive since its bonding to molybdenum is different.

The esr Spectrum of a mixture containing only a 1:2 ratio of molybdenum to thiocyanate is shown in Figure (10) This indicates no nitrogen interaction. However, it cannot be concluded from this that the 1:2 complex does not form but rather that only a minor amount of the 1:4 complex forms in this case. This is confirmed by the optical spectrum which show little change of a 1:2 mixture even upon long standing.

That ligand substitutional equilibria exist in a solution containing molybdenum (V) and thiocyanate was established by D. I. Ryabchikov and his co-workers (62, 63). It was decided to analyse the system on the basis of a simple kinetic law. Preliminary investigation with the stopped-flow apparatus showed, at very low ratios of molybdenum to thiocyanate, a very rapid formation of an absorbing species. As the thiocyanate to molybdenum ratio was increased, it appeared that this initially-formed species was "swamped-out" by the slower build-up of a more highly absorbing species. It is speculated that the first species formed is the 1:1 complex and this is regarded as the starting species for the subsequent absorbance build up at higher thiocyanate concentrations caused by the appearance of a 1:2 complex.

Table (4) shows the values of K_{pseudo} for the different thiocyanate concentrations when the concentration of molybdenum is 0.004113M and ionic strength 0.26M. Figure (13) is the plot of K_{pseudo} against the concentration of thiocyanate. It is evident that as the thiocyanate concentration increases initially the value of K_{pseudo} decreases and reaches a minimum when the ratio of molybdenum to thiocyanate is between 1:2 and 1:3. In this region it is assumed that there is a rapid formation of some species, presumably the 1:1 complex. This build up, as shown in picture IA, page (56), is complete in less than 0.025 second. It is speculated that at higher thiocyanate concentrations this complex becomes the starting species for the subsequent build-up of the 1:2 complex.

After this minimum, K_{pseudo} increases with the concentration of the thiocyanate. The values of K_{pseudo} in this region is taken as that appropriate to the formation of the 1:2 complex. It is speculated that with further increase in the concentration of the ligand the 1:2 species is slowly replaced by a 1:4 complex. This was shown by following the formation of the 1:4 species using a Unicam Sp. 800 with a constant wavelength scanner. It was noted that the initial absorbances (i.e. after one minute) for all mixtures with ratios greater than 1:2, were equal. However the subsequent build-up depended upon the thiocyanate concentration. It is reasonable to conclude that the equal absorbances at short times is due to the presence of the 1:2 complex.

In order to investigate this system further the rapid scanning monochromator was used. It was observed that an absorbing species formed rapidly. This formation soon reached a maximum and the absorbance suddenly began to decrease. The decrease also reached a minimum after which the absorbance built up to and above the former value. It was thought that such an irregular behavior was due to a leak in the solenoid. The same behavior was noted

