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A KINETIC STUDY OF THE OXIDATION OF THE 2, 3, AND 4 PYRIDINE ALDEHYDES BY COBALT(III) PERCHLORATE IN AQUEOUS SOLUTION.

A Thesis
Presented to
the Graduate Faculty
Central Washington State College

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in Chemistry

by

Ronald Barry Giuntoli

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APPROVED FOR THE GRADUATE FACULTY

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INTRODUCTION

Cobalt(III) perchlorate has been shown to be a powerful oxidizing agent and kinetic investigations of the mechanism of oxidation of many organic compounds including organic acids have been performed (1-15). Oxidation reactions between cobalt(III) and organic compounds are considered to be free radical processes in which the rate determining step involves abstraction of a hydrogen atom from the organic molecule by cobalt(III).

Bawn and Jolly (13) demonstrated the free radical nature of the autoxidation of benzaldehyde by cobalt(III) ion in glacial acetic acid. The authors verified that free radicals were involved in the reaction mechanism by radical inhibition studies. For example, the addition of known radical sources hydroquinone diphenylamine or B-napthol to the reaction mixture retarded the reaction. These molecules inhibit reaction by forming stable free radicals. A study of the variation of the time of induction to the concentration of B-napthol was also performed by the authors. They found the time of induction to vary linearly with the inhibitor concentration. The authors were able to determine the rate of chain initiation from a plot of inhibitor concentration <u>vs</u> the time of inhibition at different temperatures. They also found the rate of iniation to be identical to the rate of reaction. This suggested that the rate of reaction is directly proportional to the rate of formation of free radicals.

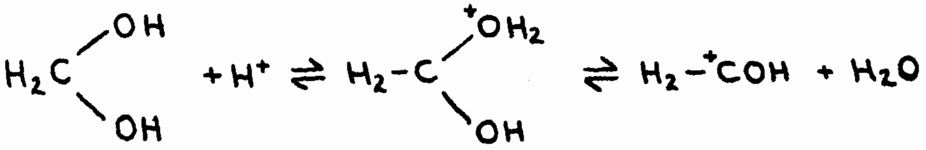
Kinetic studies performed on a wide variety of organic compounds i.e. butyl alcohol, cyclohexanol, diethyl ketone formaldehyde toluene, benzaldehyde, aliphatic carboxylic acids, benzyl esters, etc. have shown these reactions to be first-order in the organic molecule and Cobalt(III) and inversly proportional to the hydrogen ion concentration.

The kinetics and mechanism of the oxidation of formaldehyde has been the object of several studies. Hargreaves and Sutcliff (2) studied the oxidation of formaldehyde by cobalt(III) in perchloric and sulfuric acids. The progress of the reaction was followed by: (1) spectrophotometric measurement of the rate of disappearance of cobalt(III) upon addition of formaldehyde, (2) measurement of the concentration of formaldehyde at intervals during the course of the reaction. The latter method was accomplished by removing samples of the reaction mixture, quenching the reaction with excess ferrous ammonium sulfate, and estimating formaldehyde spectrophotometrically using 4,5-dihydroxy-2,7 napthelene disulfonic acid (chromotropic acid) (19). The kinetic measurements showed the oxidation reaction to be first-order with respect to both Co(III) and formaldehyde.

Comparison of the decrease of cobalt(III) concentration to the decrease in the concentration of formaldehyde during the same time interval allowed the authors to show that 2 Co(III) ions are required to oxidize 1 molecule of formaldehyde. They also found the rate of reaction to be unaffected by the presence of Co(II) ion and oxygen, and to be inversly proportional to the hydrogen ion concentration.

