KINETICS AND MECHANISM OF HYDROLYSIS OF *TRANS*-DINITROBIS(ETHYLENEDIAMINE)COBALT(III) NITRATE AND RELATED DINITRO COMPLEXES OF COBALT(III) IN HIGH CONCENTRATIONS OF ACIDS

by

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I. INTRODUCTION

A subject of continuing interest in this laboratory is the polarographic behavior of coordination compounds. This research was started to find some correlation between hydrolysis rates and half-wave potentials for reduction of some cobalt(III) dinitro complexes. Since the mechanisms of the two processes now do not seem to be related, this initial objective could not be realized.

At the time this investigation was begun, little information was available on the hydrolysis reaction

$$[Co(AA)_2(X)(Y)]^{+1} + H_2O \text{ —— } [Co(AA)_2(X)(Y)(H_2O)]^{+2} + Y^-$$

where "Y" is not a halide. Theories of hydrolysis of these complexes have emphasized the electronic properties of "X"; if "X" is electron-releasing, SN_1 reaction is likely and if "X" is electron-withdrawing, SN_2 reaction is promoted. Study of the hydrolysis of the dinitro compounds might show the effect of "Y" on the rate if the observed rate law were simple, particularly since "X" should promote SN_2 reaction.

Another objective of this work was to attempt to formulate a mechanism for the hydrolysis of the dinitro groups. In a series of complexes containing different inert ligands "AA", increasing size of the inert ligand accelerates the rate of a reaction occurring by an SN_1 mechanism but decelerates the rate if reaction occurs by an SN_2 mechanism.

In fact, the complexes were unusually resistant to hydrolysis in low concentrations of acid at 25° Centigrade. Contrary to rate laws reported for hydrolysis of other complexes, the first-order rate constant was a complicated function of the acid concentration. No prediction of this behavior could have been made before this work was begun, but using Bunnett's ideas about the rates of hydrolysis of organic compounds in acid, a mechanism consistent with all the data could be formulated. It is satisfying that good correlation with current postulations was possible.

II. HISTORICAL

A. Introduction

Interest in the reactivity of transition metal complexes has been so great that the subject has been reviewed repeatedly (14, 19, 61, 87, 88, 100, 104, 108) since the appearance of Basolo and Pearson's book (18) in 1958. Most reviews have been concerned with formulating criteria for deciding whether a given compound reacts by a dissociative (SN_1) or by a bimolecular (SN_2) process. Determination of detailed mechanisms is complicated by participation of the solvent in aqueous solution; few cases are known in which a clear distinction between the SN_1 and SN_2 processes is possible.

Because so many recent reviews of the area are available, this review will be limited mostly to acid hydrolysis reactions of coordination compounds. Catalysis by hydrogen ion has been observed for two broad classes of compounds: (1) complexes containing a ligand which is an anion of a weak acid or a ligand which can hydrogen bond to the solvent, and (2) complexes containing multidentate ligands.

B. Complexes containing an anion or a weak acid or hydrogen-bonding ligands.

i. Compounds of the type MA_5Y

Most investigators have proposed an SN_1 mechanism for the reaction

$$[Co(A)_5(Y)]^{+2} + H_2O \longrightarrow [Co(A)_5(H_2O)]^{+3} + Y^- .$$

When acid accelerates the rate, the rate law observed has been

$$\text{(I)} \qquad k_1 = k_o + k_h(H+)$$

where k_1 is the first-order rate constant, k_o is a constant, and k_h is a catalytic constant. When acid retards the rate, the rate law observed has been

$$\text{(II)} \qquad k_1 = k_o + k_c(OH^-) .$$

At least three mechanisms are consistent with rate law I: (1) direct SN_2 reaction of the complex S with a proton, (2) formation of a protonated species SH^+ which reacts faster with water than the original complex S, and (3) an SN_1 mechanism in which the complex S dissociates to an intermediate species which reacts with a proton in the rate-determining step. Analogous mechanisms could be formulated for rate law II by substituting "hydroxide ion" for "proton" in the preceding sentence. We see that determination of the rate law does not point to a unique mechanism of reaction, yet many workers seem to be committed to only one point of view when they discuss their results.

In the series $[Co(NH_3)_5(Y)]^{+2}$, three cases of acid catalysis have been reported so far, but there are probably others. Basolo, Bergmann, and Pearson (15) studied several complexes of various metals where Y is acetate in 4×10^{-3} and 8×10^{-3} molar acid and could not detect any effect of acid concentration on the rate. Later Monacelli, Basolo, and Pearson (80) examined the same compounds over a wider range of acid concentrations and found rate law I applies. Chan (37) studied the fluoride and observed the same rate law; Chan proposed a mechanism in which aggregates of water molecules are involved to emphasize the role of hydrogen bonding in hydrolysis of this compound. Schmidt and Taube (96) examined the hydrolysis of the phosphate as a part of the preparation of the complex. Although only a few rate constants were obtained, the variation of rate constant with acid concentration was not simple.

Because direct studies of the variation of the rate constant with acid concentration have not led to a unique mechanism, many workers have tried other approaches. Haim and Wilmarth (51) demonstrated that the aquation of $[Co(CN)_5(N_3)]^{-3}$ in the presence of SCN^- is an SN_1 mechanism with dissociation of a protonated species rate determining. This is probably the only case in which the results of competitive experiments point to a unique mechanism.

In contrast, interpretation of results of competitive experiments with $[Co(NH_3)_5(Y)]^{+2}$ compounds is still controversial. Most of the disagreement concerns small differences in mechanisms proposed by various workers. Taube (47, 93) used H_2O^{18} enriched water and found the same fraction of H_2O^{18} in the $[Co(NH_3)_5(H_2O)]^{+3}$ formed from several different compounds. The fraction was independent of the nature of "Y" and of whether the hydrolysis was performed in acid or in base. Taube suggested that an SN_1 mechanism is probable both in acid and base hydrolysis of these compounds. This same idea has recently been proposed for other cobalt(III) complexes by Jordan and Sargeson (64), who call attention to the fact that the product cis/trans ratio is independent of whether the product is formed by acid or base hydrolysis. Agreement that hydrolysis of $[Co(NH_3)_5(Y)]^{+2}$ occurs by an SN_1 path is general, but the nature of the intermediate is not clear.

Haim and Taube (50) hydrolyzed $[Co(NH_3)_5(N_3)]^{+2}$ in the presence of different anions Z^- and showed that the proportion of $[Co(NH_3)_5(Z)]^{+3}$ formed is dependent on the anion Z^-. Haim and Taube calculated competitive factors for the five coordinate intermediate which are consistent with the equilibria, rates, and water exchange rates, by assuming that the five-coordinate intermediate has a lifetime long enough to discriminate between nucleophiles. Pearson and Moore (91) failed to verify some of these competitive factors and concluded that the solvent-assisted SN_1 mechanism (63, 89) is more probable.

Recently, Langford (68) has shown that for the equilibrium

$$[Co(NH_3)_5(Y)]^{+2} + H_2O \rightleftharpoons [Co(NH_3)_5(H_2O)]^{+3} + Y^-$$

there is a linear relationship between the rate of the forward reaction (hydrolysis) and the equilibrium constant. This suggests "The role of the Y^- group in the transition state of acid hydrolysis is strongly similar to its role in the product: namely, that of a solvated anion." Langford shows that assistance of the solvent is not required, but points out that no simple experiment can determine whether the solvent participates. He emphasizes the need for "operationally satisfactory mechanistic categories."

The $[Co(NH_3)_5(Y)]^{+2}$ complexes are not ideal for mechanistic study for several reasons. Laurie and Monk (70) have studied the rates of hydrolysis in several acidified salt solutions and have shown that the rate constants obtained can be correlated with the ion-pair constants for the interaction of $[Co(NH_3)_5(Y)]^{+2}$ with anion Z^- present in the NaZ solutions. This ion-pairing is no doubt a consequence of the high charge these complexes possess. In two studies (86, 102) it was shown that the rate of hydrolysis of the complexes is slower in D_2O than in H_2O but interpretation of the results was not unambiguous because the importance of hydrogen-bonding in the reaction could not be assessed. Because of these and other disadvantages no unequivocal proof of the mechanism of acid hydrolysis of the $[Co(NH_3)_5(Y)]^{+2}$ is available from a single experiment; when all the evidence is examined, an SN_1 mechanism is reasonable.

King and his school have recently examined the hydrolysis of the $[Cr(H_2O)_5(Y)]^{+2}$ system (11, 42, 49). Swaddle and King (102) have shown that when Y is fluoride or azide (10) acid catalysis is observed but for the other halides, base catalysis is found. They favor the initial formation of the hydroxy complex in all cases; the difference in fluoride and azide was said to be that HF and HN_3 are released rather than F^- or N_3^-. Aquation of $[Cr(H_2O)_4(Cl)_2]^{+1}$ has been shown to be base catalyzed also (79); these results indicate that the nature of the halide is important in determining the mechanism.

Espenson and Birk (43) have studied the aquation of the $[Cr(H_2O)_5(Cl)]^{+2}$ ion catalyzed by mercury(II). Both Hg^{+2} and $HgCl^{+1}$ are effective catalysts, which suggests that reaction occurs by way of a chloride-bridging mechanism. We are reminded by the investigations of King and his co-workers that even complexes as formally similar as $[Co(NH_3)_5(Cl)]^{+2}$ and $[Cr(H_2O)_5(Cl)]^{+2}$ may hydrolyze by completely different paths.

ii. Compounds of the type $[M(A)_n(X)(Y)]$.

Studies of the hydrolysis reaction

$$[M(A)_n(X)(Y)] + H_2O \longrightarrow [M(A)_n(X)(H_2O)] + Y^-$$

where A is either a monodentate (n = 4) or a bidentate (n = 2) ligand have usually been conducted with the chloro complexes (Y = Cl) because several methods are available for measuring the rate constants.

In systems of the type $[Co(en)_2(X)(Cl)]^{+1}$, much evidence is available (108 and references therein) to show that the nature of "X" determines the rate of reaction. When "X" is electron-donating an SN_1 reaction is promoted and when "X" is electron-withdrawing an SN_2 reaction is promoted. Much work was required before this correlation could be made; a typical example of one of the many publications on this subject is Baldwin, Chan, and Tobe's (10) determination of rate constants and products for the hydrolysis of the <u>cis</u> and <u>trans</u> isomers or $[Co(en)_2(OH)(Cl)]^{+1}$. The correlation of rate with the nature of "X" has been accepted rather uncritically and investigators have tried to make sharp distinctions between SN_1 and SN_2 reactions on this basis. Baker and Gaesser (9) synthesized a series of compounds

$[Co(en)_2(tu)(Cl)]^{+1}$, where "tu" is a substituted thiourea, and measured the rates of hydrolysis. In spite of the different groups attached to the thiourea, the measured rate constant was almost independent of the nature of the thiourea. This result is expected only if the electronic effect of the group attached to the thiourea is not transmitted to the cobalt(III). More information is necessary before the correlation of mechanism with the nature of "X" can be accepted without reservation.

Probably the best-documented case for an SN_1 reaction is the hydrolysis of $[Co(AA)_2(Cl)_2]^{+1}$ complexes. Changing the ligand from ethylenediamine to 1,3-diaminopropane increases the rate by a factor of at least a thousand (18). Sargeson (95) has examined the mercury(II) catalyzed hydrolysis of $[Co(en)_2(Cl)_2]^{+1}$ and showed that the products are 70% cis d, and 30% trans-$[Co(en)_2(H_2O)(Cl)]^{+2}$. These products are consistent only with the pentagonal bipyramid intermediate formed in an SN_1 reaction. This suggests that the uncatalyzed hydrolysis may occur by the same path. Recently, Chan has found the same rate reductions in D_2O for $[Co(en)_2(Cl)_2]^{+1}$ and $[Co(en)_2(NO_2)(Cl)]^{+1}$; the cis or trans isomers give the same results. For the N-deuterated compounds, the reduction in rate is less for the nitrochloro than for the dichloro complex. This result is good evidence that $[Co(en)_2(Cl)_2]^{+1}$ is hydrolyzed by an SN_1 reaction and $[Co(en)_2(NO_2)(Cl)]^{+1}$ is hydrolyzed by an SN_2 reaction. In fact, the dichloro and the nitrochloro complexes have now assumed the status of typical examples of SN_1 and SN_2 reactions, respectively. The $[Co(en)_2(X)(Cl)]^{+1}$ complexes in which X is an organic compound capable of being varied greatly in its electronic characteristics should be systematically studied to see if such division into SN_1 and SN_2 reactions is actually fruitful for estimating rates of unknown reactions.

Several investigators have studied systems which do not contain chloride as a ligand. Tobe (103) examined the rates of hydrolysis of trans-$[Co(en)_2(NH_3)(Y)]^{+2}$ where Y is chloride, bromide, or nitrate and found results consistent with a mechanism involving attack of a water molecule adjacent to the outgoing group with some hydrogen bonding between the water and outgoing ligand. This conclusion was reached by study of three compounds at a single pH at a few temperatures. No doubt other mechanisms would also be consistent with the data. Martin and Tobe (75) studied the isomerization, racemization, and water exchange reactions of the trans-$[Co(en)_2(NH_3)(H_2O)]^{+2}$ complex. They showed that the isomerization is base catalyzed.

Staples (98, 99) has recently measured the rates of hydrolysis of $[Co(en)_2(N_3)_2]^{+1}$ and $[Co(en)_2(NO_2)_2]^{+1}$ up to 3.5 molar perchloric acid. The exact dependence of the rate on acid concentration is difficult to determine, since deviations are apparent in a graph of log k_1 versus log (H^+). Staples used perchloric acid-sodium perchlorate mixtures at a total ionic strength of 3.5 molar. For example, one rate constant was determined in 0.2 molar perchloric acid and 3.3 molar sodium perchlorate; another rate constant was found for 3.0 molar perchloric acid and 0.5 molar perchloric acid; the final rate constant was determined in 3.5 molar perchloric acid. Values of the rate constants then were listed under 0.2, 3.0, and 3.5 molar acid concentrations. This procedure is no better than determining the rate as a function of perchloric acid concentration because Staples made massive replacements of sodium ion in his investigation. The principle of keeping the activity coefficients constant by addition of a high concentration of inert electrolyte is well known to be valid only for small replacements of one ion for another.

We have studied the $[Co(en)_2(NO_2)_2]^{+1}$ system in some detail. The rate constants determined for the trans isomer agree fairly well; in 3.5 molar perchloric acid, Staples lists 10.4×10^{-5} sec.$^{-1}$ and we obtain 7.68 and 7.69×10^{-5} sec.$^{-1}$ in 3.534 molar perchloric acid. All Staple's data were obtained at 400 millimicrons, where the cis and trans $[Co(en)_2(NO_2)(H_2O)]^{+2}$ isomers have the same extinction coefficient. We found that the changes in absorbance are very small at this wavelength, which would increase the uncertainty in the computed rate constant. Several wavelengths chosen to obtain large differences in absorbance were used in our research. Staple's rate constants for the hydrolysis of cis-$[Co(en)_2(NO_2)_2]^{+1}$ drastically disagree with ours. He lists a rate constant in 3.5 molar perchloric acid at 25° C. of about 5×10^{-5} sec.$^{-1}$; our value would be about 2×10^{-7} sec.$^{-1}$ under the same conditions. Both our preparation and that of Staples gave good elemental analyses, but if the preparations were not stereochemically pure, elemental analysis would not be informative. We believe that Staples had some trans isomer in his preparation of the <u>cis</u> compound, and that his rate constant refers to a mixture of isomers. This belief is strengthened by our finding that the <u>cis</u> and <u>trans</u>-$[Co(NH_3)_4(NO_2)_2]^{+1}$ complexes are hydrolyzed at markedly different rates. The fact that two investigators can prepare a compound by the same standard method and obtain markedly different rate constants indicates the need for a detailed study of the methods of preparation of the dinitro complexes, with a careful determination of products under various conditions.

Chan (36) and Chan and Tobe (39) have determined rate constants and activation energies for acid and base hydrolysis of <u>trans</u>-$[Co(en)_2(CN)(Y)]^{+1}$ where Y is chloride or bromide for comparison of cyanide and nitrite as "orienting" groups. These results are listed below together with the result obtained in this investigation for the dinitro complex. Examination of these results

Comparison of cyanide and nitrite as orienting groups

Orienting group ("X")	Replaced group ("Y")	Acid Hydrolysis		Base Hydrolysis	
		ΔE	$\Delta S^{\ddagger}$	ΔE	$\Delta S^{\ddagger}$
CN	Cl	22.6	-4.0	23.2	20.0
CN	Br	24.0	4.4	23.4	26.5
NO_2	Br	23.1	6.0	--	--
NO_2	NO_2	23.6*	2.9*	--	--

*This investigation.

shows that there is little difference in the activation energy for hydrolysis of these complexes; our uncertainty is about 0.8 kcal. at the 95% confidence interval. If the other activation energies are uncertain by about the same amount, the activation energies are seen to be constant at 23.3 kcal. (standard deviation 0.4 kcal.); the differences in rate are seen to be related mostly to the entropy factor. Since our entropy is uncertain by 2.3 eu. at the 95% level of confidence, one may conclude that the entropy of activation is very similar for the acid hydrolysis of both nitro and cyano groups. This suggests that the mechanism of these reactions is the same, but values of the entropy of activation may not be sensitive indicators of mechanism in these systems.