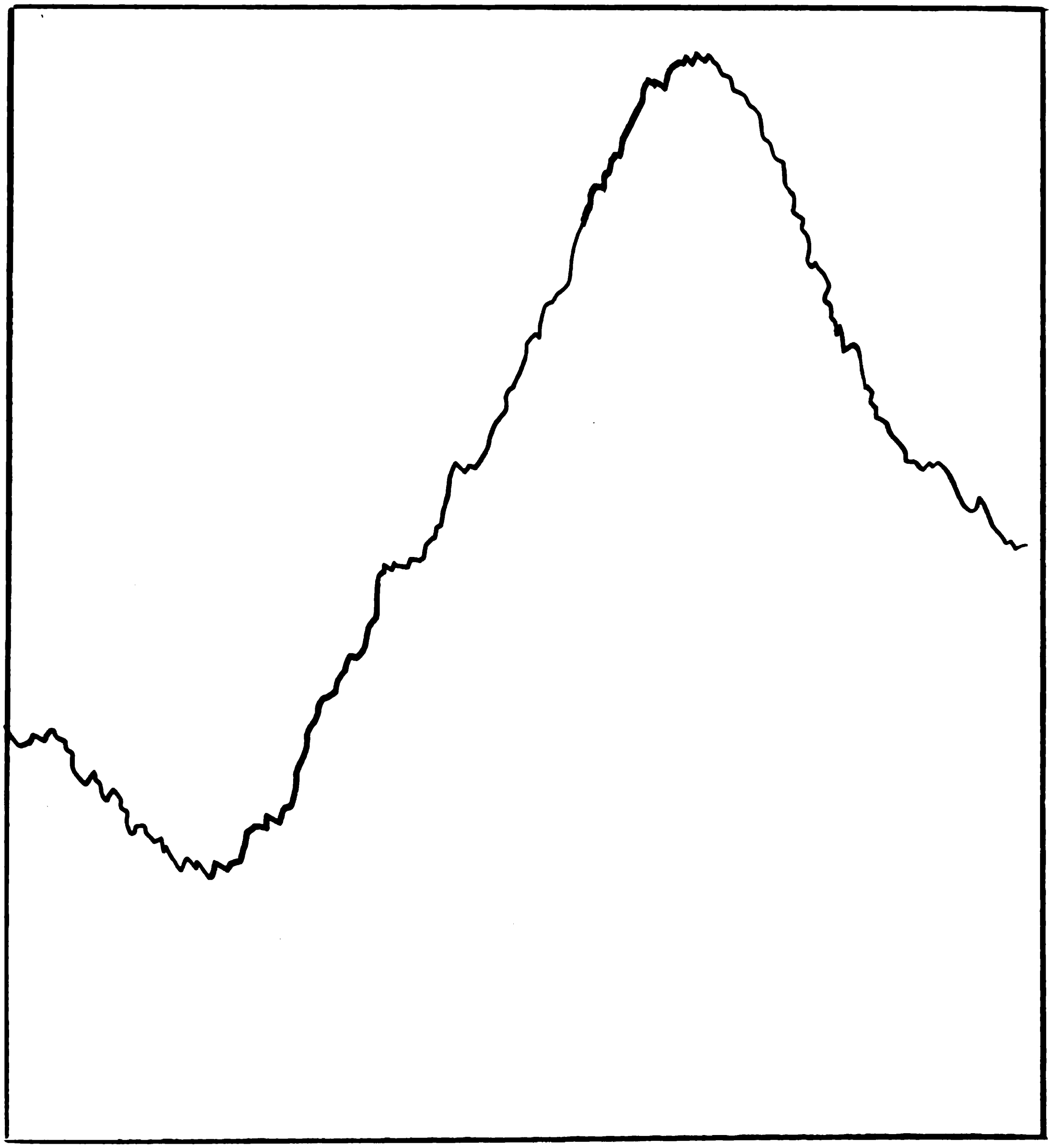


Fig. 12

Frozen glass epr spectrum of 1:2 complex

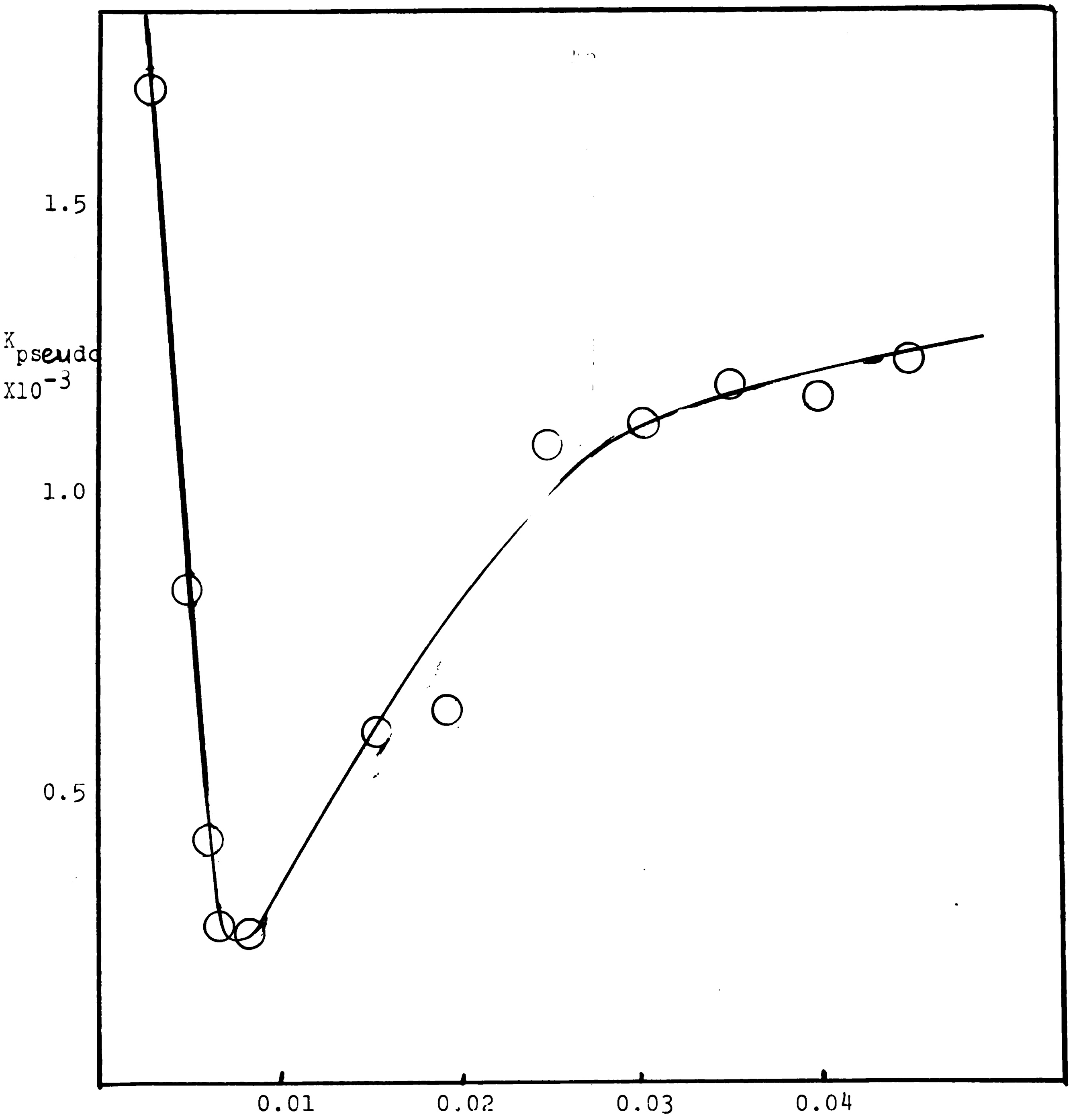


Fig. 13

Plot of K_{pseudo} versus ligand concentration

Table 4

$(NH_4)_2MoOCl_5$ = 0.004113M μ = 0.26

Valves of K_{pseudo} for Different (SCN^-)

$[SCN^-]$	K_{pseudo}
0.0025967	1670 sec^{-1}
0.0047606	834
0.005798	415
0.00669	245
0.008028	260
0.0103869	593
0.0151475	554
0.020241	623
0.0251017	1083
0.0302951	1091
0.0350558	1184
0.0402492	1148
0.0450099	1233
0.0502034	1313

even when the stop-cock close to this solenoid was closed after mixing. Such a behavior could not be effectively accounted for but the analysis of the initial rise in absorbance gave results which agreed with those of the fixed-wavelength stopped-flow apparatus at high thiocyanate concentrations. However, at low concentrations the values of K_{pseudo} were much smaller. This could probably have resulted from subtraction of the background absorbance which could have eliminated the very fast part of the build-up. Table (III) shows the values of K_{pseudo} obtained from the Rapid Scanning Monochromater.

It was observed that during the initial build up in absorbance there was a pronounced change in the peak shape as shown in Figures (14a,b,c,d). The change in peak shape is more pronounced at low thiocyanate concentrations. A well-shaped peak is formed one minute after mixing. From this change in the peak shape one concludes that at least one new species was being formed in the solution. This is supported by the fact that as the peak forms it moves towards a longer wavelength. Increasing the ratio of molybdenum to thiocyanate, as seen in Figure 14 (c & d) gives a smooth peak much earlier than at lower ratios.

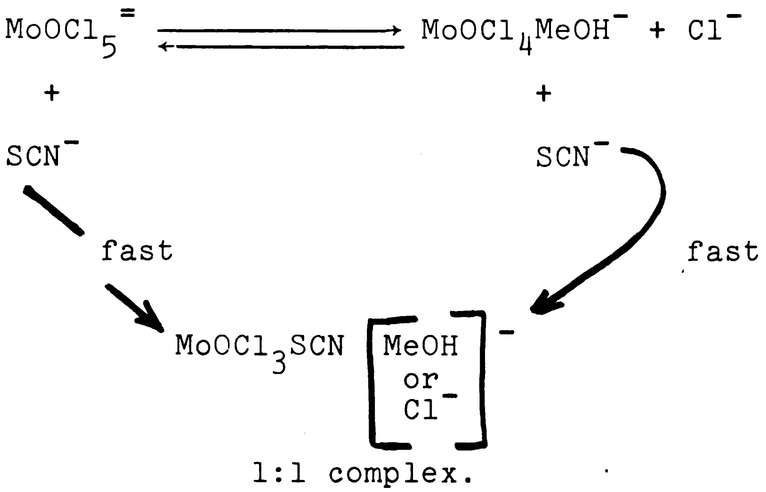
This observation supports the speculation that at very low ratios of molybdenum to thiocyanate, the 1:1 complex forms rapidly and becomes the starting species for the formation of the 1:2 species.