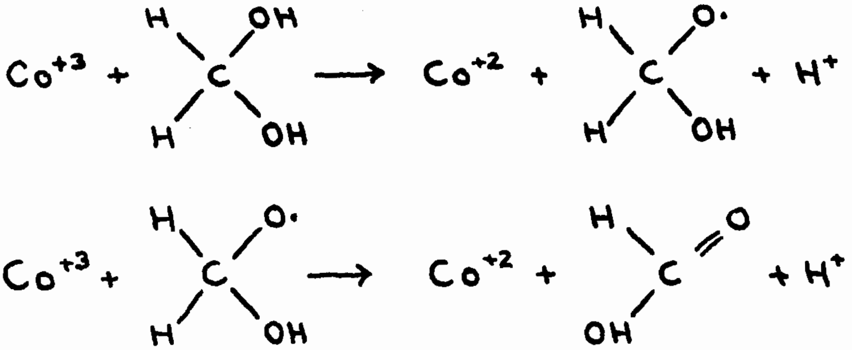
Since formaldehyde is 99.99% hydrated in acid solution (24), the authors concluded that the reaction mechanism involved the hydrated aldehyde. Thus, they attributed the inverse acidity dependence to the following equilibrium (19).

(1)



They proposed the following reaction mechanism.

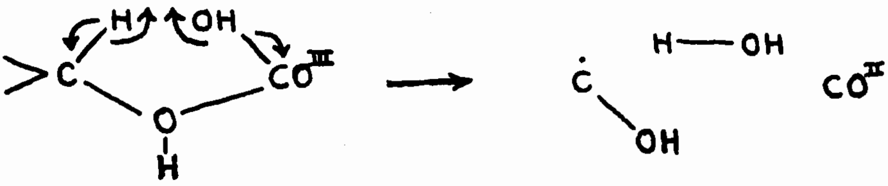
(2)



The authors viewed this mechanism as being the only one which satisfied the condition of endothermicity and inverse acid dependence. The activation energy $\Delta H^{\ddagger}$ was determined to be 22±1 kcal/mole and the heat of reaction ΔH was 2±.5 kcal/mole.

Kemp and Waters (1) in a study of isotope effects on the rate of oxidation of formaldehyde by Co(III) concluded that the rate determining step involved some degree of C-H bond fission. The authors found a kinetic deuterium isotope effect of 1.54. They accounted for this low kinetic isotope effect by postulating that the C-H bond breaking did not involve a linear extension of the C-H or C-O bond and that a considerable amount of vibrational energy could exist between the transition state structures involved in C-H and C-O cleavage. It was concluded that the low kinetic isotope effect observed would be consistant with the formation of the cyclic transition state shown below.

(3)

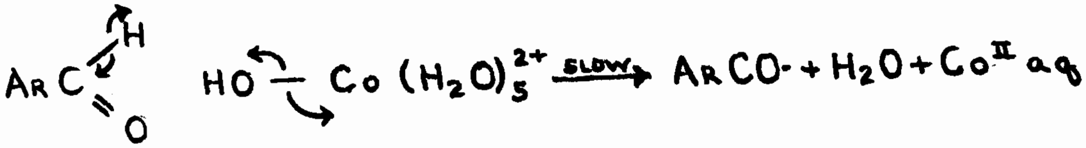


Cooper and Waters (5) investigated the oxidation of m and p-nitrobenzaldehyde by cobalt(III) perchlorate in acetyl nitrile-water solutions. The reaction was followed spectrophotometrically by measuring the decrease in cobalt (III) ion concentration at 594 mμ upon injection of cobalt (III) into solutions containing *m* or *p*-nitrobenzaldehyde. The reaction rate was found to be first-order with respect to both cobalt(III) ion and *m* and *p*-nitrobenzaldehyde and inversly proportional to the hydrogen ion concentration. Rate studies on the oxidation by cobalt(III) ion of deutero-m-nitrobenzaldehyde revealed the reaction rate to be 2.3 times slower than for the non-deuterated species. This evidence suggested that fission of the C-H bond is involved in the rate determining step.

The inverse acidity dependence was accounted for by the equilibrium reaction between water and the hexaquo cobalt(III) ion (16,17,18). The hydrolyzed species is presumably responsible for the acid-dependent path.

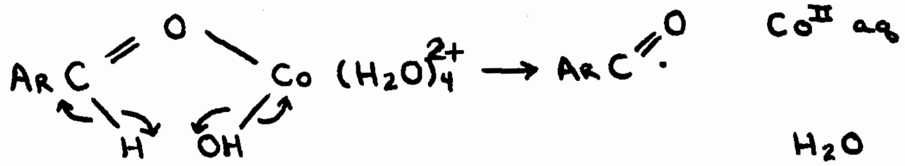
(4) $[Co(H_2O)_6]^{+3} + H_2O \rightleftharpoons [Co(H_2O)_5OH]^{+2} + H_3O^+$

The authors proposed the following three mechanisms, each consistant with the available data, for the rate determining step.