Garner and his co-workers (76, 77, 84, 94) have examined the $(Cr(en)_2(X)(Y)]^{+1}$ complexes for comparison with the corresponding cobalt(III) compounds. In general, the behavior found for the chromium complexes is the same as that for the corresponding cobalt compound. For instance, the aquation of $[Cr(en)_2(F)_2]^{+1}$ is acid catalyzed (84) as is $[Co(en)_2(F)_2]^{+1}$ (17). Activation energies for the chromium complexes are usually lower by two or three kilocalories as has been predicted from ligand field theory (18).

This survey shows that when a ligand that is an anion of a weak acid is present, acid catalysis of the hydrolysis reaction may be expected. Rate constants for these hydrolyses have not been examined over an extensive range of acid concentrations, and some investigators have allowed massive replacement of one positive ion by hydrogen ion in an effort to control the ionic strength. Systems containing anions of weak acids such as nitrite, fluoride, acetate, and phosphate should be examined over a large range of acid concentration to see what behavior is observed.

C. Complexes containing multidentate ligands.

i. Oxalate and carbonate.

These ligands are anions of weak acids and could have been included in the survey above, but since their hydrolysis behavior is complex, they are listed here. This complex dependence of the rate constants on acid concentration is a result of the fact that a multidentate ligand can be affected by acid in ways other than simple protonation. For example, one bond to the metal ion may be broken to form a "unidentate" intermediate which could then be protonated and react with the solvent. A mechanism similar to this has recently been proposed by Harris and Sastri (53) for the hydrolysis of $[Co(en)_2(CO_3)]^{+1}$. Lamb and Mysels (67) had briefly examined the hydrolysis of the carbonate complex and had shown that the rate constant depended on pH before Lapidus and Harris (69) investigated the carbonate exchange reaction over a wide pH range. Tong, St. Andre Kean, and Hall (105) apparently had not seen the carbonate exchange results when they proposed a mechanism for the hydrolysis based on their study of a limited pH range. Although Harris and Sastri (53) show that their mechanism gives an excellent fit of their data, some caution is necessary in such cases where the observed rate constant in effect is fitted to a complex polynomial function of the hydrogen ion concentration. Some other polynomial expression (another mechanism) probably could be found to fit the data just as well.

The subject of the chemistry of the metal oxalato complexes has been reviewed by Krishnamurty and Harris (65); only a few recent papers will be mentioned here. Andrade and Taube (4) showed that when $[Co(en)_2(C_2O_4)]^{+1}$ is subjected to base hydrolysis in the presence of H_2O^{18}, one C-O bond is broken for release of each oxalate, and that oxygen exchange accompanies hydrolysis. The first act is thought to be C-O scission followed by Co-O scission. Acid hydrolysis may follow a similar path.

Bunton, Carter, Llewellyn, O'Connor, Odell, and Yih have recently studied the hydrolysis of $[Co(C_2O_4)]^{-3}$ and $[Cr(C_2O_4)]^{-3}$. These workers first studied the H_2O^{18} exchange reaction (30) and demonstrated the equivalence of the Co-O and C-O bonds in the exchange reaction. They then (31) examined the hydrolysis of the cobalt and chromium oxalates in acid concentrations up to 10 molar. When the log k_1 was plotted versus H_o, the Hammett acidity function, straight lines were obtained in hydrochloric, perchloric, and sulfuric acids at concentrations of 1-8 molar. At higher or lower concentrations of acid, deviations from H_o are observed. These workers have apparently not seen the papers of Bunnett (25, 26, 27, 28, 29) which show that a better indication of mechanism can be obtained from a plot of $[\log k_1 + H_o]$ versus $\log a_w$, where a_w is the activity of water. Recently Odell, Olliff, and Seaton (82) extended their study to the rhodium complex; the rate was acid dependent but increased at a rate greater than the acid concentration increased. Some hint of the interests of this group of workers can be obtained from the paper of Olliff and Odell (82) dealing with the correlation of rates with absorption spectra for $[M(C_2O_4)_3]^{-3}$ complexes. They give absorption spectra for several metals (M) and the crystal field stabilization energy difference between the ground state of the complex and the five coordinate intermediate or the seven coordinate intermediate. This difference is the activation energy; from the activation energy, an order of reactivity is deduced. Olliff and Odell show that the proposed order of reactivity is consistent with the observed order of reactivity in oxalate exchange. We may suppose that these workers are interested in acid catalysis reactions only as a means of obtaining data to correlate with theory so that they might not have seen Bunnett's treatment of acid catalysis.

ii. Other multidentate ligands.

Not all reactions involving multidentate ligands are acid catalyzed. The critical factor would seem to be the reactivity of the protonated intermediate which might be formed in acid solution; if the intermediate is no more reactive than the original complex, then no acid catalysis would be observed. Some caution is necessary because the ranges of pH in some investigations are very small. Such reactions as the racemization of $[Co(EDTA)]^{+1}$ (91) and $[Co(PDTA)]^{+1}$ (60) and dissociation of some nickel polyamines (78, 81) seem to be independent of pH.

Reactions of polydentate complexes with other species may also be either acid or base catalyzed. Busch and Swaminathan (32) show that the reaction of $[Co(PDTA)]^{+1}$ with ethylenediamine depends on base concentration in a complex manner. The iron(III) (62) and nickel(II) (73) ethylenediaminetetraacetate complexes exchange with other metals; the rate constants for this exchange depend on acid in a complicated manner. Recent studies of the exchange M(EDTA) with M' (24, 32, 34, 35, 74) show that in some reactions no acid catalysis is observed. This lack of acid catalysis again appears to be related to the reactivity of the protonated intermediate.

Clearly, substitution of a multidentate liquid is a more complicated process than substitution of a monodentate ligand because additional paths are available for reaction. This complexity was first realized in studies of complexes containing bipyridine or orthophenanthroline (12, 16, 20, 66, 71). From these studies a general mechanism for electrophilic reactions of multidentate ligands was formulated (16). In this mechanism, a "unidentate" intermediate is formed which can then react with other species in solution. In view of the additional complication in these multidentate systems, it is not surprising that no separation of the various reaction steps into SN_1 and SN_2 paths has been possible.

D. Summary

Acid catalysis is observed in reactions involving ligands which are either multidentate or are anions of weak acids. On this basis, it is expected that trans-$[Co(en)_2(NO_2)_2]^{+1}$ would be hydrolyzed by an acid-dependent path. Staple's study (99) of this hydrolysis cannot be used to formulate a mechanism of hydrolysis because the rates were obtained under conditions in which the activity coefficients were probably changing drastically.

In few cases has it been possible to obtain a mechanism for hydrolysis of complex compounds in water because of the uncertainty of deciding what role water plays in the reaction. Little direct evidence is available on the role of water.

Little use has been made of studies of the hydrolysis in high concentrations of acids in trying to decide between alternate mechanisms in which water is (SN_2) or is not (SN_1) directly involved as a reactant.

III. EXPERIMENTAL

A. Preparation of Compounds.

Except where noted the chemicals used were Reagent Grade. All compounds were dried in an evacuated drying pistol over phosphorous pentoxide at the temperature of boiling methanol (about 55° C.) for 24 hours before analysis. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Analyses are reported because in most of the preparations in the literature analysis of only one element is given.

Equivalent weights were determined by pipetting a standard solution of complex onto Dowex 50W-X12 ion exchange resin in the acid form, then titrating the effluent with standardized sodium hydroxide as a function of time. An initial linear portion, a sharp rise, and another linear portion almost parallel to the first was seen in the curve of milliliters of base versus time. The volume of base used in computation of the equivalent weights was found by extrapolating the two linear portions to the time of half-volume change. Results accurate to 0.5% were obtained by this method.

Trans-$[Co(AA)_2(NO_2)_2]NO_3$ complexes were prepared by the method which Holtzclaw, Sheetz, and McCarty (58) used to prepare the ethylenediamine complex. This procedure will be referred to hereafter as the "HSM" procedure. In the HSM procedure, two moles of diamine partly neutralized with 1.2 moles of concentrated nitric acid is added to one mole of $Co(NO_3)_2 \cdot 6H_2O$ and 2.3 moles of sodium nitrite. Air is bubbled through the solution until precipitation of product is complete, then the product is filtered and recrystallized two or three times, usually from boiling water.

Trans-dinitrobis(ethylenediamine)cobalt(III) nitrate, trans-$[Co(en)_2(NO_2)_2]NO_3$, was prepared by the direct HSM procedure in batches using from 0.04-0.4 moles of $Co(NO_3)_2 \cdot 6H_2O$. Extinction coefficients of the product were within 0.1 log unit or better of published values (13). Anal. Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]NO_3$: Co, 17.7; C, 14.4; H, 4.86; N, 29.4; eq. wt., 333. Found: Co, 17.4; C, 14.2; H, 4.60; N, 29.1; eq. wt., 333.

Trans-dinitrobis(1,3-diaminopropane)cobalt(III) nitrate, trans-$[Co(tn)_2(NO_2)_2]NO_3$, was also made by the HSM procedure. Eastman Practical Grade 1,3-diaminopropane was distilled from sodium bicarbonate; 67 ml. of the middle fraction boiling at 133-134° C. (710 mm.) was collected and used immediately in the HSM procedure. Oxidation was continued for three hours and the two recrystallizations were done by dissolving the product in hot water, then quickly cooling the filtered solution. Some decomposition of the complex was noted if the solution was boiled. Bailar and Work (8) could not prepare $[Co(tn)_2(Cl)_2]Cl$ by air oxidation because of side reactions and decomposition; the dinitro complex is more stable but care must be used to avoid decomposition in the recrystallization step. Anal. Calcd. for $[Co(C_3H_{10}N_2)_2(NO_2)_2]NO_3$: Co, 16.3; C, 20.0; H, 5.58; N, 27.2. Found: Co, 16.3; C, 20.1; H, 5.60; N, 26.9.

Trans-dinitrotetramminecobalt(III) chloride, *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, was synthesized by the method of Blitz, Hall, and Blanchard (21) which involves air oxidation of an ammoniacial solution of cobalt(II) chloride in the presence of sodium nitrite and ammonium chloride. The crude product was twice recrystallized from water. Anal. Calcd. for $[Co(NH_3)_4(NO_2)_2]Cl$: Co, 23.1; H, 4.74; N, 32.9; Cl, 13.9. Found: Co, 23.1, H, 4.76; N, 33.1; Cl, 13.6.

Trans-dinitrobis(2,2'-bipyridine)cobalt(III) nitrate, *trans*-$[Co(bipy)_2(NO_2)_2]NO_3$, was made by the HSM procedure except that the solution was boiled during the half-hour air oxidation. The chloride salt had been synthesized (90) by nitrosation of $[Co(bipy)_2(Cl)_2]Cl$. *Anal*. Calcd. for $[Co(C_{10}H_8N_2)_2(NO_2)_2]NO_3$: Co, 11.2; C, 45.7; H, 3.07; N, 18.7. Found: Co, 11.5; C, 45.5; H, 3.27; N, 18.5.

Trans-dinitrobis(1,10-phenanthroline)cobalt(III) nitrate, *trans*-$[Co(phen)_2(NO_2)_2]NO_3$, was made by the HSM procedure except that the solution was boiled during the air oxidation. At room temperature, the HSM procedure gave low yields of complex and high yields of unidentified grey material. In both cases, the product was recrystallized first from ethanol and then from water. These preparations dissolved in concentrated hydrochloric acid to give the green color characteristic of *trans*-dichloro complexes.

Ablov's method (1) of chlorination of a solution containing cobalt(II) chloride and 1,10-phenanthroline was used to prepare the dichloro complex (solution after chlorination was dirty violet in color), which was nitrosated in situ by the addition of three moles of sodium nitrite. After the precipitate had been filtered, it was dissolved in warm water; yellow-brown crystals that gave a green solution in concentrated hydrochloric acid were obtained.

Attempts to purify the green $[Co(phen)_2(Cl)_2]Cl$ were frustrated by the extremely rapid hydrolysis of this compound. In "absolute" ethanol subjected to no special drying, hydrolysis was complete in less than two minutes; the product was orange, then became purple. This suggests that Ablov's assignment of the cis-dichloro configuration to the purple product isolated from the reaction mixture is incorrect. Even taking into account the later work of Ablov and Palade (2), the structure of the dinitro complex is not proved conclusively.

By analogy with products obtained with other amines and because the trans-dichloro complex is obtained by dissolution in concentrated hydrochloric acid, our dinitro complex is assigned the trans configuration. Anal. Calcd. for $[Co(C_{12}H_8N_2)_2]NO_3 \cdot H_2O$: Co, 10.0; C, 48.7; H, 3.08; N, 16.6. Found: Co, 10.0; C, 48.7; H, 3.30; N, 16.6.

Attempted preparation of trans-dinitrotetrapyridinecobalt(III) nitrate, trans-$[Co(py)_4(NO_2)_2]NO_3$.

Russian workers (6) made a compound which they claim is this compound by reacting hot pyridine with sodium hexanitritocobaltate(III), but the stereochemical form was not determined. They state that the compound is decomposed by water.

The direct procedure of HSM gave rise to polymeric material even when acetic acid was substituted for nitric acid. Cooling in an ice bath during oxidation gave a brown material which was decomposed in water to a red product. Oxidation using hydrogen peroxide instead of air in the HSM procedure was unsuccessful.

Werner's method (106) of synthesis of trans-$[Co(py)_4(Cl)_2]Cl$ gave the dichloro complex in good yield when chlorine was passed into the flask containing cobalt(II) chloride and pyridine at 0° Centigrade. Nitrosation of the dichloro complex led to formation of polymeric material or red solutions even at room temperature. Only when a huge excess of sodium nitrite was added did the solution become yellow.

Trans-chloronitrobis(ethylenediamine)cobalt nitrate, trans-$[Co(en)_2(NO_2)(Cl)]NO_3$, was made by dissolving the trans-dinitro complex in concentrated hydrochloric acid at room temperature and using the resulting solution.

Werner (107) prepared the compound in the same way except the solution was heated on a water bath; more recently Japanese workers (44) obtained the compound using 1:4 hydrochloric acid.

Trans-chloronitrobis(1,3-diaminopropane)cobalt(III) nitrate, trans-$[Co(tn)_2(NO_2)(Cl)]NO_3$, was made in the same way as the ethylenediamine complex.

Cis-dinitrobis(ethylenediamine)cobalt(III) nitrate, cis-$[Co(en)_2(NO_2)_2]NO_3$, was made by a procedure involving reaction of potassium hexanitritocobaltate(III) with ethylenediamine (58).

Reaction of cobalt(II) nitrate with potassium nitrite in the presence of acetic acid gave $K_3Co(NO_2)_6$. After being washed with water, alcohol, and ether, the product was dried overnight at 110° C., ground and used immediately.

The instructions given for the preparation of the cis-complex were followed explicitly, particularly the warning about heating above 60° C., and the product was twice recrystallized from water which was always cooler than 50° Centigrade. Extinction coefficients, although not a sensitive criterion of purity, agreed with published values (13) to 0.1 log unit or better. Anal. Calcd.

for $[Co(C_2H_8N_2)_2(NO_2)_2]NO_3$: Co, 17.7; C, 14.4; H, 4.86; N, 29.4; eq. wt., 333. Found: Co, 17.8; C, 14.3; H, 4.90; N, 29.6; eq. wt., 331.

Harbulak and Albinak (52) have criticized the above method of preparation of the *cis*-dinitro complex and recommend making it by treating *trans*-$[Co(en)_2(Cl)_2]Cl$ with a twenty-fold excess of sodium nitrite. Staples (99) says that he obtained the same rate constant from either preparation. Our rate constants for the cis complex are so different from those reported by Staples that this claim must be questioned. A very recent method (97) of synthesis of potassium triscarbonatocobaltate(III) and ethylenediamine in our hands led to product contaminated with some *trans* isomer.

Cis-dinitrotetramminecobalt(III) nitrate, *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$, was made by nitrosation of the carbonate (22) which had been synthesized by air oxidation of an ammoniacal solution of cobalt(II) nitrate containing ammonium carbonate (24). The crude *cis*-dinitro product was twice recrystallized from water. *Anal*. Calcd. for $[Co(NH_3)_4(NO_2)_2]NO_3$: Co, 21.0; H, 4.30; N, 34.9. Found: Co, 20.9; H, 4.58; N, 35.1.