The dependence of K_{pseudo} on the ionic strength was investigated in order to determine the charges on the reactants. A graph of log K_{pseudo} against the square root of the ionic strength, shown in Figure 15, was made. From this plot a slope of 4.1 was obtained. The calculated value of the slope, by use of the Debye-Huckel limiting law and by assuming a charge of -2 on the principal reactant, is 16. The value actually obtained indicates that two species each having a unit negative charge are involved in the rate determining step. Such a unit charge on the principal reactant would be possible if one of the chloride ions were displaced by a molecule of methanol prior to the reaction. A second possibility is the formation of ion-pairs in solution. Methanol has a low enough dielectric constant that over the concentration range used, ion pairs such as

$$M^{+} . MoOX_5^{=}$$

are probably important.

This behavior suggests the following as the initial mechanism:



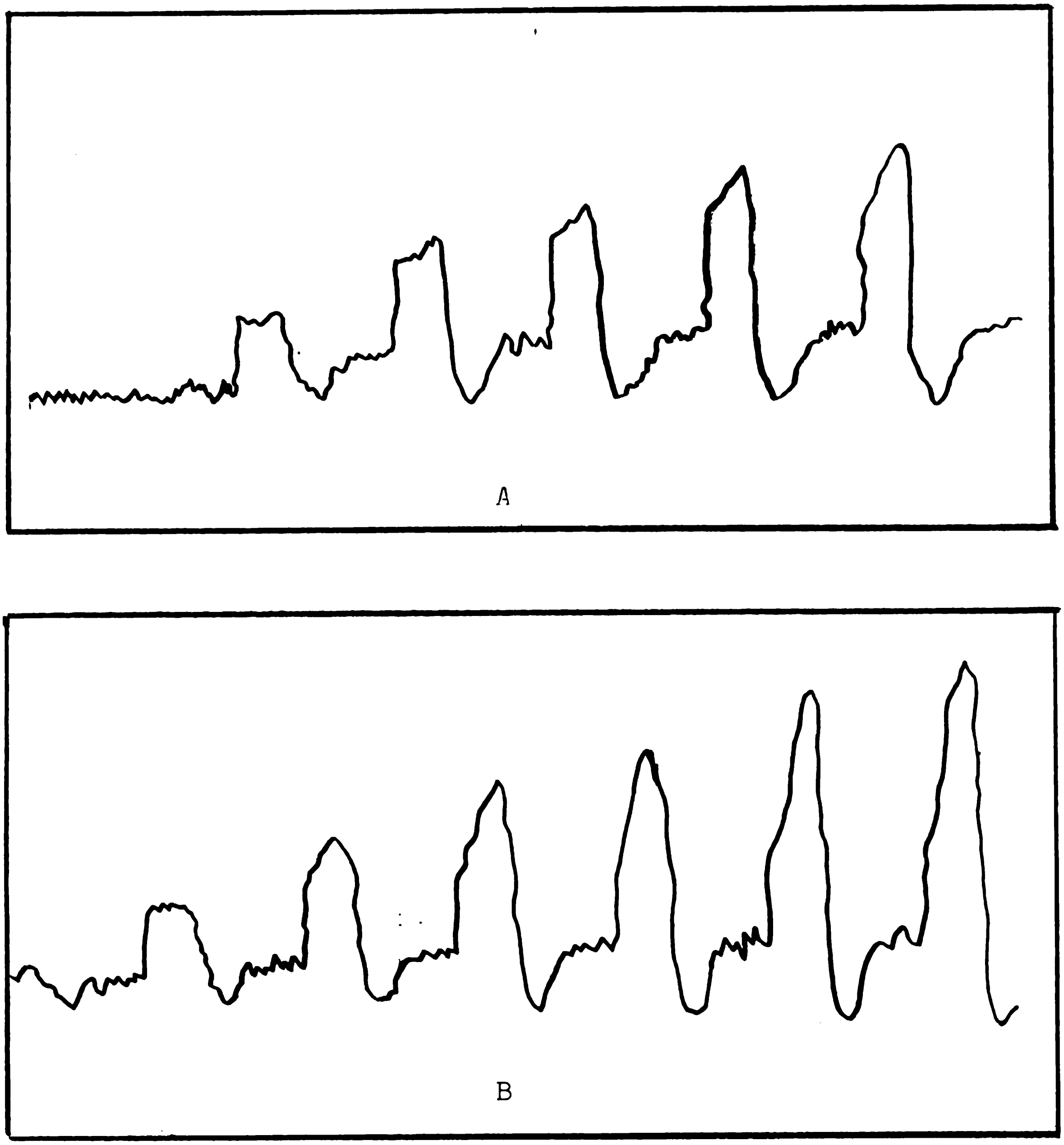
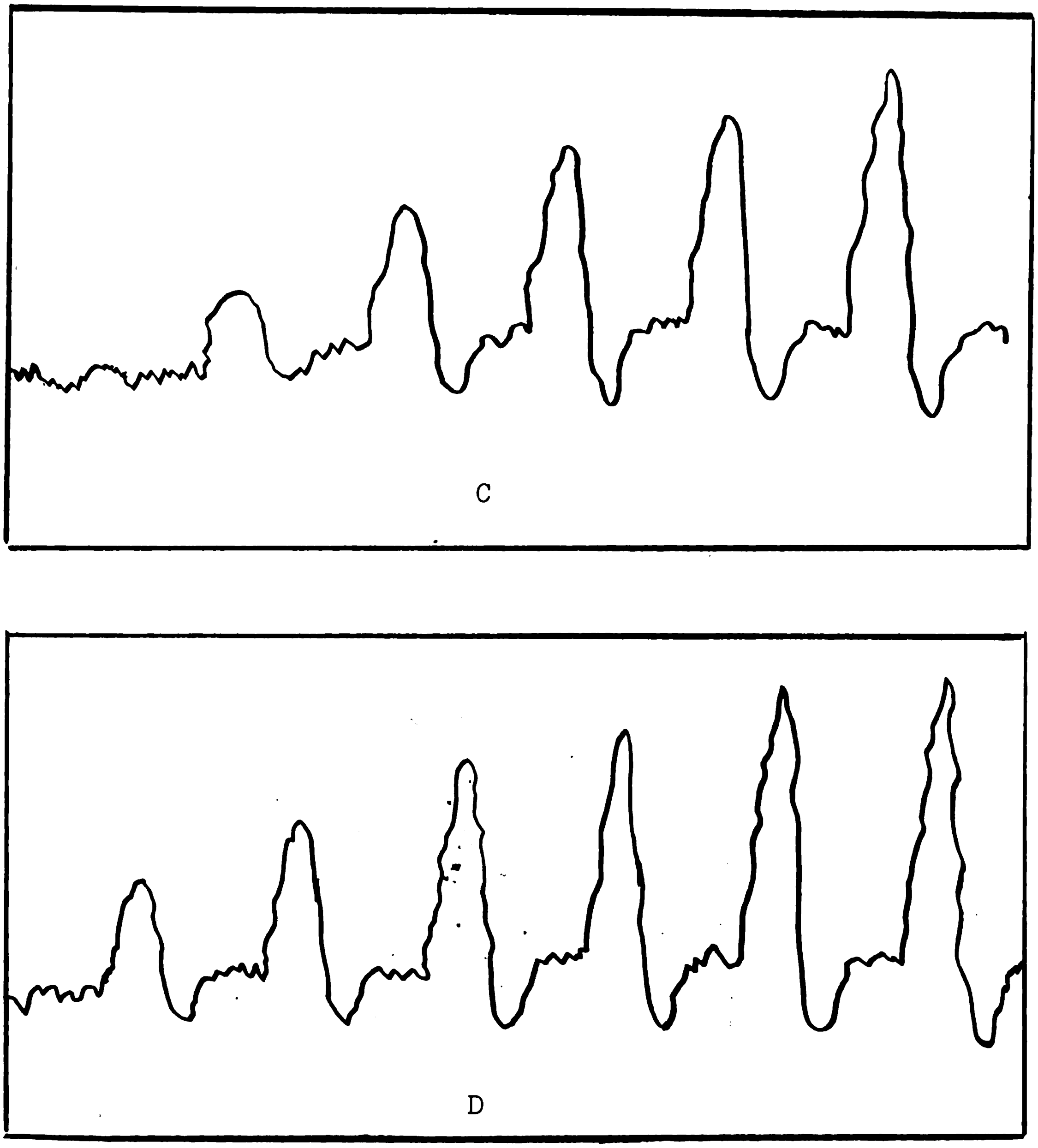