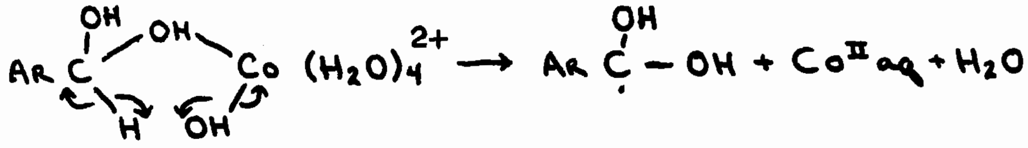
(5) 

$$\mathrm{Ar}\overset{H}{\underset{O}{C}} \quad HO{-}Co(H_2O)_5^{2+} \xrightarrow{slow} ArCO\cdot + H_2O + Co^{II}\,aq$$

(6)



(7)



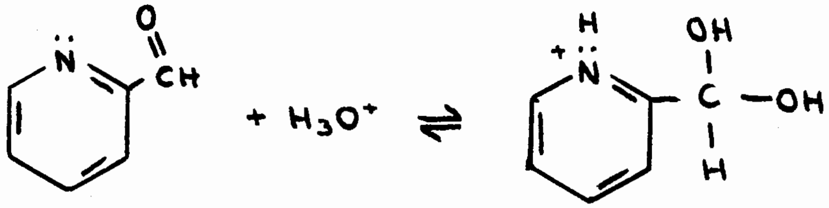
Route (7) was believed to be least likely as hydration of the m and p-nitrobenzaldehyde is slow under the reaction conditions employed. Enthalpies and entropies of activation for m and p-nitrobenzaldehyde were determined by the investigators from Arrhenius plots. The values reported were 20.1 kcal/mole and 12.1 e.u. for p-nitrobenzaldehyde and 20.7 kcal/mole and 14.1 e.u. for m-nitrobenzaldehyde. In actuality the reported entropies and enthalpies are apparent enthalpies and entropies of activation since the authors neglected to account for the enthalpy and entropy of hydrolysis of the aquo cobalt(III) ion.

In the preceeding discussion some contradictory evidence appeared regarding the mechanism of the oxidation of formaldehyde. Hargreaves and Sutcliff (2) proposed a mechanism in which the O-H atom was abstracted in the rate determining step. Kemp and Waters (1) concluded from their kinetic isotope studies that the C-H hydrogen atom is involved in the rate determining step. Furthermore, two equilibrium reactions (1)(4) have been proposed which could account for the observed inverse acidity dependence of formaldehyde.

In the present investigation the 2, 3, and 4-pyridine aldehydes were studied with the hope that this system would be amenable to solving some of the problems mentioned above.

The 2, 3, and 4-pyridine aldehydes were employed as reducing agents for the oxidation by cobalt(III) perchlorate because of their unique properties in acid solution. Unlike nitrobenzaldehydes, the pyridine aldehydes are essentially 100 percent hydrated in aqueous acid solutions (20). Furthermore, the nitrogen atom on the pyridine ring is protonated in acid solution (20).

(8)



A portion of the study was therefore devoted to determining the effect of N-protonation on the relative rates of oxidation of the 2, 3, and 4-pyridine aldehydes. It was also hoped that the system chosen would allow estimations of the relative importance of inductive, resonance, and complexation effects and that the information gained would be useful in the elucidation of the reaction mechanism.

EXPERIMENTAL

I. Chemicals:

Cobalt(II) Perchlorate - Cobalt(II) Perchlorate was prepared in the following manner: 70 g. of Mallinckrodt Analytical Reagent $CoCl_2 \cdot 6H_2O$ was dissolved in 100 ml. of distilled water and filtered. Approximately 100 ml. of concentrated (70%) perchloric acid was added to the filtrate and the resulting dark red solution was heated until evolution of copious white fumes. The solution was cooled in an ice bath and filtered. The crystals obtained were dissolved in 50 ml. of distilled water.