Cis-chloronitrobis(ethylenediamine)cobalt(III) nitrate, *cis*-$[Co(en)_2(NO_2)(Cl)]NO_3$, was synthesized by nitrosation of *trans*-$[Co(en)_2(Cl)_2]Cl$ which had been prepared by the method of Bailar (7), and subsequent precipitation of the *cis*-chloronitro complex with hydrochloric acid (107). After a second precipitation with hydrochloric acid, the product was converted to the nitrate salt by dissolving in concentrated hydrochloric acid and adding a concentrated solution of potassium nitrate. *Anal.* Calcd. for $[Co(C_2H_8N_2)_2(NO_2)(Cl)]NO_3$: Co, 18.3; C, 14.9; H, 4.99; N, 26.1; Cl, 11.0. Found: Co, 18.6; C, 15.0; H, 5.02; N, 26.1; Cl, 10.8.

B. Kinetic measurements

All measurements of rate constants were made with a Beckman DU Spectrophotometer equipped with a Beckman Dual Thermospacer Set. Data were taken at wavelengths ranging from 250 to 605 millimicrons during the course of this investigation. Water from a well-insulated Fisher Unitized constant temperature bath was pumped through the thermospacers. Measurement of the cell temperature showed that the temperature of the cells varied less than 0.1° from the thermostat temperature. All temperatures are reported in degrees Centigrade.

A Precision Scientific Company Time-It was used for measurement of time.

All volumetric glassware was of Kimax quality and was used without calibration.

For the slower rate constants, 50 or 100 milliliter volumetric flasks were used as reaction vessels. The required number of milliliters of acid which had been standardized by titration with sodium hydroxide which in turn was standardized against Primary Standard Potassium Acid Phthalate was pipetted into each of three volumetric flasks. Some water was then added and the flasks were placed in the constant temperature bath. In the meantime, the cells were put in the cell holder of the spectrophotometer. After about one-half hour, the appropriate number of milliliters of complex were pipetted into the volumetric flasks, and the volume brought to exactly 50 to 100 milliliters with water maintained at the bath temperature. The flasks were inverted to mix the solutions thoroughly, and then some of the solution was transferred to a cell. After all cells had been filled, the timer was started and the optical density of each cell was determined at various times. For some runs, the data were taken at equal time intervals for one half-life of the reaction, and then more data were taken after two half-lives so that the method of Guggenheim could be readily applied. In other cases, the subsequent reactions were slow enough that an "infinite time" reading could be made.

For the fastest reactions, essentially the same procedure was used except that a solution of acid in the volumetric flask was placed in the constant temperature bath; some of the solution was placed in the cell. Solid complex was then added, the timer started, and the cell was inverted and returned to the cell holder. Readings of optical density were made at very short time intervals in these cases. This procedure is valid because it was repeatedly shown that the reactions are first order in complex, and so the concentration of the complex is not a critical factor in finding the rate law.

C. Analysis of data

Several methods were used to find the first order rate constant from the optical density data. When an "infinite time" reading of the optical density could be taken, first order rate constants were obtained from a plot of the logarithm of the corrected optical densities versus time (Method I). When the method of Guggenheim (48) was used, the logarithm of the difference in optical densities at a constant time interval was plotted versus time (Method II). When direct comparison was possible, Method I and Method II gave the same rate constant.

As a check on the graphical procedure, some rate constants were found directly from the first order equation

$$(1) \qquad k_1 = \frac{2.303}{t} \operatorname{Log} \frac{D_o - D_{oo}}{D_t - D_{oo}}$$

where t is the time in seconds; D_o is the optical density at an arbitrary starting time, t_o; D_t is the optical density at time t; and D_{oo} is the optical density at the end of the reaction (Method III).

Finally, some rate constants were computed by the method of least squares (85) from a plot of the logarithm of $(D_t - D_{oo})$ versus time (Method IV).

Rate constants computed by all methods were within the limits of the 95% confidence interval found in the least squares treatment. This was usually about 2% for most of the rate constants, although for the very fast or very slow rate constants, the error was up to 5%.

IV. DATA AND RESULTS

A. Hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ in hydrochloric, hydrobromic, perchloric, sulfuric, and nitric acids.

The rate constant as a function of acid concentration was found for five different acids at 25°. Figure 1 shows that even at low concentrations differences in the rate constant are found for perchloric and hydrochloric acids.

Data for the activity of water versus molarity for hydrochloric acid less than 10 molar, for sulfuric acid, and for perchloric acid given by Bunnett (26) were plotted. The activity of water was read off this graph for a specific acid concentration. For hydrochloric acid concentrations above 10 molar, the equations of Akerlof and Teare (3) were solved for the specific acid concentration needed. Davis and De Bruin's recent results (41) for nitric acid were plotted and the activity of water read off the graph.

The activity of water in hydrobromic acid was obtained indirectly. A graph of the Hammett acidity function, H_o, versus activity of water was constructed

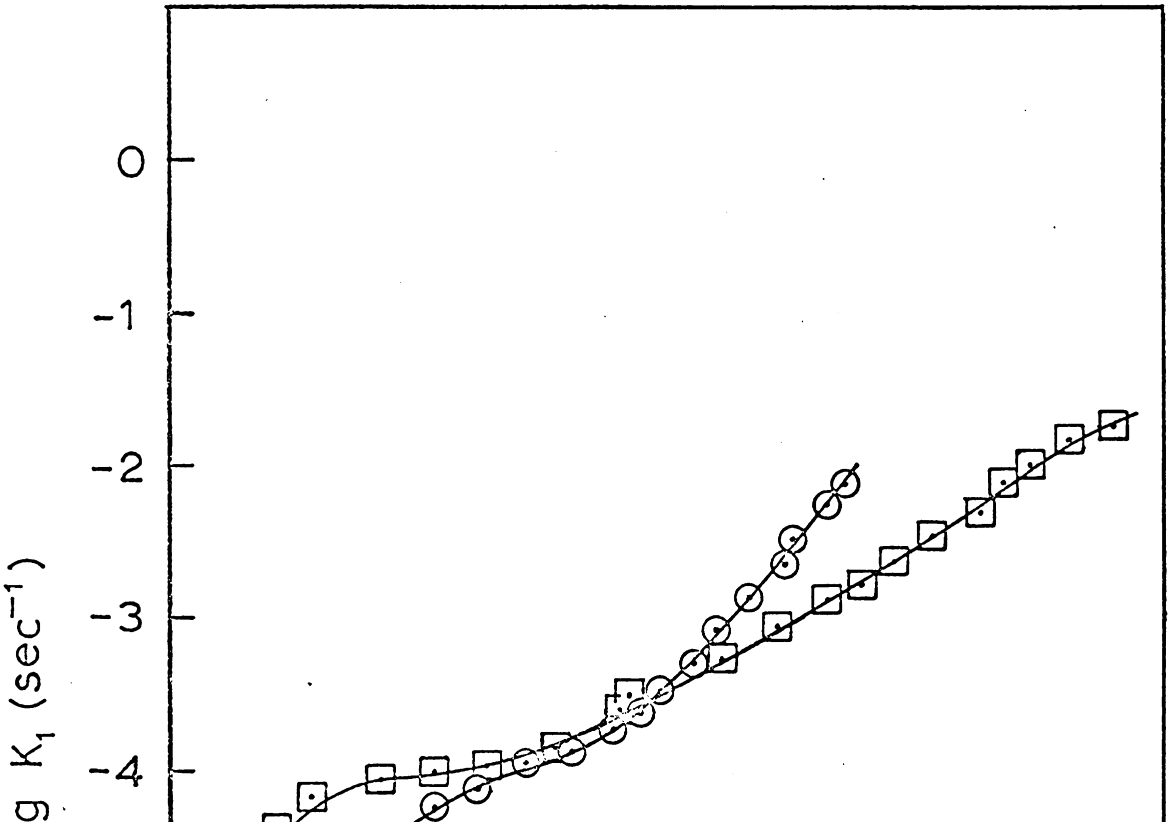

Figure 1. Hydrolysis of <u>trans</u>-$[Co(en)_2(NO_2)_2]NO_3$ in hydrochloric and perchloric acid at 25°, log k_1 versus acid concentration.

for sulfuric, nitric, hydrochloric, and perchloric acids; the H_o values were obtained from Long and Paul's review (72). All the points formed one curve, as Wyatt (109) first pointed out. Recently Yates and Wai (110) have confirmed this relationship up to high concentrations of sulfuric and perchloric acids.

Hogfeldt (55) showed that hydrobromic acid falls on the same activity of water versus H_o curve as the other acids. Therefore, the H_o values listed by Long and Paul for hydrobromic acid were used to obtain the activity of water for a given concentration of acid. The H_o value for a given hydrobromic acid concentration was read from a large-scale graph of H_o versus concentration of acid. The H_o value so obtained was located on the graph of H_o versus water activity, and the value of the activity of water was read off.

In Table 1, the first-order rate constant is shown as a function of the concentration of hydrochloric acid at 25°. These data were obtained at a wavelength of 520 millimicrons.

Table 1

First-order rate constant versus acid concentration for hydrolysis of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ in hydrochloric acid at 25°.

HCl, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	$-\log k_1$	$-\log a_w$
0.1042	0.00805	6.094	-
0.2718	0.0564	5.249	-
0.4526	0.141	4.851	-
0.6797	0.275	4.561	-
0.9053	0.403	4.395	-
1.358	0.661	4.180	0.024
2.263	0.875	4.058	0.046
2.970	0.981	4.008	0.068
3.621	1.18	3.928	0.090
4.501	1.52	3.818	0.130
5.423	2.60	3.585	0.177
5.950	3.23	3.491	0.207
6.751	5.43	3.265	0.260
7.483	9.20	3.362	0.318
8.118	13.7	2.863	0.364
8.552	16.5	2.783	0.403
9.001	25.1	2.600	0.443
9.507	35.9	2.445	0.490
10.11	53.3	2.273	0.526
10.42	81.9	2.087	0.582
10.70	101.	1.996	0.604
11.25	137.	1.863	0.661
11.88	183.	1.738	0.733

A similar variation of the rate of hydrolysis of the complex was done at 40° for calculation of the activation energy in hydrochloric acid. These data presented in Table 2 were obtained at a wavelength of 520 millimicrons, except where specifically noted in the table.

Table 2

First-order rate constant versus acid concentration for hydrolysis of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ in hydrochloric acid at 40°.

HCl, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	$-\log k_1$	$-\log a_w$
0.07985	0.0409	5.389	-
0.3944	0.810	4.092	-
0.7985	2.45	3.611	-
1.183	2.72	3.565	-
1.562	3.04	3.517	0.029
1.986	5.04	3.298	0.039
2.760	6.10	3.215	0.059
3.925	8.32	3.080	0.102
	8.17(a)		
4.722	11.1 (a)	2.955	0.140
5.915	19.2	2.717	0.204
6.388	24.3	2.614	0.210
6.786	32.5	2.488	0.261
7.187	41.8	2.379	0.290
7.870	48.3 (b)	2.316	0.339
	48.6 (b)	2.314	
	48.4 (b)	2.315	
	47.9 (b)	2.320	
7.985	60.3	2.220	0.349
8.450	86.9	2.061	0.411
9.001	122. (c)	1.914	0.443

(a) Wavelength, 430 millimicrons.
(b) Concentration of complex varied from 1.7×10^{-3} to 18.0×10^{-3} m/l.
(c) Wavelength, 350 millimicrons.

Examination of the data in Tables 1 and 2 shows that the first-order rate constant is independent of the concentration of complex, indicating a simple first-order rate law is followed at a given acid concentration; the rate constant is also independent of the wavelength used in measurement. Variation of the first-order rate constant with concentration of acid is extremely complex.

Because the data in Tables 1 and 2 seemed to show that the rate constant was related to the water activity, the hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ was examined in other acids at 25°.

The data in Table 3 show that the reaction in hydrobromic acid is also complicated. Optical density readings were made at 440 millimicrons in all cases.

Table 3

First-order rate constant versus acid concentration for the hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ in hydrobromic acid at 25°.

HBr, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	-log k_1	-log a_w
1.419	0.698	4.156	0.030
2.837	0.977	4.010	0.073
3.547	1.19	3.925	0.092
4.965	2.19	3.660	0.163
	2.20	3.658	
5.674	2.92	3.535	0.211
6.383	5.53	3.257	0.280
6.738	8.04	3.095	0.322
7.097	10.6	2.973	0.355
	10.7	2.971	

In seeking to explain the results in Tables 1-3 where the final product is the trans nitrohalide, we sought a simpler system. In perchloric acid the product is the trans nitroaquo (99), and we confirmed this observation.

Table 4 shows the observed variation of the first-order rate constant with concentration in perchloric acid at 25°. Unless specifically noted, the data in Table 4 were obtained at a wavelength of 350 millimicrons.

The data in Table 4 are compared with the data in Table 1 in Figure 1. Differences in the rate constant are apparent even at low acid concentrations.

From Table 4 we see that the hydrolysis probably is not catalyzed by small amounts of impurities such as cobalt(II) ion, because unrecrystallized compound gives the same rate constant as the thrice recrystallized material usually used.

Table 4

First-order rate constant versus concentration of acid for hydrolysis of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ in perchloric acid at 25°.

HClO$_4$, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	$-\log k_1$	$-\log a_w$
0.3278	0.00541	6.277	-
0.6555	0.0176	5.754	-
1.093	0.0511	5.292	-
1.639	0.157	4.804	0.035
2.356	0.350	4.456	0.058
2.945	0.566	4.247	0.079
3.534	0.768	4.115	0.108
	0.768(c)	4.114	
4.187	1.12 (a)	3.952	0.148
4.712	1.32	3.881	0.185
5.301	1.98	3.704	0.245
5.698	2.74 (a)	3.563	0.285
5.890	3.28	3.485	0.317
	3.16 (b)	3.500	
6.361	5.06	3.296	0.375
6.662	8.41 (a)	3.075	0.425
7.068	12.8	2.892	0.505
7.598	22.7 (a)	2.643	0.620
7.653	32.6 (d)	2.487	0.634
8.128	55.2 (d)	2.258	0.740
8.246	72.7 (d)	2.139	0.776

(a) Wavelength, 440 millimicrons.
(b) Different preparation of complex, not recrystallized.
(c) Different preparation of complex, once crystallized.
(d) Wavelength, 329 millimicrons.

Several runs were made in perchloric acid at 40°; these data are collected in Table 5. The wavelength unless otherwise stated is 350 millimicrons.

Table 5

First-order rate constant versus perchloric acid concentrations for hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ at 40°.

$HClO_4$, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	$-\log k_1$	$-\log a_w$
1.093	0.379	4.421	0.021
1.639	0.968	4.014	0.035
2.356	2.28	3.642	0.058
2.945	3.59	3.445	0.079
3.534	4.85	3.314	0.108
4.123	6.83	3.166	0.143
4.123;0.43 M. LiCl	7.91	3.102	-
4.123;0.87 M. LiCl	8.90	3.051	-
4.712	9.06	3.043	0.185
5.301	13.8	2.860	0.245
5.890	23.6 (a)	2.627	0.317
	23.9 (b)	2.620	
	24.5 (c)	2.611	
	23.5 (d)	2.629	
6.419	51.3	2.289	0.393
	51.8	2.286	
7.068	106.	1.975	0.505

(a) Wavelength, 250 millimicrons; complex 5×10^{-5} molar.
(b) Wavelength, 350 millimicrons; complex 5×10^{-4} molar.
(c) Wavelength, 400 millimicrons; complex 3×10^{-3} molar.
(d) Wavelength, 440 millimicrons; complex 3×10^{-3} molar.

Table 5 shows that when small amounts of lithium chloride are added to perchloric acid, the rate constant is not changed drastically although the product is the nitrochloro complex instead of the nitroaquo. The changes in the rate are no more than would be expected for small changes in the activity of water. Also, the data in the table make clear that the rate constant is independent of both the wavelength and concentration of complex for a fixed acid concentration.

Hydrolysis of the trans dinitro complex was examined in sulfuric acid at 25°. In this acid, the first product appears to be the nitroaquo complex. Activation energy data point to a different final product.

In Table 6 the rate constants obtained as a function of the sulfuric acid concentration at a wavelength of 440 millimicrons are reported. The rate constants were divided by two when logarithms of the rate constant were taken in an attempt to make a statistical correction.

Bunnett (10) has pointed out that no mechanistic conclusions can be drawn from rate constants determined in sulfuric acid below four molar because of the changing ional distributions in the dilute acid region.

In nitric acid the product is the nitronitrate. Ganieve (19) has synthesized the trans nitronitrate by reacting trans-$[Co(en)_2(NO_2)_2]NO_3$ with six molar nitric acid at room temperature. Ganieve reports that the cis dinitro complex gives no reaction under the same conditions. This indicates that the rate of reaction of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ with nitric acid is much greater than the rate of reaction of the *cis* isomer.

Table 6

First-order rate constant for the hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ in sulfuric acid at 25° versus concentration of acid.