Fig. 14

Rapid-scanning monochromater traces

Fig. A for 1:1 mixture

Fig. B for 1:2 mixture



Rapid-scanning monochromater traces

Fig. C for 1:4 Mixture

Fig. D for 1:10 Mixture

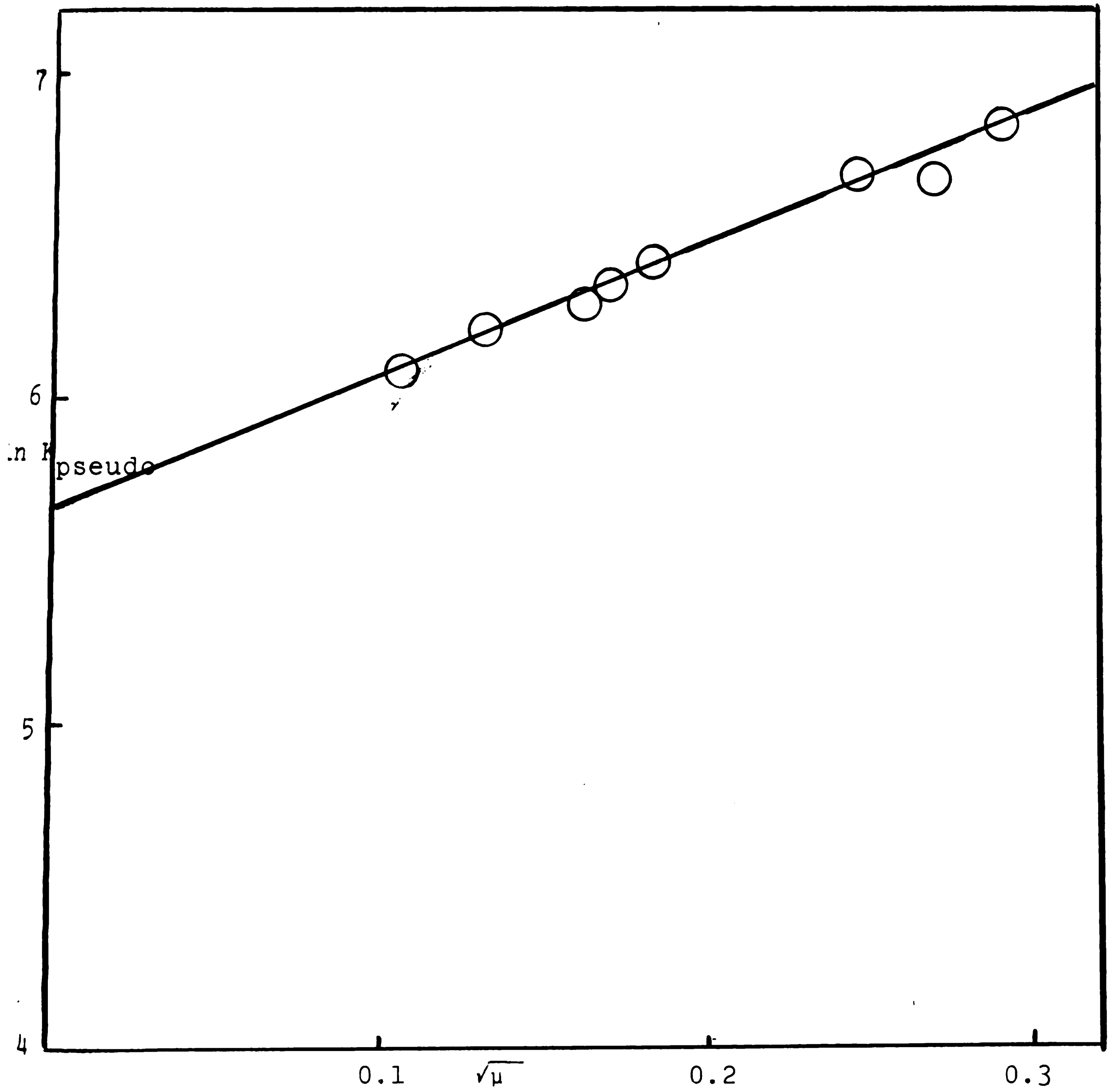


Fig. 15

Variation of ln K_{pseudo} with the square root of the ionic strength. Slope obtained is 4.1:expected value is 16.