The concentration of the cobalt(II) perchlorate solution was determined in the following manner: A 1 ml. portion of the solution was pipetted into an erlnmeyer flask and approximately 50 ml. distilled water added. To the solution was added 10 ml. of saturated solutions of ammonium acetate and the disodium salt of ethylenediamine tetraacetic acid as well as 7 drops of 30% H_2O_2. The resulting mixture was boiled for ten minutes and 4 more drops of a 30% solution of hydrogen peroxide was added. The solution was boiled an additional 30 minutes and allowed to cool. This solution was then transferred to a 1 liter volumetric flask and diluted to volume. A portion of the sample was placed in a 10 mm. cell and its absorbance measured spectrophotometrically at 540 mu. Concentration was determined by comparing the observed absorbance at a 1000 fold dilution to the absorbancy index of 312 liters/ $mole^{-1}$ $cm.^{-1}$ which has been reported for the cobalt(II) perchlorate-EDTA complex (25).

<u>Cobalt(III) Perchlorate</u> - Cobalt(III) perchlorate was prepared by the anodic oxidation of 1 x 10^{-2} M cobalt(II) perchlorate in 1.0 M perchloric aicd. A platinum mesh electrode was used for the cathode and a standard platinum electrode used for the anode. The anode and cathode compartments were separated by a sintered glass frit and the whole electrolysis cell was immersed in a Dewar flask filled with an ice-water mixture. The concentration of cobalt(III) ion was determined by addition of excess standard ferrous ion solution and titration of the excess ferrous ion by standard Ce(IV) ion solution using barium diphenylamine sulfonate as the indicator. The appearance of a red-purple color was taken as the end point. It was found necessary to add 5 ml. of phosphoric acid to the ferrous ion solution in order to obtain reproducible results at the low concentrations at which these titrations were performed. From the cobalt(III) perchlorate solution whose concentration had been determined in the manner described above, dilutions were made and a standard Beer's

Law plot constructed. All subsequent estimations of cobalt (III) ion concentration were determined by measuring the absorbancy of the solution and comparing with the Beer's Law plot. The absorbancy index for cobalt(III) perchlorate was determined to be 36.2 liters/mole^{-1} cm.$^{-1}$ at 605 mu. (2). Concentration of perchloric acid in the cobalt(III) perchlorate solution was determined by titration with standard sodium hydroxide solution and the solution was adjusted to 1.025.

<u>Pyridine Aldehydes</u> - Reagent grade 2, 3, and 4-pyridine aldehydes were obtained from the Aldrich Chemical Co. The aldehydes were purified by multiple distillation under nitrogen at a pressure of 12 mm. Hg. The pyridine aldehydes were stored under nitrogen at -5° C until used. Analysis by gas chromatography showed the aldehydes to contain less than 1% impurities.

<u>Pyridine Carboxylic Acids</u> - Reagent grade 2, 3, and 4-pyridine carboxylic acids were obtained from Matheson, Colman and Bell. No further purification was deemed necessary.

<u>Perchloric acid</u> - Mallinckrodt Analytical Reagent grade 70% perchloric acid was used. The concentration of various solutions of the acid was determined by titration with standard sodium hydroxide solution.

Miscellaneous Chemicals - All other chemicals used in this research were of reagent or better.

II. Glassware:

Syringes - A 1 ml. Cyanamide VIM surgical syringe was used for all procedures requiring the addition of a specific volume of sample. The syringe was calibrated at 0.50, 0.75, and 1.00 ml. by determining the difference in the weight of syringe when filled to the corresponding mark with mercury and when empty. The syringe was found to be accurate to within 0.5% for the three volumes determined.

Spectrophotometer Cells - Absorbance above 320 mu. was measured using Beckman 10 mm. grade A pyrex cells. For the determination of absorbance below 320 mu. Beckman standard silica 10 mm. cells were employed.

Miscellaneous Glassware - All glassware used was grade A pyrex.