H_2SO_4, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	$-\log k_1/2$	$-\log a_w$
0.8583	0.157	5.105	-
1.716	0.530	4.577	-
2.575	0.746	4.428	0.066
4.292	1.76	4.056	0.165
5.150	3.12	3.806	0.236
5.579	4.01	3.698	0.276
6.008	6.66	3.478	0.320
6.437	8.52	3.376	0.370
6.866	11.1	3.255	0.418
7.296	22.5	2.947	0.486
7.725	26.9	2.857	0.551
8.145	50.5	2.598	0.612
	49.5	2.607	
8.583	76.9	2.414	0.688
	77.0	2.415	

Kinetic data for hydrolysis of the *trans* dinitro complex are given in Table 7.

Table 7

First-order rate constant versus concentration of acid for the hydrolysis of <u>trans</u>-$[Co(en)_2(NO_2)_2]NO_3$ in nitric acid at 25°.

HNO_3, m/l.	$k_1 \times 10^4$, sec.$^{-1}$	$-\log k_1$	$-\log a_w$
3.074	0.983	4.007	0.059
4.611	1.47	3.833	0.109
5.379	1.61	3.793	0.137
6.148	2.37	3.625	0.166
6.917	2.54	3.595	0.200
7.685	2.69	3.570	0.238
9.222	4.47	3.351	0.311
10.76	5.34	3.273	0.392
	5.58	3.253	
12.30	9.89	3.005	0.488
	9.94	3.003	
13.83	14.2	2.845	0.615
15.37	24.0	2.620	0.767

In all acids, there seemed to be a relation between the rate constant and the activity of water. Other parameters such as H_o did not seem to be related to the rate constants.

In Figure 2 the log k_1 is plotted versus log a_w; examination of the graph shows that for all acids except nitric a good linear relationship is observed at higher concentrations of acid. At low concentrations of acid, this relationship fails to describe the data at all.

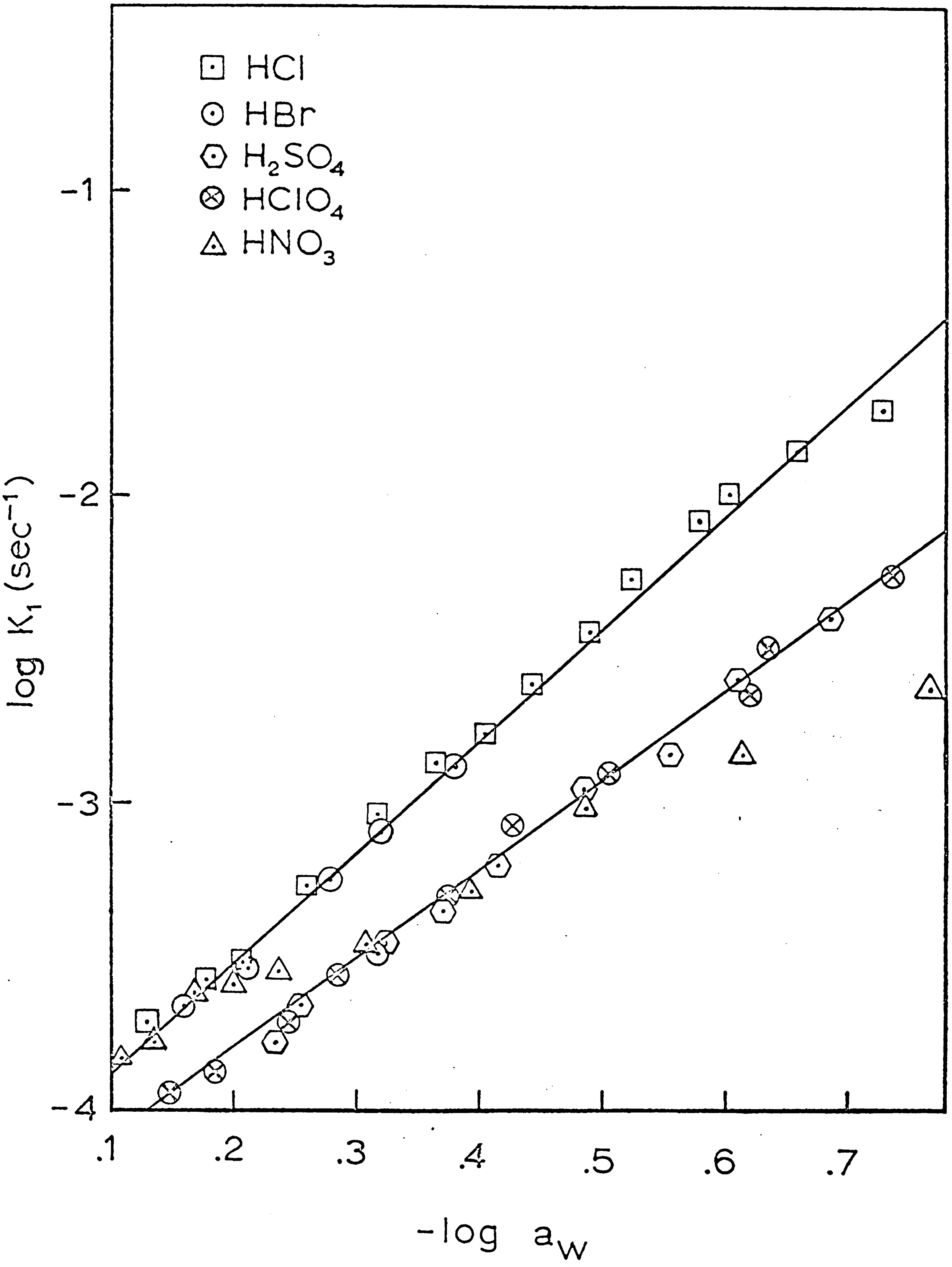

Figure 2. Hydrolysis of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ in five acids at 25°, log k_1 versus log a_W.

Nitric acid does not obey this relation. One might argue that complex behavior is observed in nitric acid and attempt to rationalize the observed rate constants. A more satisfying correlation of the data was found and will be presented in the section entitled "The Rate Laws."

B. Activation energy data for hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$.

The first-order rate constant was measured as a function of temperature for two different concentrations of perchloric acid. These data are collected in Table 8 and the Arrhenius plot of log k_1 versus 1/T is shown in Figure 3.

Table 8

Variation of $k_1 \times 10^4$ in $sec.^{-1}$ with temperature for the hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ in two concentrations of perchloric acid.

t, °C.	4.123 M. $HClO_4$	5.890 M. $HClO_4$
0.0	0.0306	0.0910
25.0	1.08	3.28
40.0	6.83	24.0
55.0	31.2	135.

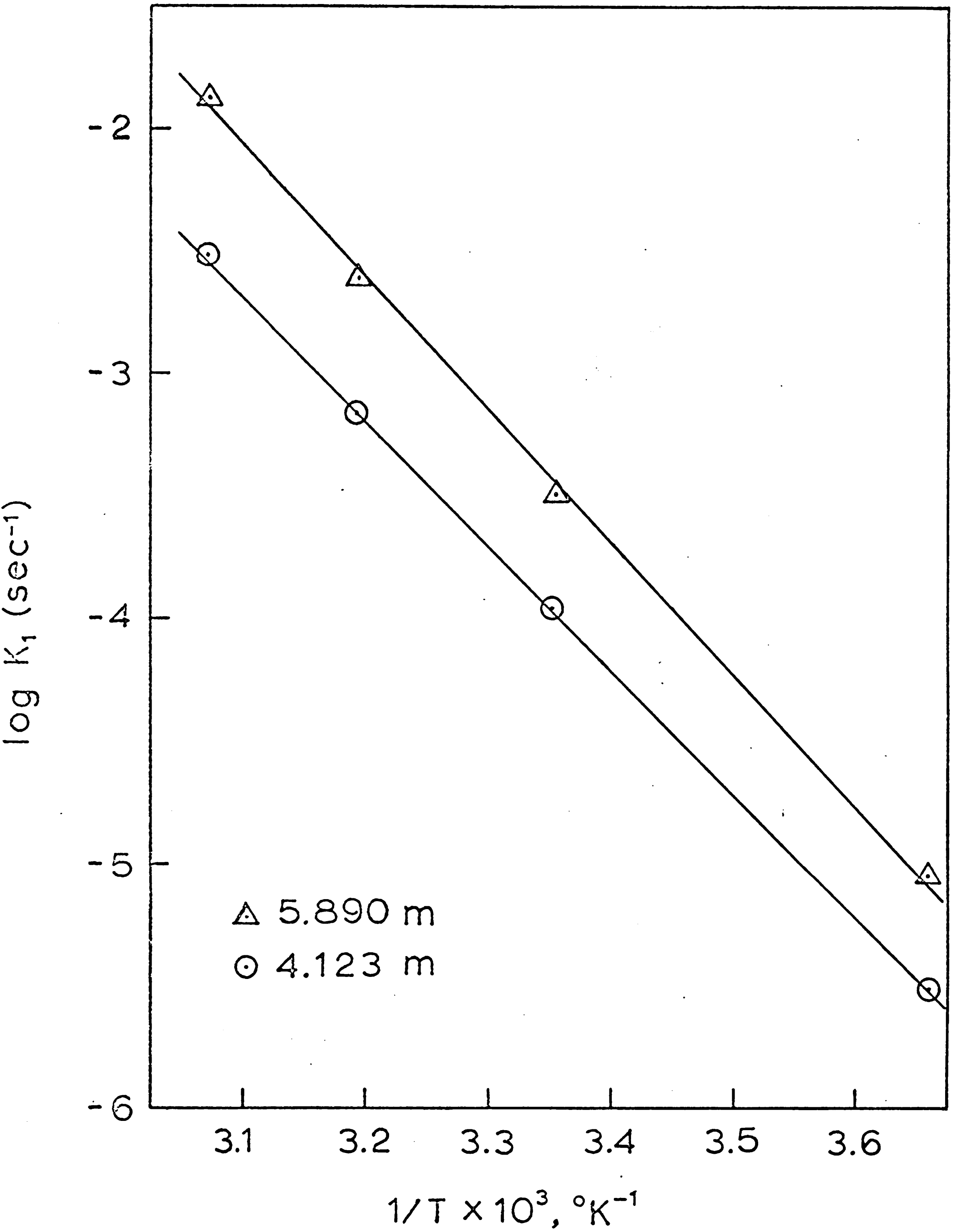

Figure 3. Arrhenius plots for hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ in perchloric acid.

Examination of Figure 3 shows that in this simple case where the product is the nitroaquo complex good linear Arrhenius plots are obtained. Activation energies obtained are 22.7 kcal. for 4.123 molar perchloric acid and 23.6 kcal. in 5.890 molar acid, with the 95% confidence interval 0.9 kcal./mole.

Another approach was used to find the activation energy and activation entropy using the data in Tables 4 and 5. Empirically it was found that up to about 5 molar acid, the rate constants could be fitted to an equation of the form

$$(1) \qquad k_1 = A(HClO_4)^2 .$$

Figure 4 shows a plot of eq. 1. From the least-squares values of "A" at 25 and 40°, the energy of activation is 23.6 ± 0.8 kcal./mole and the entropy of activation is 2.9 ± 2.7 eu., both at the 95% confidence level. Staples (99) lists 24.9 kcal./mole for the activation energy and 2.0 eu. for the activation entropy of hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ in 3.5 molar perchloric acid.

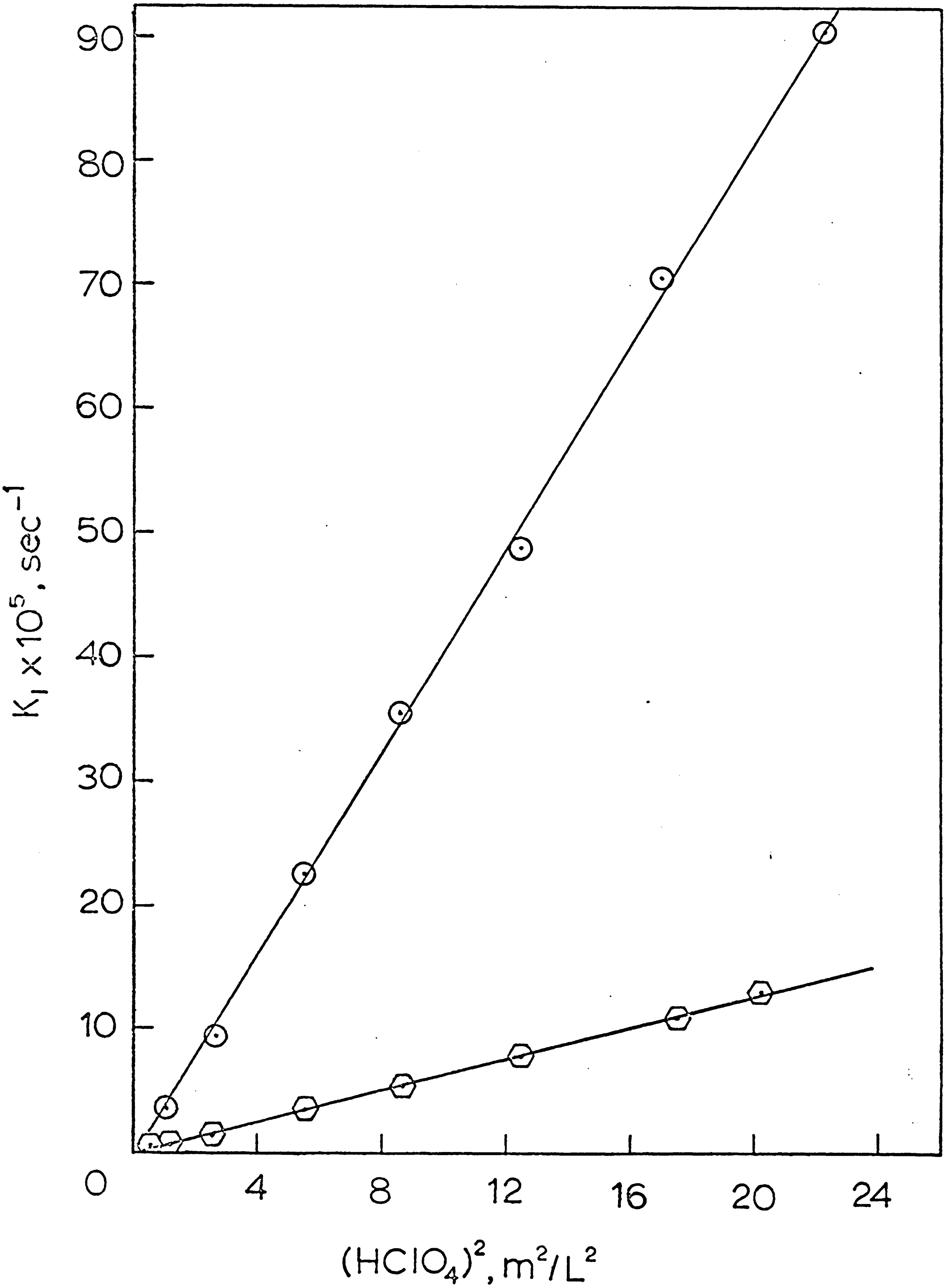

Figure 4. Hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ in perchloric acid at two temperatures, k_1 versus $(HClO_4)^2$; hexagons, 25°; circles, 40°.

Arrhenius plots in sulfuric, hydrobromic, hydrochloric, and nitric acids were curved with an activation energy of 23 kcal. at the lower temperatures decreasing to as low as 12 kcal. at higher temperatures. If the nitroaquo complex is an intermediate, we would have the reactions

(2) $[Co(en)_2(NO_2)_2]^{+1} + H_2O \longrightarrow [Co(en)_2(H_2O)(NO_2)]^{+2}$

(3) $[Co(en)_2(H_2O)(NO_2)]^{+2} + Z^- \longrightarrow [Co(en)_2(Z)(NO_2)]^{+1}$

where Z^- is an anion. Qualitative experiments show that the addition of Z^- in concentrated acid solutions is not instantaneous; on the basis of color changes, addition of chloride ion to a 6 molar perchloric acid solution of the nitroaquo complex appears to have a half-life of about one minute. This would mean that reaction 3 is faster than reaction 2.

Hulett (59) has recently reviewed reasons for deviation from the Arrhenius equation. Medium effects have been observed to give curved Arrhenius plots in the hydrolysis of neutral organic compounds. In most of these cases, a polar transition state is likely; an example of such a reaction is the hydrolysis of tertiary butyl chloride, in which dE/dT has been found to be -183 cal. mole^{-1} deg.$^{-1}$ over the temperature range 0-25°.

If a pre-equilibrium is involved and the rate depends on the concentration of species formed, a curved Arrhenius plot may be observed. This curvature would be due to the variation of the equilibrium constant with temperature. Neither medium effects nor variation of an equilibrium constant with temperature seem to be adequate explanations of the curvature of the Arrhenius plots in our system. Perchloric acid should give the same results as other acids by either of these explanations.