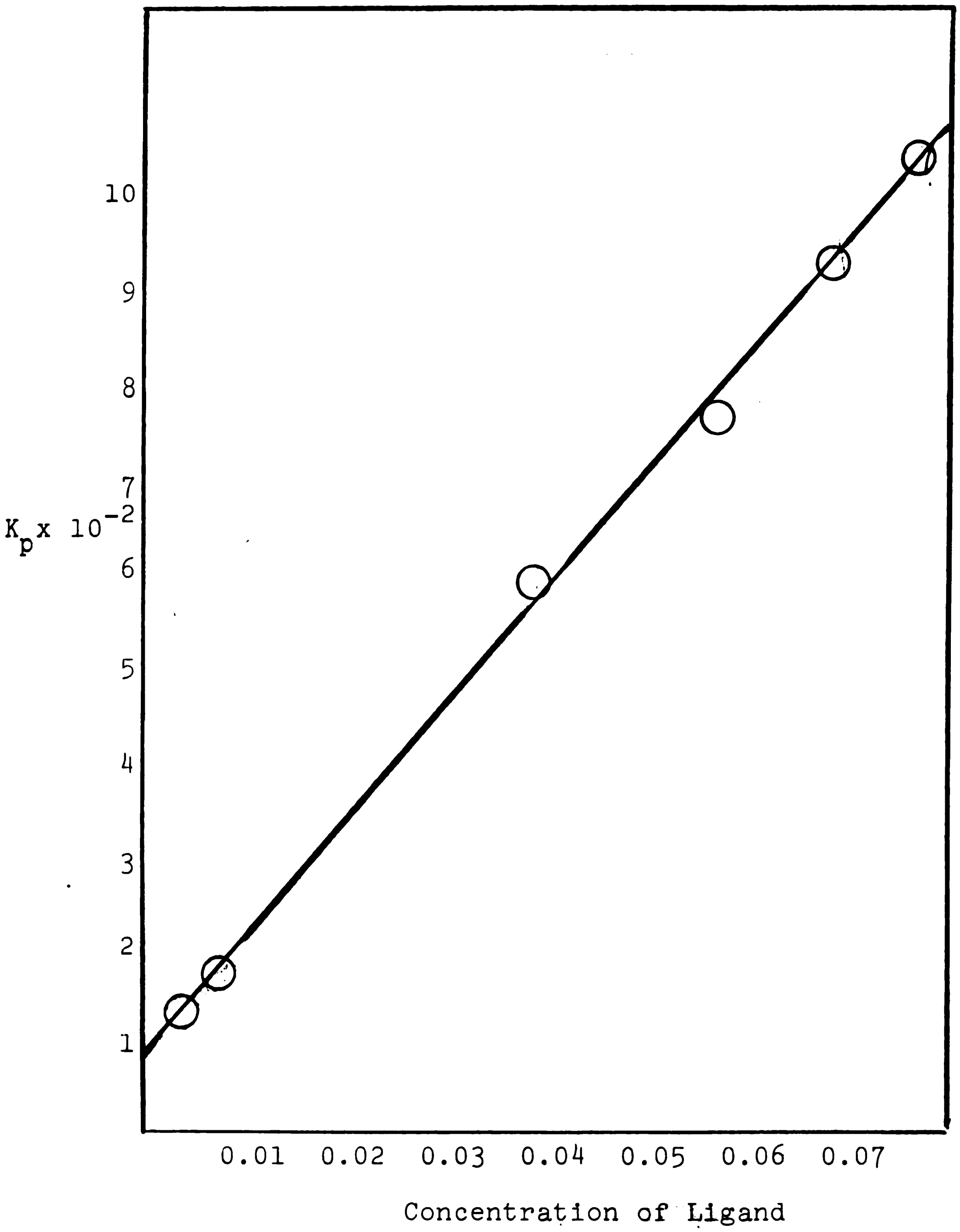


Fig. 16

Variation of K_{pseudo} with ligand concentration at .
The line is expected to pass through the origin.

The rate constant for the formation of the 1:1 complex was not determined but is estimated to be about 10^4 M^{-1} sec^{-1}.

After this rapid formation of the 1:1 complex the build-up of the 1:2 complex begins. At very high thiocyanate concentrations the plot of K_{pseudo} against the ligand concentration, Figure 16, gives a straight line which does not pass through the origin. This suggests the following scheme:

$$MoOCl_3(SCN)MeOH^- + SCN^- \rightleftharpoons MoOCl_3(SCN)_2^= + MeOH$$

$$MoOCl_3(SCN)_2^= \xrightarrow{k_1} MoOCl_2(SCN)_2\ MeOH^- + Cl^-$$

$$\text{or} \xrightarrow{k_1} MoOCl_2(SCN)_2Cl$$

The second step will be represented by

$$A \xrightarrow{k_1} B$$

The first step involves the rapid displacement of a solvent molecule to form the 1:2 complex with an equilibrium constant K. In the second step an internal rearrangement is postulated in which the axial thiocyanate ion displaces one of the equatorial chloride ions. The rate constant for this process is represented by k_1 and can be obtained from the pseudo-first order rate constant.

It is speculated that at higher thiocyanate concentrations the 1:2 complex is rapidly formed and thus becomes the starting species for the build up of the 1:4 and ultimately the 1:5 complex.

For convenience the pseudo-first order rate constant was determined by the method applicable to the kinetics of formation of ferric thiocyanate (51, 52). Although this treatment is only valid for an excess of complexing agent, the same treatment was formally used at low thiocyanate concentrations. Plots of log (absorbance) versus time were slightly curved but an average slope was used.

Assuming the mechanistic scheme described above the following is derived:

I

$$\frac{dB}{dt} = k_1 A$$

$$K = \frac{[MoOCl_3(SCN)_2^{=}]}{[MoOCl_3SCN\ MeOH^-][SCN^-]} = \frac{A}{[MoOCl_3SCN\ MeOH^-][SCN^-]}$$

$$[Mo]_T = [MoOCl_3(SCN)_2^{=}] + [MoOCl_3SCN\ MeOH^-] + B$$

$$[Mo]_T - B = A + \frac{A}{K[SCN^-]}$$

$$= A\ \{1 + \frac{1}{K[SCN^-]}\}$$

$$A = \frac{[Mo]_T - B}{1 + \frac{1}{K[SCN^-]}}$$

$$\frac{dB}{dt} = \frac{K_1\ \{(Mo)_T - B\}}{1 + \frac{1}{K[SCN^-]}}$$

$$= \frac{k_1 K(SCN^-)\{Mo)_T - B\}}{1 + K(SCN^-)}$$

$$\frac{dB}{dt} = K_{pseudo}\ \{(Mo)_T - B\}$$

Hence $$K_{pseudo} = \frac{k_1K(SCN^-)}{1 + K(SCN^-)}$$

$$\frac{K_{pseudo}}{(SCN^-)} = \frac{k_1K}{1 + K[SCN^-]} = K_{obs}$$

At high thiocyanate concentration a plot of

$$\log \frac{[MoO(SCN)_2Cl_3^{=}]_\infty - [MoO(SCN)_2Cl_3^{-}]}{[MoO(SCN)_2Cl_3^{=}]_\infty - [MoO(SCN)_2Cl_3^{=}]_o} \quad \text{versus time}$$

gives a straight line from which $K_{ps\ \ do}$ is obtained. The observed second order rate constant K_{obs} is calculated as follows.

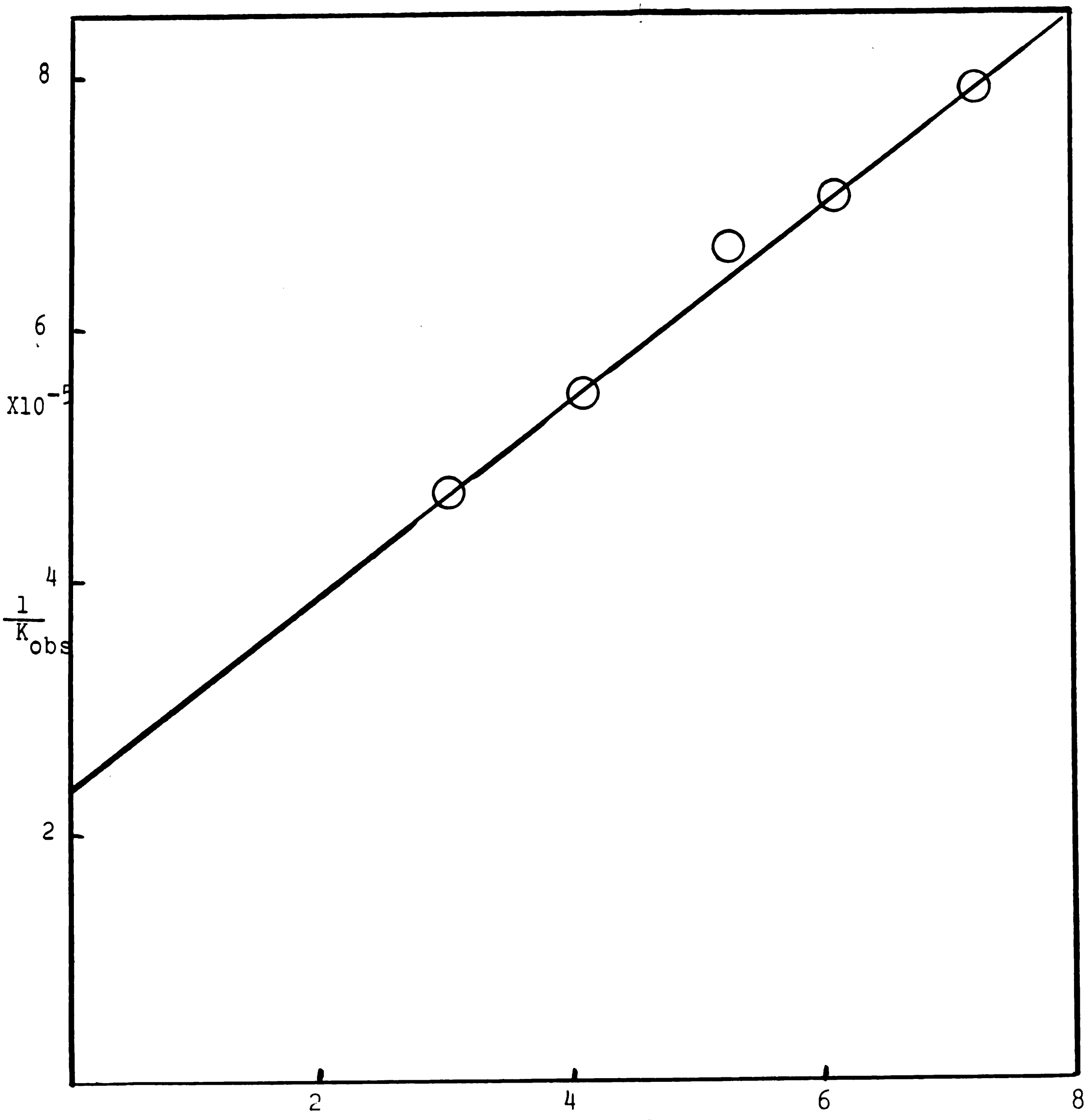
$$K_{obs} = \frac{K_{psuedo}}{[SCN^-]}$$

Since $$K_{obs} = \frac{K_1K}{1 + K_1(SCN^-)}$$

$$\frac{1}{K_{obs}} = \frac{1}{K_1K} + \frac{(SCN^-)}{K_1}$$

A plot of $\frac{1}{K_{obs}}$ against the thiocyanate concentration gives a straight line whose slope is $\frac{1}{K_1}$ and intercept $\frac{1}{K_1K}$.

Figure 17 shows such a plot while Table 5 gives the various values of K_1 and K. Both K_1 and K are independent of ionic strength.