Hulett says: "If two consecutive reactions have different activation energies, the Arrhenius plot is concave downwards in the region where the two rates are comparable, that with the low activation energy controlling at high temperature and *vice versa*." In perchloric acid, only reaction 2 occurs so a linear Arrhenius plot would be expected; in the other acids both reactions 2 and 3 take place, leading to curvature of the Arrhenius plots.

The activation energy data obtained in hydrobromic acid are listed in Table 9 and are plotted in Figure 5.

Table 9

Variation of $k_1 \times 10^4$ in sec.$^{-1}$ with temperature in three concentrations of hydrobromic acid for trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$.

t, °C.	3.547 M. HBr	4.965 M. HBr	6.383 M. HBr
25.0	1.19	2.19	5.53
40.0	7.98	14.9	35.1
55.0	37.9	51.2	91.2
70.0	120.	-	213.

Table 10 contains rate constants obtained in sulfuric acid; the Arrhenius plot of these data is shown in Figure 6.

Table 10

Variation of $k_1 \times 10^4$ in sec.$^{-1}$ with temperature in four sulfuric acid concentrations for trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$.

t, °C.	2.575 M. H_2SO_4	4.292 M. H_2SO_4	5.150 M. H_2SO_4	6.866 M. H_2SO_4
15.0	0.214	-	0.549	2.95
25.0	0.746	1.76	3.12	11.1
40.0	5.60	11.2	18.2	69.3
55.0	24.9	45.3	73.6	224.
70.0	79.8	-	244.	-

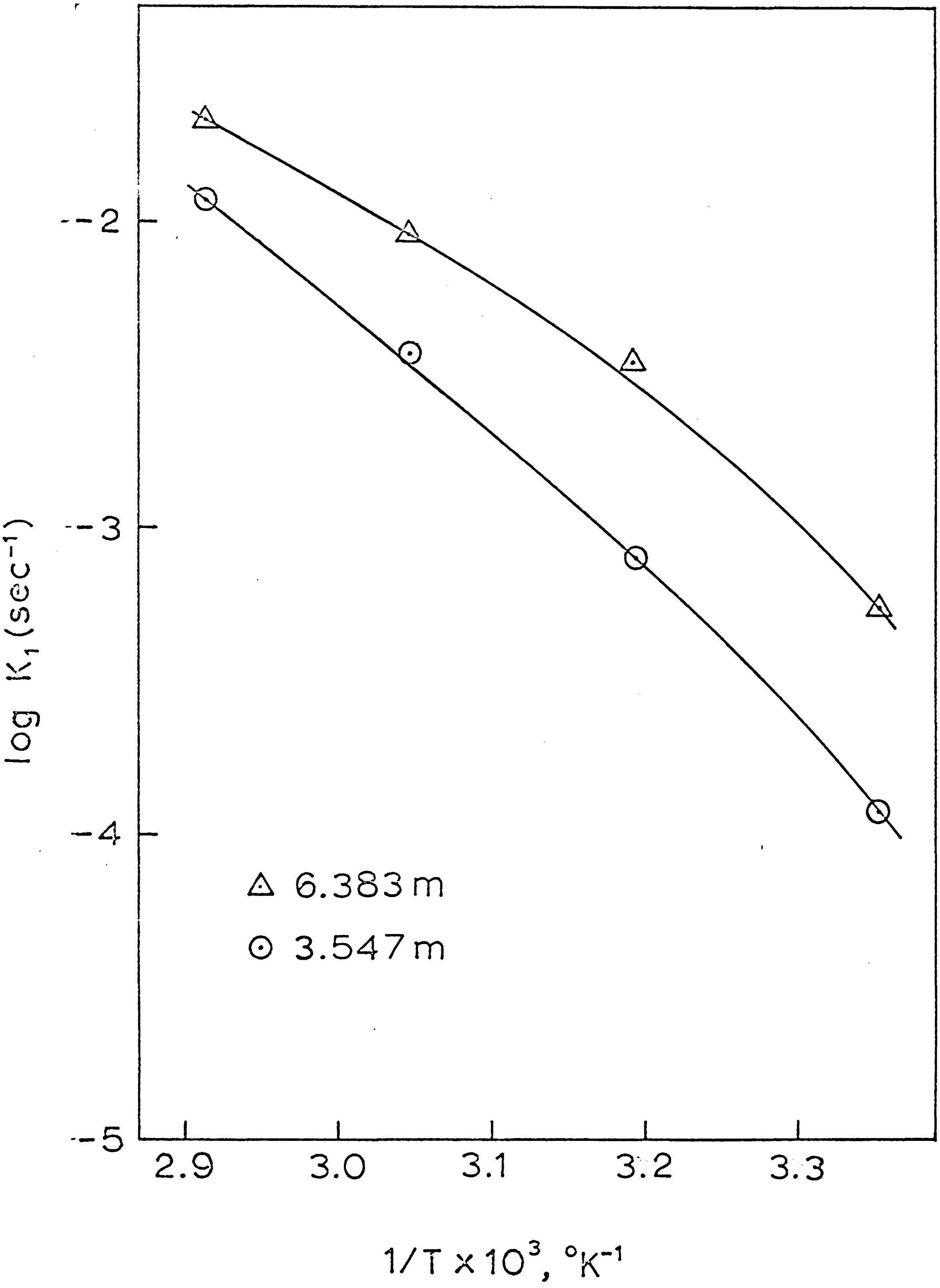

Figure 5. Arrhenius plots for hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ in hydrobromic acid.

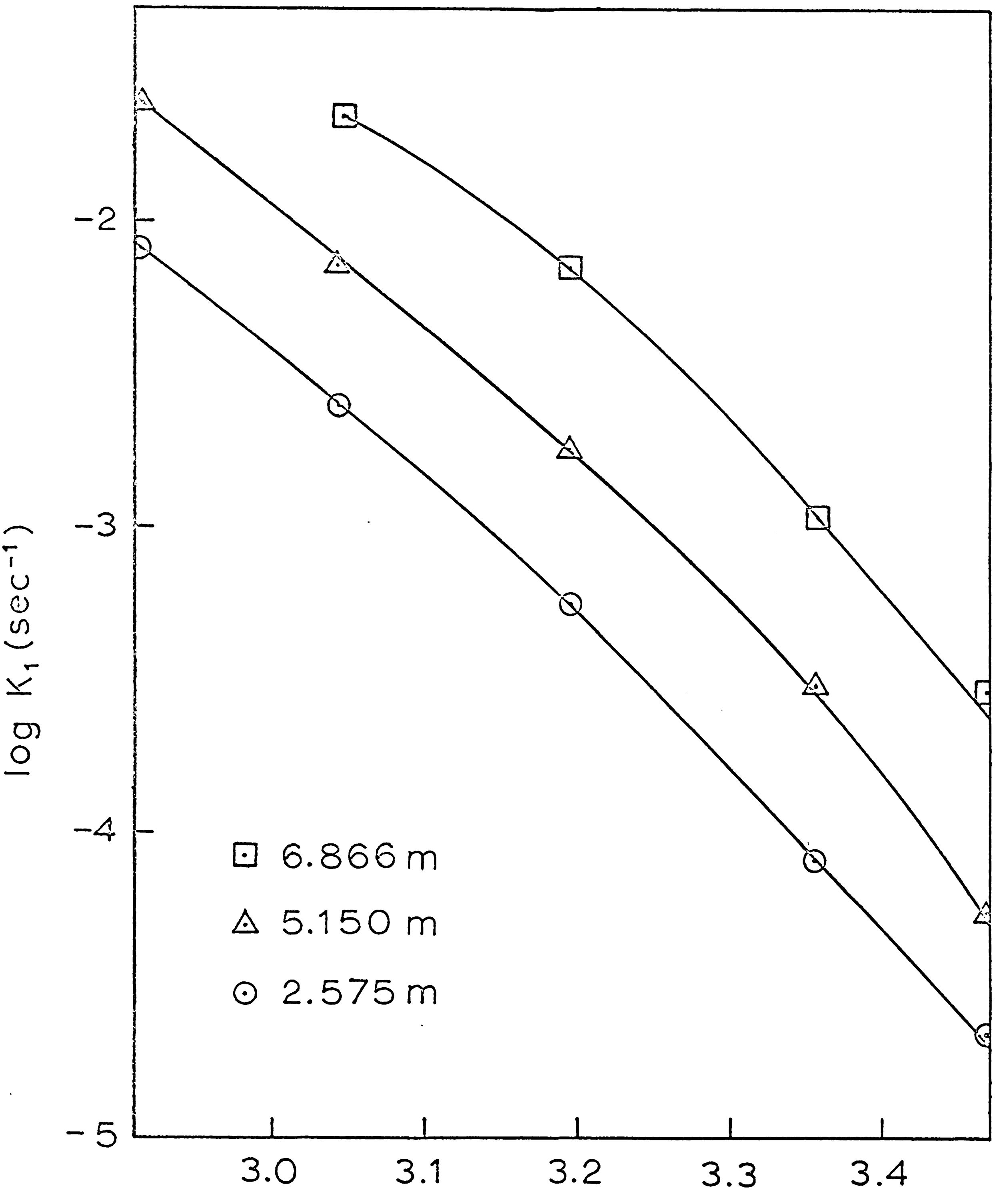

Figure 6. Arrhenius plots for hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ in sulfuric acid.

In Table 11 are given the activation energy data for nitric acid; the Arrhenius plot of these rate constants is shown in Figure 7.

Table 11

Variation of $k_1 \times 10^4$ in sec.$^{-1}$ with temperature in four concentrations of nitric acid for trans-$[Co(en)_2(NO_2)_2]NO_3$.

t, °C.	3.074 M. HNO_3	6.148 M. HNO_3	9.222 M. HNO_3	12.30 M. HNO_3
15.0	-	0.597	1.05	2.65
25.0	0.983	2.37	4.47	9.89
40.0	4.66	10.5	23.4	55.4
55.0	21.1	44.7	68.6	135.
70.0	-	166.	-	-

Smooth curves of the data in Tables 1 and 2 were drawn and the rate constants were read off the graphs at round concentrations of hydrochloric acid; these rate constants were used to compute an activation energy from the two rates (at 25° and 40°). The computed activation energies were constant at 23.2 kcal. with an uncertainty of 0.5 kcal. at the 95% confidence interval up to 6 molar acid. Above this concentration a linear decrease in the activation energy with concentration of acid was noted.

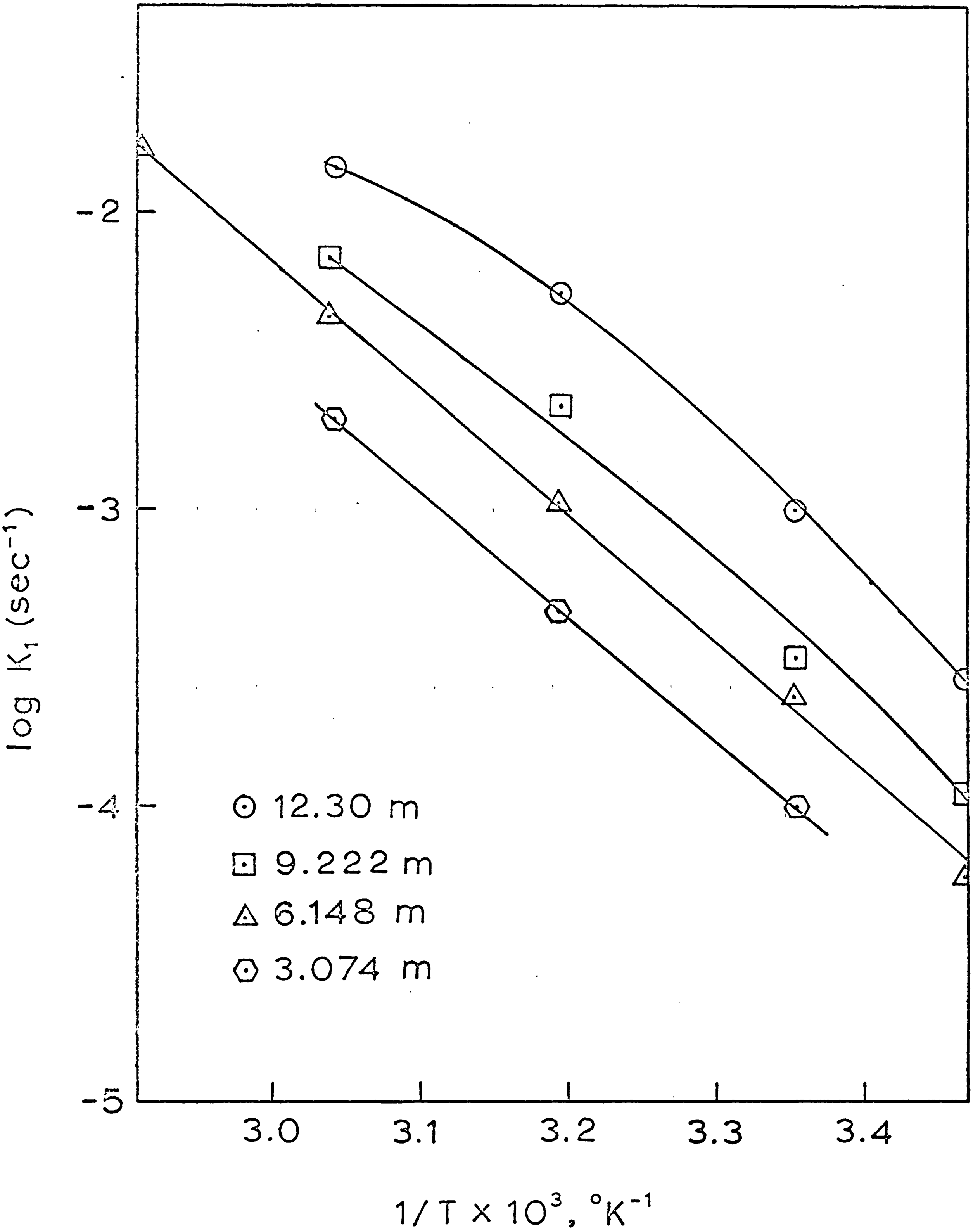

Figure 7. Arrhenius plots for hydrolysis of <u>trans</u>-$[Co(en)_2(NO_2)_2]NO_3$ in nitric acid.

Three concentrations of hydrochloric acid were examined in more detail. In Figure 8 the data in Table 12 are plotted.

Table 12

Variation of $k_1 \times 10^4$ in $sec.^{-1}$ with temperature in three concentrations of hydrochloric acid for *trans*-$[Co(en)_2(NO_2)_2]NO_3$.

t, °C.	0.9054 M. HCl	2.380 M. HCl	11.88 M. HCl
0.0	-	-	14.4
15.0	-	-	94.9
25.0	0.403	0.890	183.
40.0	2.50	5.35	-
45.0	-	8.55	-
60.0	22.8	49.6	-

Examination of Figures 5-8 shows that the curvature of the Arrhenius plots is greater in higher acid concentrations. This may indicate that the addition of the anion Z^- is a second-order reaction, but other interpretations are possible. The observed curvature can most easily be explained on the basis of two consecutive reactions; the first is the addition of water to form the nitroaquo intermediate and the second is the reaction of an anion with the intermediate to yield product.