Concentration of (SCN^-)

Fig. 17

Plot of $\frac{1}{K_{obs}}$ vs Ligand Concentration

$K = 33.6$

$K_1 = 1.3 \times 10^3$ Mole^{-1} Sec^{-1}

Table 5

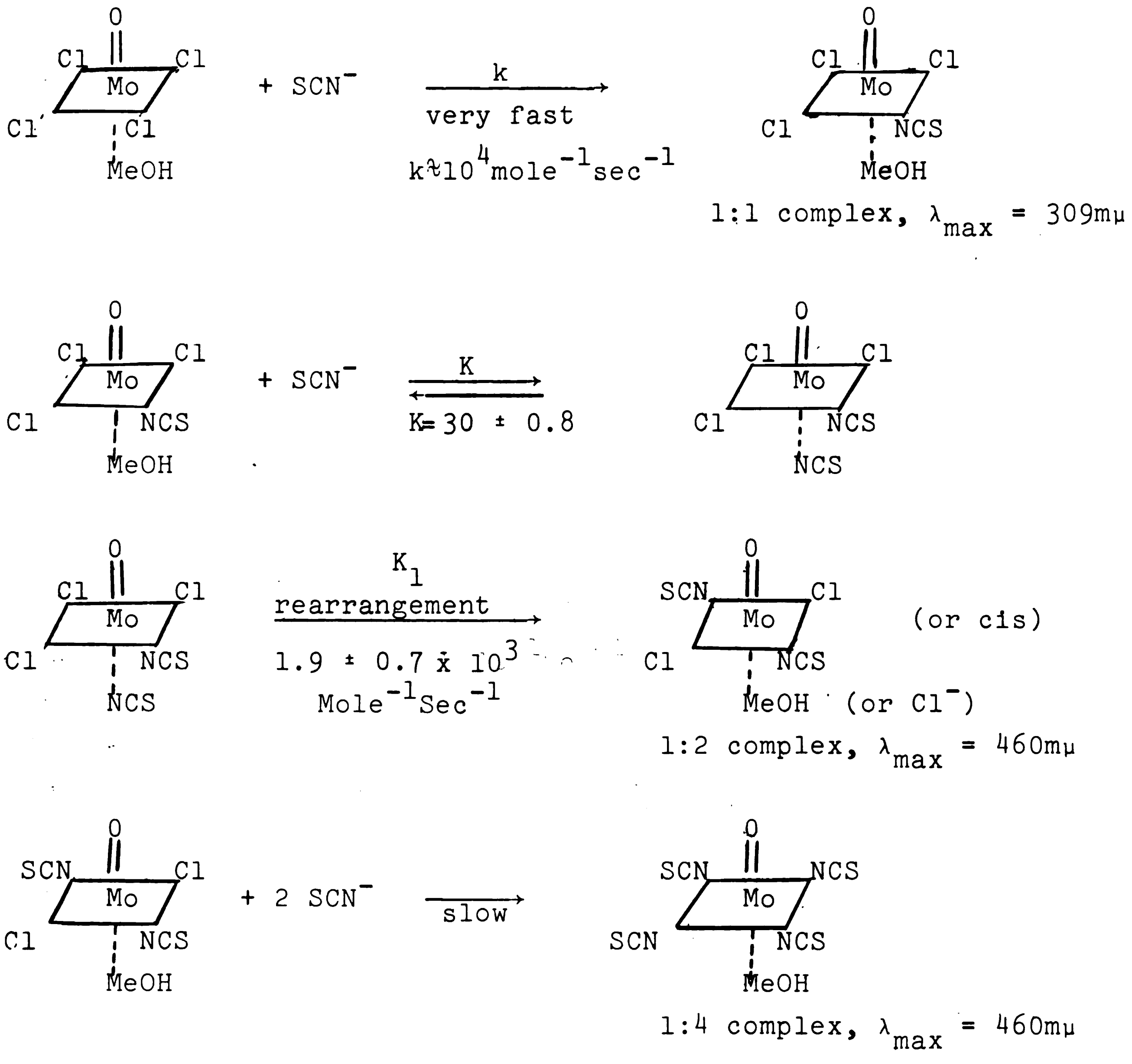
Table of values of k_1 and K

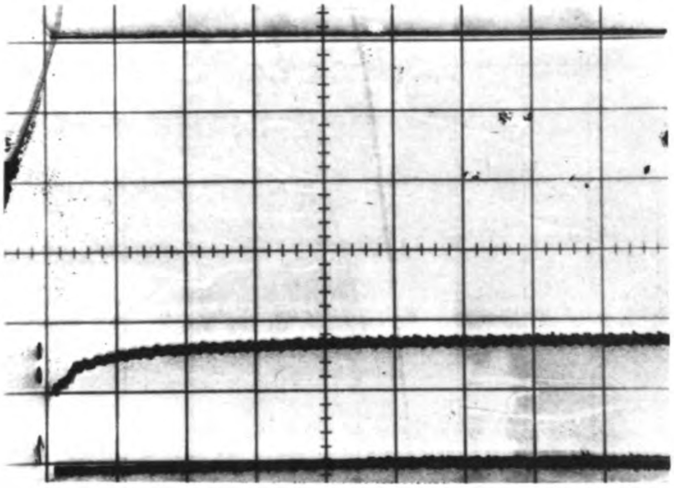
$[MoOCl_5^=]$	k_1 in $mole^{-1}sec^{-1}$	K
0.004113	$2.0 \pm 0.15 \times 10^3$	31.88 ± 0.25
0.0030	$1.3 \pm 0.10 \times 10^3$	33.6 ± 0.40
0.00226	$1.6 \pm 0.12 \times 10^3$	29.4 ± 0.2
0.0029	$1.8 \pm 0.11 \times 10^3$	30.2 ± 0.21

SUMMARY

The present investigation has established the presence of two molybdenyl thiocyanate complexes in methanol. These are the 1:2 and 1:4 Species.

A reaction scheme consistent with the observed reaction is postulated as follows:





IA

IB

Picture I

Oscilloscope traces from the stopped flow apparatus.

IA for Mo: SCN^- ratio of 1:1

IB for Mo: SCN^- ratio of 1:10

V Appendix

A Theoretical

Association constants for the complexes. Absorbance measurements have been used to determine the formation constants of complexes (40, 41, 42). In this study the method due to Hume was used to calculate these constants and a summary of the theory follows.

For a series of complexes the absorbance is a function of the extinction coefficient E, stepwise formation constants K, ligand concentration X, and the central atom concentration M.

Thus:

$$A = E(M) + E_1K_1(M)(X) + E_2K_1K_2(M)(X)^2 + \ldots \qquad (1)$$

The two highest stepwise formation constants are defined as

$$K_n = \frac{(MX_n)}{(MX_{n-m})(X)^m} \qquad (2)$$

$$K_{n-m} = \frac{(MX_{n-m})}{(MX_{n-m-p})(X)^p} \qquad (3)$$

If all the three species MX_n, MX_{n-m} and MX_{n-m-p} absorb then:

$$A = E_n(MX_n) + E_{n-m}(MX_{n-m}) + E_{n-m-p}(MX_{n-m-p}) \qquad (4)$$

where A is the absorbance for the mixture of all three species.

With X in large excess of M such that only the highest complex is formed

$A_o = E_n M_o$ where M_o is the concentration of the central atom nearly all of which is present in the form of the highest complex MX_n.

$$M_t = (MX_n) + (MX_{n-m}) + (MX_{n-m-p}) \tag{5}$$

Manipulation of equations (1), (3) and (4) in (5) gives the following:

$$E_n = \frac{A_o}{M_o}; \qquad (MX_n) = K_n(MX_{n-m})(X)^m \tag{6}$$

From (3)

$$(MX_{n-m-p}) = \frac{A - E_n(MX_n) - E_{n-m}(MX_{n-m})}{E_{n-m-p}}$$

$$= \frac{A - \frac{A_o}{M_o} K_n(MX_{n-m})(X)^m - E_{n-m}(MX_{n-m})}{E_{n-m-p}} \tag{7}$$

putting these in (5) we obtain

$$M_t = K_n(MX_{n-m})(X)^m + (MX_{n-m}) + \frac{A - \frac{A_o}{M_o} K_n(MX_{n-m})(X)^m - E_{n-m}(MX_{n-m})}{E_{n-m-p}} \tag{8}$$

$$M_t(E_{n-m-p}) = (E_{n-m-p})(MX_{n-m})\{(K_n X^m + 1)\} + A - \frac{A_o}{M_o} K_n(MX_{n-m})(X)^m - E_{n-m}(MX_{n-m}) \tag{9}$$

$$A - M_t E_{n-m-p} = (MX_{n-m})\{(K_n X^m + 1)E_{n-m-p} + \frac{A_o}{M_o} K_n(X)^m + E_{n-m}\} \tag{10}$$

$$(MX_{n-m}) = \frac{A - M_t\ E_{n-m-p}}{E_{n-m} + \frac{A_o}{M_o} K_n(X)^m - E_{n-m-p}(K_n(X)^m + 1)} \tag{11}$$

Similarly

$$(MX_{n-m-p}) = \frac{M_t(E_{n-m} + \frac{A_o}{M_o} K_n(X)^m) - A\{1 + K_n(X)^m\}}{E_{n-m} + \frac{A_o}{M_o} K_n(X)^m - E_{n-m-p}(1 + K_n(X)^m} \qquad (12)$$

Substitution of (12) and (13) into (3) gives

$$K_{n-m} = \frac{A - M_t\ E_{n-m-p}}{[M_t(E_{n-m} + \frac{A_o}{M_o} K_n(X)^m] - A(1 + K_n(X)^m)X^p} \qquad (13)$$

Rearranging (14) gives for the case of 3 species absorbing when $X >> M_t$

$$A = K_{n-m}\underbrace{\{(K_n(Ao\frac{M_t}{M_o} - A)(X_t)^m - A + E_{n-m}M_t)\}X_t^p}_{Y} + (E_{n-m-p})M_t \qquad (14)$$

in which X_t is the total concentration of ligand.

A plot of A versus Y gives a straight line whose slope is K_{n-m} and whoses intercept gives E_{n-m-p}.

If both (MX_n) and (MX_{n-m}) absorb at a particular wavelength, and $E_{n-m-p} = 0$, we obtain for 3 species present with 2 absorbing

$$A = K_n(Ao\frac{M_t}{M_o} - A)\ X_t^m - \frac{1}{K_{n-m}}\ \{{}^A/X_t^p\} + E_{n-m}M_t \qquad (15)$$

If only (MX_n) absorbs at a particular wavelength, then $E_{n-m}=0$, $E_{n-m-p} = 0$ and we obtain for 3 species with only one absorbing:

$$\log^{-}\frac{1}{X_t^p} = \log \frac{[K_n(Ao\frac{M_t}{M_o} - A)X_t^m - A]}{A} \qquad (16)$$

and for only 2 species present with both absorbing:

$$A = K_n(Ao\frac{M_t}{M_o} - A)X_t^m + E_{n-m}{}^{M_t} \qquad (17)$$

To use equation 17 values are assumed for m such that a straight line results. When A is plotted versus $(A_o M_t/M_o - A)\ X_t^{m}$. If a wavelength is selected such that only the higher of the two species is absorbing, E_{n-m} becomes zero and Eq. 18 upon rearrangement gives for 2 species, only 1 absorbing, $MX_{n-m-p} = 0$, $E_{n-m-p} = 0$, $E_{n-m} = 0$

$$\log \left(\frac{Ao\frac{Mt}{Mo} - A}{A}\right) = -m \log X - \log K_n \tag{18}$$

a plot of the left-hand side versus log X gives a slope of n and an intercept equal to $-\log K_n$.

In order to obtain the first formation constant it is necessary that the concentrations of both the molybdenum and thiocyanate be comparable.

As before $A = E(M) + E_q(MX_q)$ (19)

$$M_t = [M] + (MX_q) \tag{20}$$

$$X_t = (X) + q(MX_q) \tag{21}$$

Solving for K_q as before we obtain

$$K_q = \frac{A - E(M_t)}{\frac{A(E_q - E) - E_q(A-E(M_t))}{E} \quad X_t - q\left(\frac{A-E(M_t)}{E_q - E}\right)^q} \qquad (22)$$

By using $Ao' = EMo$, $Ao'' = E_q X_o$ and substituting

$\frac{Ao'}{Mo}$ for E and $\frac{Ao''}{Xo}$ for E_q we obtain for 2 species both absorbing and $MX_{q+r} = 0$, $E_{q+r} = 0$

$$\log \frac{A - Ao' \frac{Mt}{Mo}}{Ao'' \frac{Mt}{Xo} - A} = q \{\log[X_t - q \left(\frac{A - Ao' \frac{Mt}{Mo}}{\frac{Ao''}{Xo} - \frac{Ao'}{Mo}} \right)] + \log Kq \qquad (2z)$$

A plot of $\log \left(\frac{A - Ao' \frac{Mt}{Mo}}{Ao'' \frac{Mt}{X_o} - A} \right)$ versus $\log \left[X_t - q \left(\frac{A - Ao' \frac{Mt}{Mo}}{\frac{Ao''}{X_o} - \frac{Ao'}{Mo}} \right) \right]$

using suitable values for q gives a straight line of slope q. The intercept of this plot is log K_q.

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