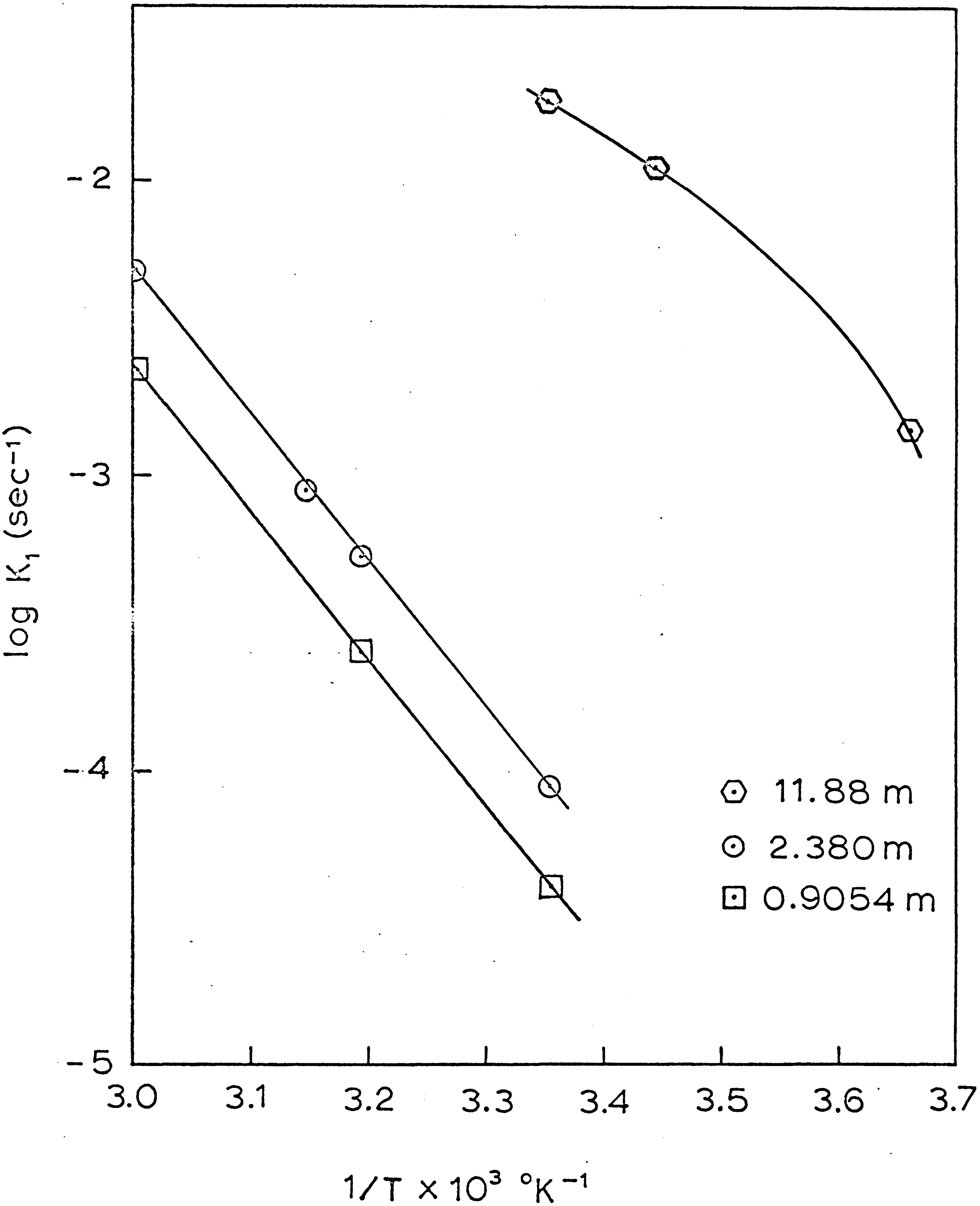

Figure 8. Arrhenius plots for hydrolysis of trans-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$ in hydrochloric acid.

C. Rates of hydrolysis of cis-$[Co(en)_2(NO_2)_2]NO_3$.

Staples (99) reports that the rate of hydrolysis of the cis isomer is about one half as fast as the rate of hydrolysis of the trans isomer in 3.5 molar perchloric acid. Results of this investigation presented in Table 13 show that there is a marked difference in reactivity between the two isomers in 11.88 molar hydrochloric acid. Two rate constants in 9.054 molar acid are included in the table. The data in Table 13 for the cis compound and the data in Table 12 for the trans in 11.88 molar hydrochloric acid are plotted in Figure 9.

Table 13

Variation of $k_1 \times 10^4$ in sec.$^{-1}$ with temperature in two concentrations of hydrochloric acid for cis-$[Co(en)_2(NO_2)_2]NO_3$.

t, °C.	9.054 M. HCl	11.88 M. HCl
25.0	-	3.02
30.0	-	5.73
35.0	-	9.30
40.0	-	19.8
45.0	4.34	31.1
50.0	-	48.0
60.0	20.9	-

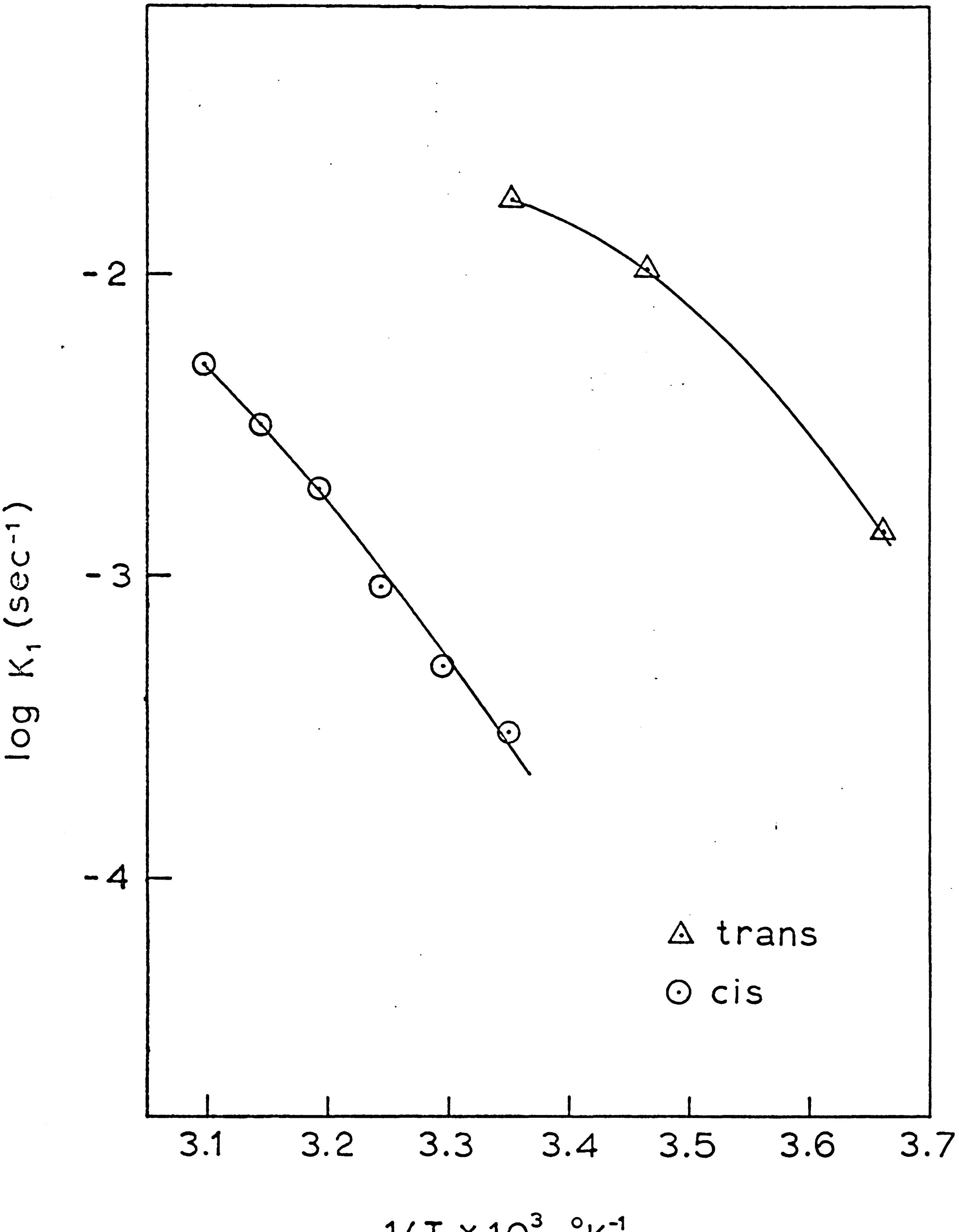

Figure 9. Reactivity of $[Co(en)_2(NO_2)_2]NO_3$ isomers in 11.88 M. HCl.

Examination of Figure 9 shows that the trans isomer reacts about 60 times faster than the cis compound. An activation energy of 21.3 kcal. is obtained for the cis complex in both concentrations of hydrochloric acid if only the data below 45° are used in the case of the 11.88 molar acid.

Because the rate of hydrolysis of the cis-$[Co(en)_2(NO_2)_2]NO_3$ complex was so slow in perchloric acid, the method of Guggenheim could not be used conveniently; the subsequent hydrolysis of the nitroaquo product prevented measurement of an "infinite time" optical density. Only the initial rates of change of the absorbance at 350 millimicrons was measured in three concentrations of acid using the same concentration of complex.

We may write

$$\text{(4)} \qquad \frac{-dD}{dt} = k_1 Q$$

where dD/dt is the initial rate of change of absorbancy with time, k_1 is the first-order rate constant, and Q is a constant if the same concentration of complex is used. From measurement of the initial absorbancy minus the absorbancy after 24 hours, Q in eq. 4 was 0.565 in

9.41 molar and 0.444 in 7.05 molar perchloric acid. We may take Q to be approximately one half.

In Table 14 are listed initial slopes measured using 5.6 x 10^{-4} molar <u>cis</u>-$[Co(en)_2(NO_2)_2]NO_3$ at a wavelength of 350 millimicrons. These initial slopes may be converted to the first-order rate constant by multiplying by a factor of approximately two.

Table 14

Initial rates of acid hydrolysis of <u>cis</u>-$[Co(en)_2(NO_2)_2]NO_3$ in perchloric acid at 25°.

$HClO_4$, m/l.	dD/dt x 10^7	-log dD/dt	-log a_w
4.712	3.54	6.456	0.190
7.068	24.3	5.614	0.505
9.410	477.	4.320	1.100

A graph of log dD/dt versus log a_w has a slope of -2.8 compared with a slope of -3.0 for the <u>trans</u>-dinitro complex, suggesting that the mechanism of hydrolysis is the same for both compounds.

We attempted to obtain rate constants in 3.5 molar perchloric acid for direct comparison with the rate constants reported by Staples (99) for the <u>cis</u>

complex but the rate was too slow to measure with any accuracy by the method of initial rates. Staples reported a rate constant of about 5 x 10^{-5} $\mathrm{sec.}^{-1}$ in 3.5 molar perchloric acid; using the data in Table 14 we can estimate a rate constant of about 2 x 10^{-7} $\mathrm{sec.}^{-1}$ at the same concentration of acid. Although our estimate is uncertain, the disagreement with Staples' rate constant is so extreme that some explanation of the difference is necessary. Our rate constant is much smaller than Staples', which might suggest that Staples had some catalytic impurity in his preparation of the cis complex. We think this is not a reasonable explanation because we have deliberately tried to add impurities. There is no difference in rate in reactions run in ordinary distilled water and carefully redistilled water for the trans complex. No difference was observed in rates obtained with unrecrystallized and with thrice recyrstallized trans complex. Unless the cis compound is unusually sensitive to catalytic impurities, which we doubt, these results for the trans complex tend to rule out catalytic impurities as the explanation.

One possible reason for this disagreement might be that Staples' preparation of the cis-dinitro complex was contaminated by some trans isomer. Staples' complexes give good elemental analyses, which tends to confirm their formulas, but does not confirm their stereochemical purity. The extinction coefficient for the trans nitroaquo is lower than that for the cis nitroaquo compound at 329 millimicrons. A mixture of cis dinitro and trans nitroaquo complexes could give the same apparent extinction coefficient as the cis nitroaquo, which is what Staples reported.

Whatever the explanation, the disagreement on the ratio of rates trans/cis is profound: Staples, 2; this investigation, 160 in 4.7 molar perchloric acid and 60 in 11.88 molar hydrochloric acid. We synthesized the cis and trans isomers of $[Co(NH_3)_4(NO_2)_2]NO_3$ and measured the rates of hydrolysis in 11.88 molar hydrochloric acid. The trans/cis ratio for these complexes is about 350, which tends to indicate that the results for the ethylenediamine complex is correct.

D. Rates of reaction of other trans-dinitro complexes.

In order to see what effect the "inert" ligand (AA) exerts, hydrolysis rates of other complexes were measured. Table 15 lists the data obtained for five trans-dinitro complexes of the type $[Co(AA)_n(NO_2)_2]^{+1}$. Several abbreviations are used in the table for the following complexes: for n = 4; "ammine" is ammonia: for n = 2; "en" is ethylenediamine; "tn" is 1,3-diaminopropane; "bipy" is 2,2'-bipyridine; and "phen" is 1,10-phenanthroline. These abbreviations are used throughout the remainder of this thesis.

Table 15

First-order rate constant, $k_1 \times 10^4$, in sec.$^{-1}$ versus perchloric acid concentration for five *trans*-dinitro complexes at 25°.

$HClO_4$, m/l.	en	tn	-log a_w
1.629	0.157	0.443	0.035
2.356	0.349	0.949	0.058
3.534	0.766	2.21	0.108
4.712	1.32	5.57	0.185
5.890	3.28	16.8	0.317
7.068	12.8	75.4	0.505

$HClO_4$, m/l.	ammine	bipy	phen
4.712	21.3	1.04	0.263
5.890	53.3	4.89	1.04
7.068	240.	40.1	6.02

Inspection of Table 15 reveals that the rate constants are surprisingly close together for this wide variation in inert ligand structure. Notice also that the rate of reaction decreases with the complexity of ligand from ammine, tn, en, bipy to phen. This is the order of reactivity expected with an SN_2 reaction. A plot of log k_1 versus log a_w of the data in Table 15 is shown in Figure 10.

In Table 16 are given the data for hydrolysis of three of the complexes in hydrochloric acid. The log k_1 versus log a_w plot for these data is presented in Figure 11.

Table 16

First-order rate constant, $k_1 \times 10^4$, in $sec.^{-1}$ versus hydrochloric acid concentration for three *trans*-dinitro complexes at 25°.

HCl, m/l.	en	tn	ammine
5.423	2.60	10.1	33.1
6.340	4.30	18.7	53.1
8.118	13.7	73.5	162.

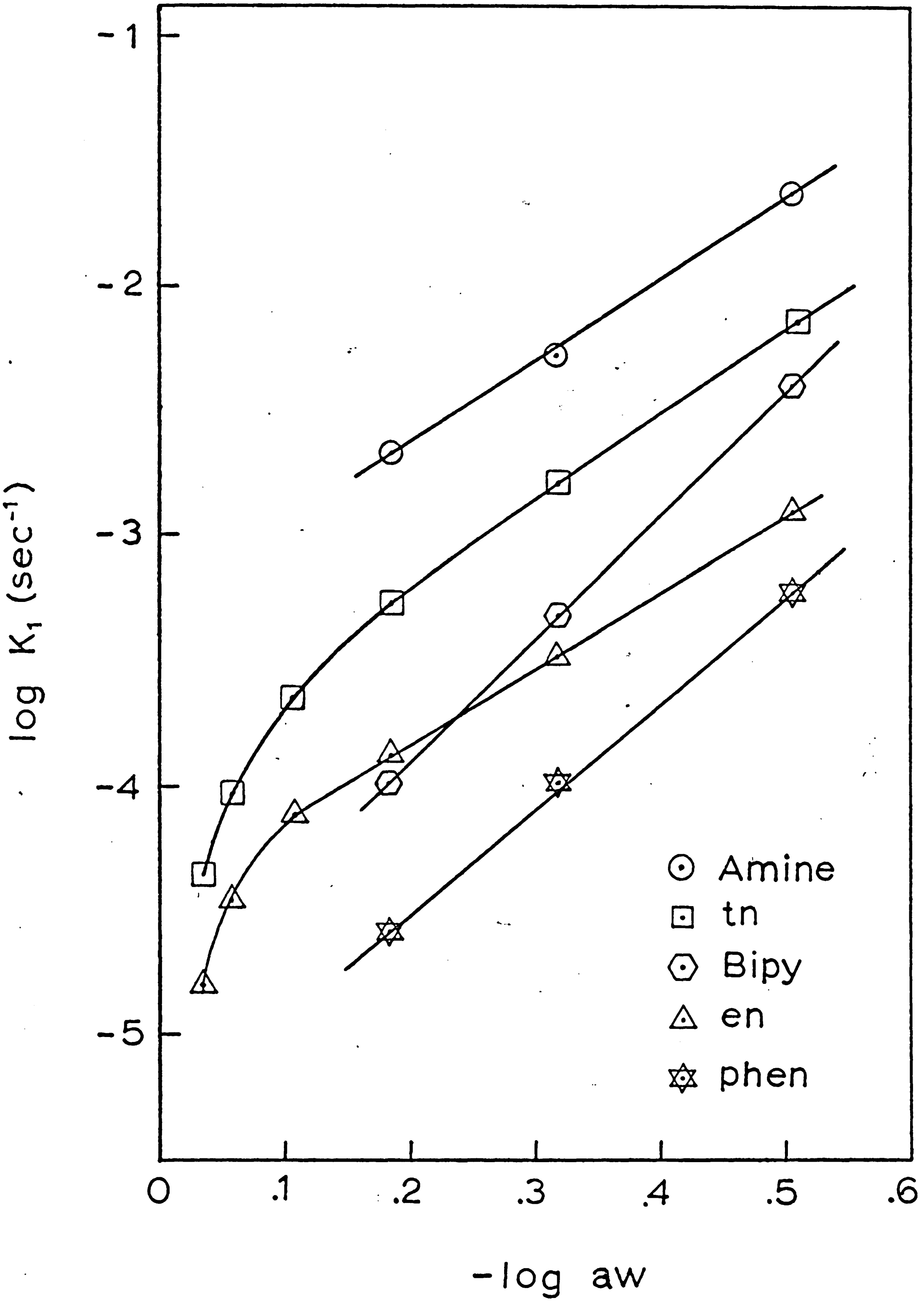

Figure 10. Reactivity of five trans-dinitro complexes in perchloric acid at 25°, log k_1 versus log a_w.

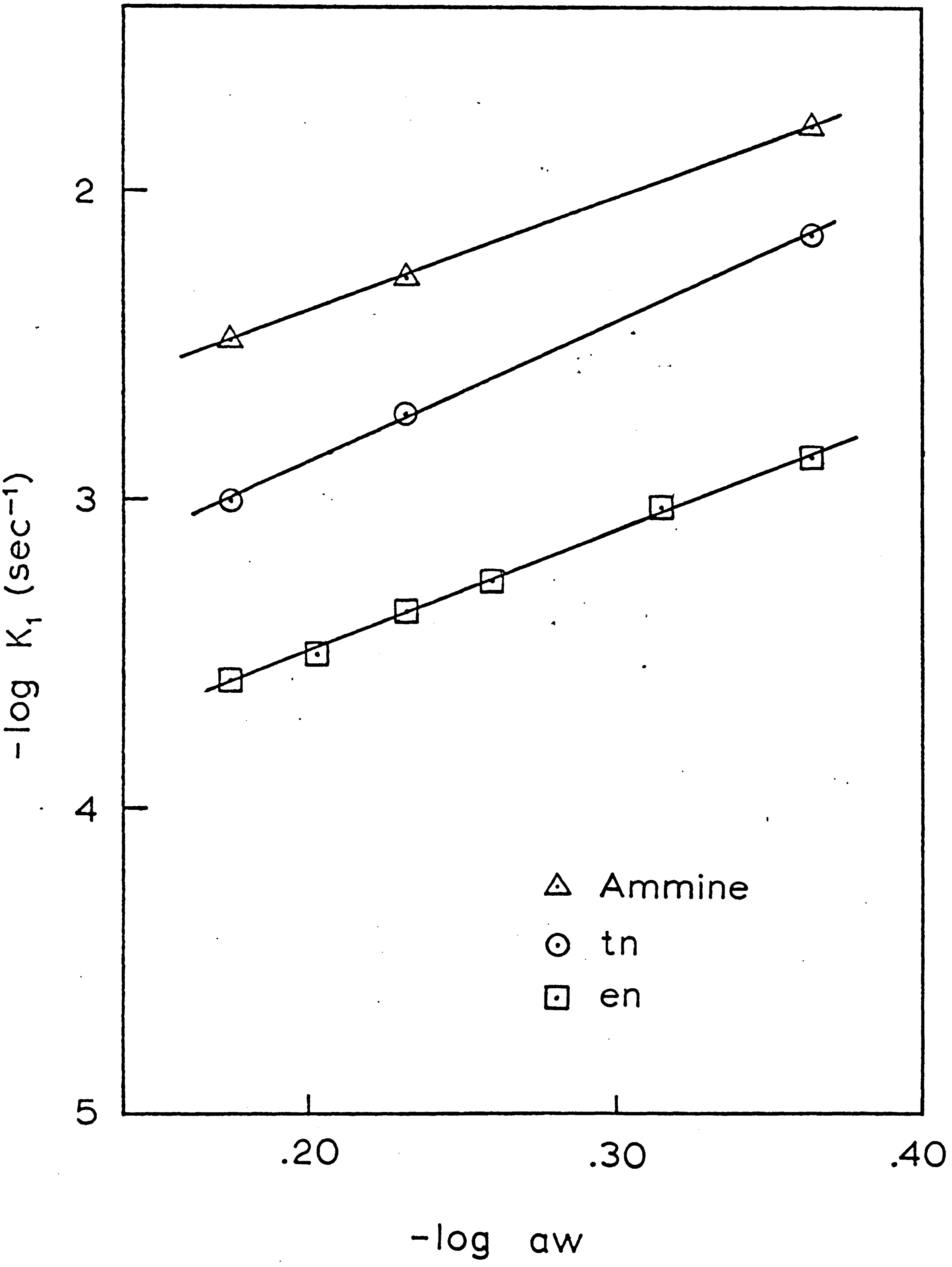

Figure 11. Reactivity of three trans-dinitro complexes in hydrochloric acid at 25°, log k_1 versus log a_w.

Notice that in Table 16 the rate constants are all within a factor of about 15 of each other. The small effect of the ligand in removal of the nitro group suggests that perhaps the removal involves a species protonated on the nitro group, in which case the ligand would have only a small effect on the rate of reaction. This idea also would explain the marked difference in reactivity between the cis and trans forms of the same complex.

E. Comparison of reaction rates in 11.88 molar hydrochloric acid.

In Table 17 are collected data obtained in concentrated hydrochloric acid. In this solvent the second nitro group was replaced, although at a much slower rate than the first. The rate constants for the nitrochloro complexes are for the removal of the nitro group.

Table 17

First-order rate constants, $k_1 \times 10^4$, in sec.$^{-1}$ for reaction of several complexes in 11.88 molar hydrochloric acid at 25°.

Complex ion	trans	cis
$[Co(NH_3)_4(NO_2)_2]^{+1}$	3,800 (a)	11.3
$[Co(en)_2(NO_2)_2]^{+1}$	185	3.00
$[Co(tn)_2(NO_2)_2]^{+1}$	3,500 (a)	-
$[Co(bipy)_2(NO_2)_2]^{+1}$	55.3	-
$[Co(phen)_2(NO_2)_2]^{+1}$	21.3	-
$[Co(en)_2(Cl)(NO_2)]^{+1}$	0.0110	7.25
$[Co(tn)_2(Cl)(NO_2)]^{+1}$	0.935	-

(a) Estimated from log k_1 versus log a_w plot.

F. The rate laws.

Bunnett (25) has examined a large number of acid hydrolyses of organic compound reported in the literature. He comments that most investigators have tended to try to fit their results to one of two rate laws; they plot either log k_1 versus H_o or log k_1 versus log (H^+). According to the Zucker-Hammett hypothesis, if the rate varies with H_o water is not involved in the rate determining step but if the rate varies with acid concentration, water is involved in the rate determining step of the reaction.

Bunnett suggested that the differences [log k_1 - log (H^+)] or [log k_1 + H_o] could be plotted against the log a_w. In some cases a good fit of the data could be obtained by plotting log k_1 versus log a_w. If protonation is not complete, the fraction protonated defined as

$$F = \frac{h_o}{h_o + K_a} \tag{5}$$

where K_a is the acid dissociation constant of the species being protonated, must be included.

Bunnett's proposed equations are then

$$[\log k_1] - \log F = w_a \log a_w + \text{Constant} \tag{6}$$

$$[\log k_1 - \log (H^+)] - \log F = w^* \log a_w + \text{Ratio} \tag{7}$$

and

$$[\log k_1 + H_o] - \log F = w \log a_w + \text{Activity} \tag{8}$$

where w, w_a, and w^* are slopes and constant, ratio, and activity are intercepts of the respective plots. We recognize eq. 6 as log k_1 versus log a_w plot if protonation is complete so that log F is zero. This kind of plot has been seen in Figures 2, 10, and 11. Bunnett shows that w_a is related to w^* so that it is necessary to consider only eq. 7 and eq. 8.

Bunnett shows that eq. 7 and eq. 8 may be used to fit the data very well. He further shows that the values of w^* and w can be related to the role of water in the reaction. The categories are listed in Table 18, for substances protonated on oxygen or nitrogen.

Table 18

Bunnett's (25) mechanistic interpretation of w and w^* values

w values	w^* values	Function of water in rate-determining step
-2.5 to 0.0	-	Is not involved
1.2 to 3.3	less than -2	Acts as a nucleophile
above 3.3	above -2	Acts as a proton-transfer agent

In Figure 12 a plot of the data for the hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ in the five acids at 25° is shown; examination of Figure 12 shows that these data follow eq. 7 very well indeed. The slopes and intercepts computed by the method of least squares are given in Table 19.

Table 19

Slopes and intercepts of eq. 7 for *trans*-$[Co(en)_2(NO_2)_2]NO_3$ hydrolysis in five acids at 25°.

Acid	Conc. range	w^*	Ratio	n(a)
Nitric	3.074-15.37	-1.03 ± 0.19	-4.64 ± 0.19	11
Perchloric	2.358- 8.247	-2.42 ± 0.12	-4.96 ± 0.05	15
Sulfuric	2.575- 8.585	-2.49 ± 0.18	-5.08 ± 0.13	11
Hydrobromic	3.547- 7.097	-2.55 ± 0.58	-4.48 ± 0.54	6
Hydrochloric	3.621-11.88	-2.74 ± 0.30	-4.84 ± 0.26	15

(a) The number of observations included.

Table 19 shows that the value of w^* is the same for all acids except nitric.

A graph of eq. 8 was constructed; a value of w of 2.3 for perchloric and nitric acids and 2.4 for hydrochloric acid was obtained if a value of K_a of 10 was assumed for calculation of the fraction protonated in eq. 5. Comparison of these w and w^* values with the

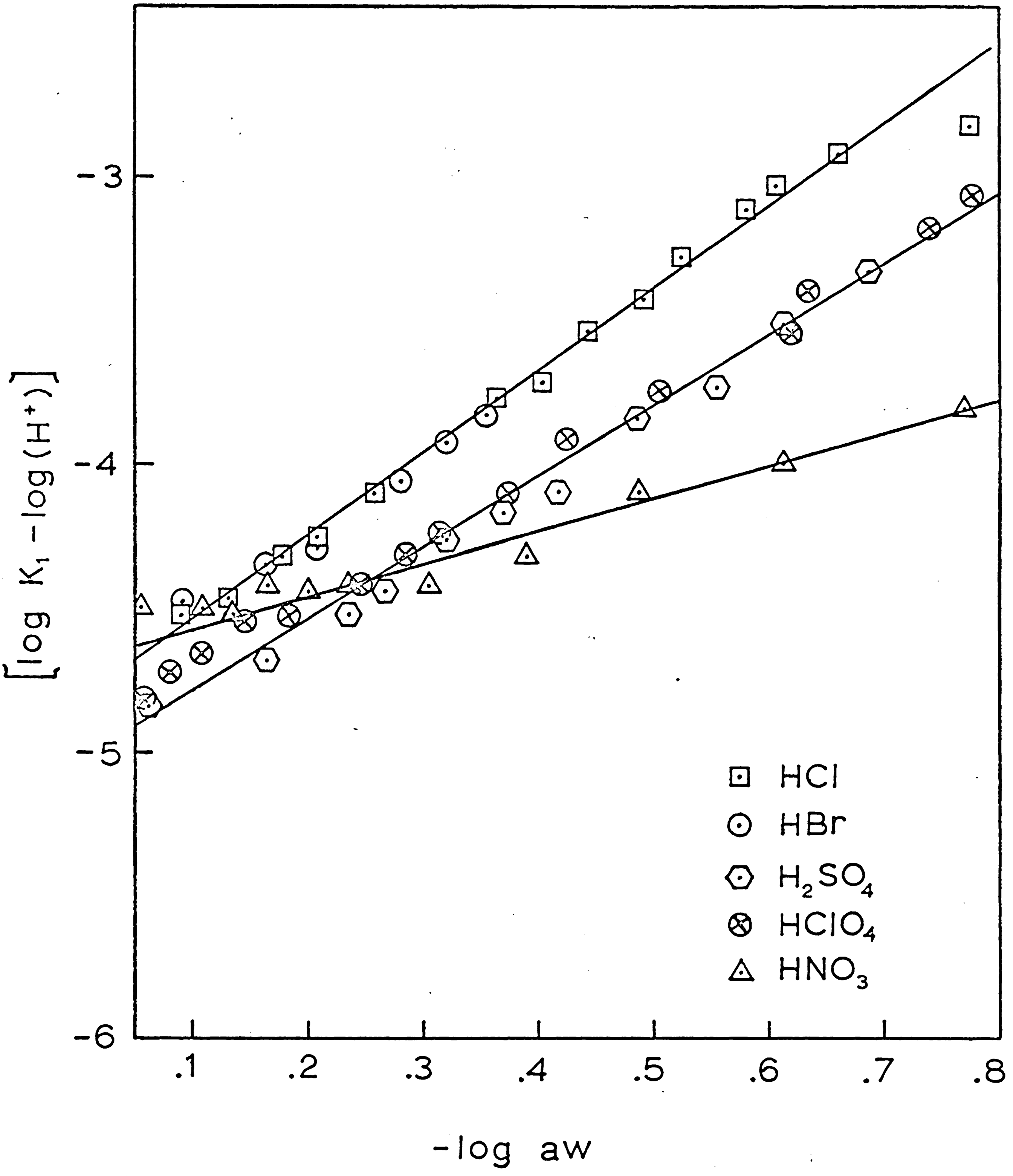

Figure 12. Hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ in five acids at 25°, [log k_1 - log (H+)] versus log a_w.

corresponding ones in Table 18 suggests that water is involved as a nucleophile in these reactions.

Figure 13 shows a plot of eq. 7 for the other dinitro complexes in perchloric acid (Table 15). Similar plots were constructed for the data in Table 16 and the slopes obtained. Plots of eq. 8 were constructed for all these complexes in both acids and the slopes were found. The parameters obtained from such plots are listed in Table 20.

Table 20

w and w^* values for the hydrolysis of five complexes in two acids at 25°

Compound	Hydrochloric acid		Perchloric acid	
	w	w^*	w	w^*
ammine	2.1	-2.7	1.5	-2.8
en	2.4	-2.8	2.3	-2.4
tn	1.3	-3.5	1.3	-3.0
bipy	-	-	0.0	-4.4
phen	-	-	1.0	-3.7

Comparison of the values in Table 20 with Bunnett's mechanistic values in Table 18 shows that all the w^* values are less than -2, indicating that water

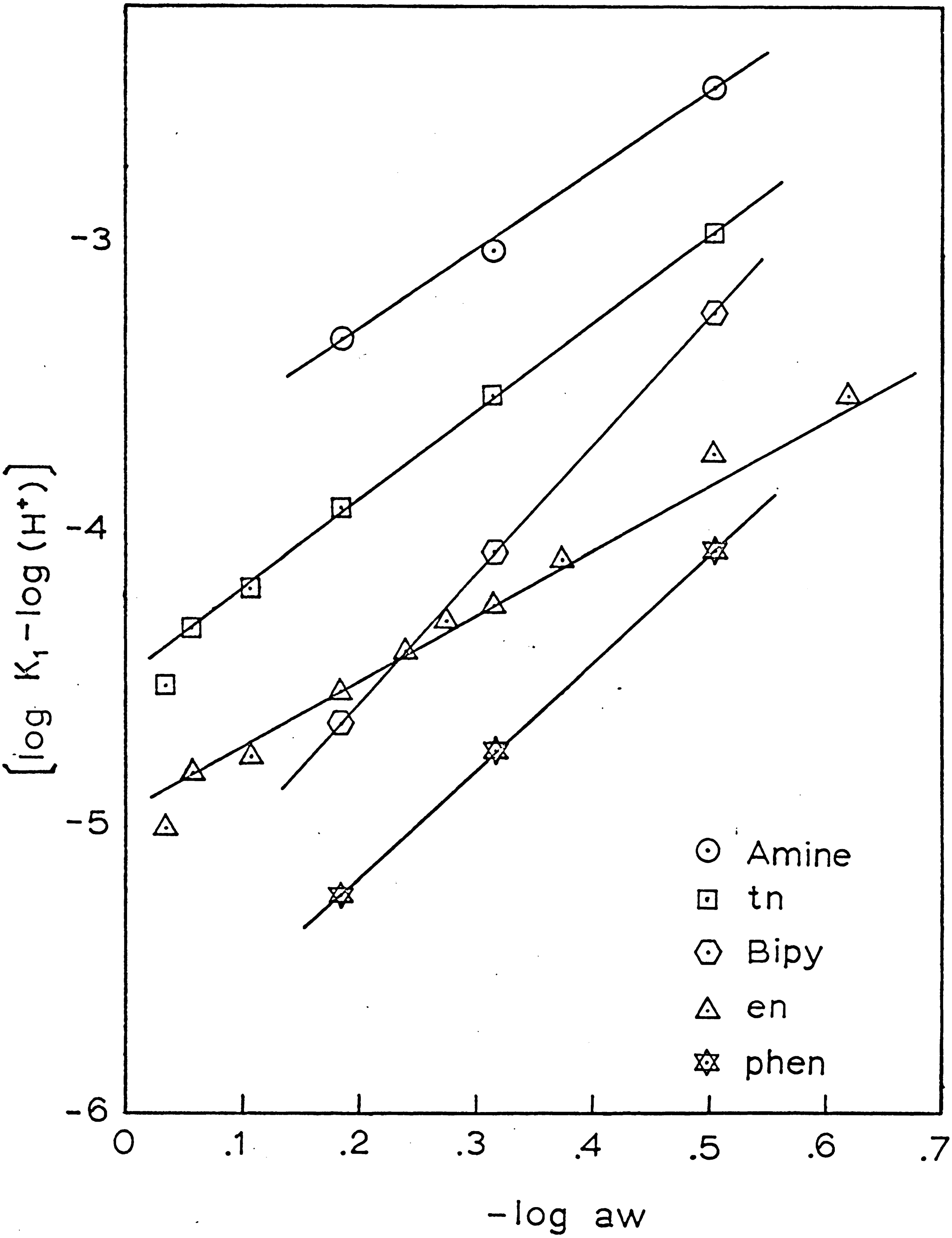

Figure 13. Hydrolysis of five trans-dinitro complexes in perchloric acid at 25°, [log k_1 - log (H+)] versus log a_w.

is probably acting as a nucleophile in these reactions also. The w values are in agreement with this conclusion except for the bipyridine and orthophenanthroline complexes.

V. DISCUSSION

A. Bunnett's interpretation of w^* values.

Bunnett, after proposing eq. 7 and eq. 8 as empirical equations to fit hydrolysis data in moderately concentrated aqueous acids (25) proposed (27) that w and w^* values could be used as an empirical criterion of mechanism. Table 18 showed Bunnett's correlation of the values of the parameters with the role of water in the reaction. All the data available to Bunnett were obtained in perchloric, hydrochloric, or sulfuric acids; only one hydrolysis had been done in nitric acid, and no data was available for hydrobromic acid.

Bunnett then (28) proposes a theory of w and w^* values. He considers the reaction scheme

$$(9) \qquad S(H_2O)_s + H(H_2O)n^{+1} \rightleftharpoons SH(H_2O)_p^{+1} + (s + n - p)H_2O$$

$$(10) \qquad SH(H_2O)_p^{+1} + (t - p)H_2O \longrightarrow \ddagger(H_2O)_t \longrightarrow \text{Products}$$

and derives the equation

(11) $$[\log k_1 - \log H(H_2O)_n{}^{+1}] = (t\text{-}s\text{-}n)\log a_w + \log f_{S(H_2O)_s}$$

$$+ \log (f_{H(H_2O)_n{}^+}/f_{\ddagger(H_2O)_t{}^+}) + \log (k/K_a)$$

from which, if the assumption is made that activity coefficient ratios for species of like charge do not change, we have

(12) $$[\log k_1 - \log H_{(H_2O)_n}{}^{+1}] = (t\text{-}s\text{-}n)\log a_w + \text{Ratio}.$$

Comparing eq. 7 and eq. 12 we see that

(13) $w^* = (t\text{-}s\text{-}n)$.

The slope w^* then is the difference in the hydration of the transition state and the substrate minus the hydration of the proton. For a given compound, in different acids, w^* should be constant if this parameter is to be used as an indicator of mechanism. Table 19 showed that for trans$[Co(en)_2(NO_2)_2]NO_3$, w^* had the same value within experimental error in all acids except nitric.

B. Deviation of the w^* value in nitric acid.

Hogfeldt has developed (54) an approach to hydration of acids in which he obtained a function related to the hydration of a single ion. From the observation (55) that the hydrogen ion activity function is the same in perchloric, sulfuric, hydrochloric, hydrobromic, and nitric acids while the negative ion activity coefficient is different, Hogfeldt concludes (54) that perchlorate and bisulfate probably contain 2-3 more water molecules in the coordination shell than does nitrate. He has extended this treatment to lithium salts (56). Hogfeldt has emphasized (57) the difference in hydration behavior found in nitric acid.

We may conclude that the different value of w^* found in nitric acid is not due to any difference in mechanism but rather is due to the difference in hydration behavior in nitric acid.

C. Bunnett's interpretation of w values.

Bunnett (28) shows that if activity coefficient ratios are again assumed constant w is given by

$$w = (t-s) - (a-b) \tag{14}$$

where t and s represent the hydration of the transition state and substrate, respectively; a and b are the hydrations of the indicators used in determining H_0. Then w is the hydration of transition state minus hydration of substrate on a scale determined by the hydration of the indicator base used in finding H_o.

The values of w listed by Bunnett for reactions involving water as a nucleophile were based on the hydrolysis of amides which were structurally not very different, and would probably be hydrated to about the same extent.

Examination of the w values in Table 20 shows that the bipyridine and phenanthroline complexes have w values less than 1.1, which Bunnett has taken as the lower limit of w for reactions in which water is a nucleophile. These complexes are probably not hydrated very much in aqueous solution because of their huge size; there is little reason to think the hydration of the transition state would be extensive. If we take the hydration number of the proton to be four, the value most often quoted, then w^* is just (t-s-4). For cases in which there is no hydration change on going from the substrate to the transition state, w^* would have a value of -4.0, which is close to the observed value. This indicates that these large complexes are probably not extensively hydrated; water can still be involved in the rate-determining step as a nucleophile.

D. A mechanism of reaction.

Some of the pertinent observations which a mechanism should take into account are: (1) the correlation of the data with Bunnett's equations giving values of the parameters which are consistent with water acting as a nucleophile; (2) the observation that the rate of reaction decreased as the "inert" ligand was varied from ammonia to 1,10-phenanthroline; and (3) the fact that linear Arrhenius plots are obtained in perchloric acid, but curvature to lower activation energies is observed in nitric, hydrochloric, hydrobromic, and sulfuric acids.

Consider the mechanism

(15) $[Co(AA)_2(NO_2)_2]^{+1} + H^+ \rightleftharpoons [Co(AA)_2(NO_2)_2H]^{+2}$

Equilibrium

(16) $[Co(AA)_2(NO_2)_2H]^{+2} + H_2O \longrightarrow [Co(AA)_2(H_2O)(NO_2)]^{+2}$

Rate determining

(17) $[Co(AA)_2(H_2O)(NO_2)]^{+2} + Z^- \longrightarrow [Co(AA)_2(Z)(NO_2)]^{+1}$

Faster than 16.

Correlation of the data with Bunnett's equations is accounted for by eq. 15 and eq. 16, if the equilibrium constant in eq. 15 has a value of about 10 for the ethylenediamine complex. Direct nucleophilic participation of water is implied by the values of the w and w^* parameters in Bunnett's equations.

The direct nucleophilic participation of water in eq. 16 is also consistent with the observation that the rates of hydrolysis decrease as the "inert" ligand (AA) is varied from ammonia to phenanthroline. Information in the literature and qualitative observations with the phenanthroline complex indicate that the rate of hydrolysis of the $[Co(AA)_2(Cl)_2]^{+1}$ complexes increases markedly as the ligand (AA) is varied from ethylenediamine to phenanthroline. Other workers have firmly established that the dichloro complexes react by an SN_1 mechanism; by contrast, the decrease in hydrolysis rates observed in the dinitro series is indicative of an SN_2 mechanism. An SN_2 mechanism for hydrolysis must mean that water is directly involved in the reaction.

Curvature of the Arrhenius plots in perchloric acid would not be expected because only reactions 15 and 16 take place. In the other acids, reaction 17 can also occur. The observed direction of curvature is consistent with that expected for two consecutive reactions, the second having the lower activation energy.

E. Comments on the intermediate in SN_2 reactions.

What does one mean by the statement that substitution follows an SN_2 path? By analogy with substitution at carbon, it has been accepted that a seven-coordinate intermediate must be formed after which the leaving group is displaced. Some reflection shows that from an operational point of view "SN_2 behavior" is possible without the postulation of a seven-coordinate species when multi-atomic ligands are being replaced. For example, suppose that protonation of the nitro group facilities reaction because the added hydrogen ion can act as a bridge between the nitro group and the attacking water molecule. If decomposition of the "bridge complex" so formed is rate determining, then a typical SN_1 five-coordinate intermediate could be formed, and so long as the "five-coordinate" intermediate reacts rapidly with water to form the nitroaquo, the observed kinetic behavior would be SN_2. This speculation would mean that eq. 16 would be written in more detail

(16a) $R\text{-}NO_2H^{+2} + H_2O \longrightarrow R\text{-}NO_2H\cdot H_2O^{+2}$ (bridged complex)

Rate determining

(16b) $R\text{-}NO_2H\cdot H_2O \longrightarrow R\text{-}^{+2}$ (five-coordinate intermediate)

Fast

(16c) $R\text{-}^{+2} + H_2O \longrightarrow R\text{-}H_2O$ Fast

where R- is $Co(AA)_2(NO_2)$-.

We see that although one may use Bunnett's approach to show that water is involved in the rate-determining step, any attempts to formulate a more detailed mechanism must be based more on prejudice than on scientific fact.

F. Conclusion.

That even the information that water is involved in the rate-determining step can be obtained from kinetic studies in acid solutions is remarkable. So far as is known, this is the first time that good evidence has been offered for the participation of water in hydrolysis reactions in aqueous solutions, although such participation has been assumed.

This is the first application of Bunnett's ideas to an inorganic system, so far as we are aware. The usefulness of these equations for correlation of the data cannot be denied.

Bunnett says (29):

"Because of the frequent ease with which reaction rates can be measured as a function of mineral acid concentration, because of the present considerable accuracy of the empirical criterion of mechanism and the probability that it will become more accurate with the passage of time, kinetic response to changing acid concentration deserves a restoration of status as a criterion of mechanism."

The present study shows that the ideas of Bunnett are at the very least useful for correlating experimental data, and probably are much more useful in arriving at a mechanism of reaction. Some time will be required before we can say how useful these ideas really are. Zollinger (111) recently has expressed the need for caution in accepting the interpretation given w and w^* values by Bunnett. Still, it is remarkable that these ideas could be applied to a wholly different system and lead to a mechanism consistent with other observations.

VI. SUMMARY

A detailed study was made of the rates of hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ as a function of acid concentration in perchloric, hydrochloric, hydrobromic, sulfuric, and nitric acids up to high concentrations of acid. All the data could be fitted to an equation proposed by Bunnett

$$(1) \quad [\log k_1 - \log (H^+)] - \log \frac{h_o}{h_o + K_a} = w^* \log a_w + \text{Ratio}$$

where k_1 is the first-order rate constant, (H^+) is the hydrogen ion concentration, h_o is the effective hydrogen ion concentration, K_a is the acid dissociation constant of the protonated intermediate, and a_w is the activity of water. "Ratio" is the intercept and w^* the slope of a plot of the left side of the equation versus the logarithm of the activity of water. Bunnett also proposed another equation like eq. 1 except that "$-\log (H^+)$" is replaced by "H_o", and the slope of this equation versus $\log a_w$ is denoted "w" instead of "w^*"; the intercept of the new equation will be another constant, not equal to "Ratio". Bunnett proposed that for the hydrolysis of organic compounds, w and w^* values are indicative of mechanism.

From the constant values of w^* obtained in hydrobromic, hydrochloric, sulfuric, and perchloric acids, a mechanism involving water acting as a nucleophile was indicated. The different value of w^* obtained in nitric acid could be correlated with the known difference in hydration in nitric acid. Values of w also were consistent with nucleophilic attack by water except for the trans-$[Co(bipy)_2(NO_2)_2]NO_3$ and trans-$[Co(phen)_2(NO_2)_2]NO_3$ complexes. Since these are very large ions which are probably unhydrated, the values of w obtained were shown to be reasonable.

Rates of hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ were also measured as a function of temperature. In perchloric acid, good linear Arrhenius plots were obtained from which the energy of activation was 23.6 ± 0.8 kcal. and the activation entropy was 2.9 ± 2.3 eu. at the 95% confidence level. Arrhenius plots in hydrochloric, hydrobromic, sulfuric, and nitric acid were curved, the amount of curvature increasing with acid concentration and temperature. At lower temperatures, the activation energy was

23-24 kcal. but decreased to as low as 12 kcal. at high acid concentrations and higher temperatures. This behavior is consistent with two consecutive reactions, the second reaction having the lower activation energy. The latter reaction was identified as the addition of an anion to the intermediate nitroaquo complex.

The following <u>trans</u>-$[Co(AA)_n(NO_2)_2]NO_3$ complexes were synthesized: n = 4; (AA) is ammonia: n = 2; (AA) is ethylenediamine; 1,3-diaminopropane; 2,2'-bipyridine; or 1,10-phenanthroline. Rate constants were obtained as a function of acid concentration for all the <u>trans</u> complexes in three concentrations of perchloric acid. Similar study was made of the ethylenediamine; 1,3-diaminopropane, and ammine complexes in three concentrations in hydrochloric acid. Values of w and w^* for these complexes in both acids were shown to be consistent with nucleophilic participation of water. The rate constants <u>decreased</u> as the ligand varied from ammonia to 1,10-phenanthroline; this behavior is consistent with an SN_2 reaction involving direct participation of water.

Two <u>cis</u> dinitro complexes were synthesized, namely the tetrammine and the ethylenediamine. These complexes reacted at a rate from 60 to 300 times slower than the trans complexes, contrary to a report that the cis complex of $[Co(en)_2(NO_2)_2]NO_3$ reacts only about one-half as fast as the trans isomer. All these observations could be explained by the following mechanism:

$$(2)\quad [Co(AA)_2(NO_2)_2]^{+1} + H^{+} \rightleftharpoons [Co(AA)_2(NO_2)_2H]^{+2}$$

Equilibrium

$$(3)\quad [Co(AA)_2(NO_2)_2H]^{+2} + H_2O \longrightarrow [Co(AA)_2(H_2O)(NO_2)]^{+2}$$

Rate determining

$$(4)\quad [Co(AA)_2(H_2O)(NO_2)]^{+2} + Z^{-} \longrightarrow [Co(AA)_2(Z)(NO_2)]^{+1}$$

Faster than 3.

This investigation has provided probably the most detailed evidence for the direct participation of water in a reaction that has been offered. It is satisfying that all the data obtained can be rationalized using current ideas about the reactivity of complex compounds and the mechanistic interpretation of acid catalysis data.

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ABSTRACT

A detailed study was made of the rates of hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ as a function of acid concentration in perchloric, hydrochloric, hydrobromic, sulfuric, and nitric acids up to high concentrations of acid. All the data could be fitted to the equations proposed by Bunnett[1].

(1) $[\log k_1 - \log (H+)] = w^* \log a_w + \text{Ratio}$

and

(2) $[\log k_1 + H_o] = w \log a_w + \text{Constant}.$

In these equations, k_1 is the first-order rate constant, (H+) is the hydrogen-ion concentration, a_w is the activity of water in the solution, and H_o is the Hammett acidity function. The w and w* are the slopes, "Ratio" and "Constant" are the intercepts, of plots of the left side of eq. 1 or eq. 2 versus the log a_w. Bunnett proposed that for the hydrolysis of organic compounds, w and w* values are indicative of mechanism.

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[1] J. F. Bunnett, J. Am. Chem. Soc., 83, 4956, 4968, 4973, 4978 (1961)

From the constant values of w^* obtained in hydrobromic, hydrochloric, sulfuric, and perchloric acids, a mechanism involving water acting as a nucleophile was indicated. The different value of w^* obtained in nitric acid was consistent with the known difference in hydration in nitric acid. Values of w also were consistent with nucleophilic attack by water.

Rates of hydrolysis of trans-$[Co(en)_2(NO_2)_2]NO_3$ were also measured as a function of temperature. In perchloric acid, good linear Arrhenius plots were obtained from which the energy of activation was 23.6 ± 0.8 kcal. and the activation entropy was 2.9 ± 2.3 eu. at the 95% confidence level.

Arrhenius plots in hydrochloric, hydrobromic, sulfuric, and nitric acids were curved, the amount of curvature increasing with acid concentration and temperature. At lower temperatures, the activation energy was 23-24 kcal. but decreased to as low as 12 kcal. at high acid concentrations and higher temperatures. This behavior is consistent with two consecutive reactions, the second reaction having the lower activation energy; the latter reaction was identified with addition of an anion to the intermediate nitroaquo complex.

A series of dinitro complexes with "inert" ligand size varying from ammonia to 1,10-phenanthroline was made; these complexes were studied in hydrochloric and perchloric acids. The first-order rate constant decreased as the size of the ligand increased, indicating direct participation of water in an SN_2 reaction. The values of w^* in both acids were consistent with nucleophilic participation of water; for the bipyridine and orthophenanthroline complexes a lower value of w was observed. This observation could be related to the expectation that these large complexes would not be hydrated as much as the smaller compounds.

A mechanism for the hydrolysis reaction consistent with the observed behavior was given. According to this mechanism, the complex is first protonated in an equilibrium step; the protonated species reacts with water to give the nitroaquo complex as the rate-determining step for all compounds in all acids. Finally, the nitroaquo complex reacts with an anion Z^- (except when Z- is ClO_4-) to give the final product of reaction.

This investigation shows that Bunnett's equations are useful for correlating data, but some caution in accepting Bunnett's mechanistic interpretations from the values of w and w^* is necessary. It is satisfying that application of these ideas to a totally different system (inorganic complexes) lead to a mechanism consistent with current ideas about the reactivity of coordination compounds of cobalt(III).