III. Preparation of solutions for kinetic runs:

Preparation of Cobalt(III) Perchlorate Solution -

Cobalt(III) perchlorate solutions for all kinetic runs were adjusted to a perchloric acid concentration of 1.025 molar by dilution with distilled H_2O.

Preparation of Pyridine Aldehyde Solution - Pyridine aldehyde was weighed into a 10 ml. volumetric flask. The desired amount of perchloric acid solution was added by pipette to protonate the pyridine aldehyde and bring the resulting solution to the desired acid strength when diluted to volume. For reactions at constant acid strength the pyridine aldehyde solution was adjusted to a perchloric acid concentration of 1.025 M. All deviations of the perchloric acid strength from 1.025 M were the result of varying the perchloric acid concentration in the pyridine aldehyde solution.

Preparation of Lithium Perchlorate Solution - A stock solution of lithium perchlorate was prepared by weighing lithium perchlorate into a 200 ml. volumetric flask and adding sufficient perchloric acid solution to bring the resulting solution to an acid strength of 1.025 M when diluted to volume. Lithium perchlorate concentration was altered by adding the desired amount of 1.025 M perchloric acid solution to portions of the stock lithium perchlorate solution.

IV. Equipment:

Kintrac VII - The Beckman Kintrac VII was used to follow all kinetic runs.

Constant Temperature Bath - The Beckman constant temperature bath that was designed to control temperature in the cell compartment was used for all kinetic runs performed with pyridine aldehyde at constant acid strength.

Unfortunately, this constant temperature bath contained a pumping system which was of insufficient force to obtain a flow rate through the cell compartment sufficient for rapid cooling. For subsequent kinetic runs involving the 2, 3, and 4-pyridines, the Beckman constant temperature bath was used to maintain syringe temperature at cell temperature.

The constant temperature bath used to follow the other kinetic runs was composed of a Sargent heater and Circulator, a Cole Palmer refrigeration unit, and a Sargent thermo controller. Liquid was circulated through the cell compartment by an Eastern B-1 type 100 pump. Temperature was held constant to ± 0.02 C.

V. Kinetic runs:

Kinetic runs were performed with the Beckman Kintrac VII by recording the decrease in the absorbance of cobalt (III) perchlorate at 605 mu. A distilled water blank was used to adjust percent absorbance and transmittance on the recorder. All kinetic runs were accomplished by pipetting 2 ml. of cobalt(III) perchlorate solution into a 10 mm. pyrex cell which was then placed in the cell compartment and allowed to equilibrate. Pyridine aldehyde of the desired volume, concentration, acid strength, and temperature was injected into the cobalt(III) perchlorate solution and the reaction was followed as described above. The resulting acid strength and pyridine aldehyde concentration was calculated from known initial volumes and the original concentrations of the two solutions. For kinetic runs where ionic strength effects were studied, the same procedure was followed with the exception that the pyridine aldehyde solution also contained lithium perchlorate. The temperature of pyridine aldehyde solution and cobalt(III) perchlorate solution were maintained to within 0.05° C of one another by employment of two independent baths. Two baths were necessary as the temperature in the cell compartment was approximately 1 degree warmer than the temperature of the bath used to cool the cell compartment.

VI. Product Analysis:

The product of the oxidation of pyridine aldehyde by cobalt(III) perchlorate was presumed to be pyridine carboxylic acid. The quantity of pyridine acid produced from the oxidation of pyridine aldehyde by cobalt(III) perchlorate solution was estimated in the following manner. Standard solutions of the pure aldehyde and acid were prepared and the pH adjusted to 8 by the addition of dilute NaOH solution. Ultra-violet spectra were obtained for the pure acid and aldehyde and for mixtures of acid and aldehyde. It was necessary to obtain UV spectra of basic solutions of aldehyde and acid as the spectra obtained in acid solution for the pyridine aldehydes and acids were nearly identical. A specific volume of pyridine aldehyde in 1.0 M $HClO_4$ of known concentration was added to an equal volume of cobalt (III) perchlorate whose concentration was twice that of the pyridine aldehyde. Sufficient time was allowed for the reaction to proceed essentially to completion (4 hrs.). The reaction mixture was then adjusted to a pH of 6 by addition of NaOH solution. Approximately 0.5 g. of amberlite CG 120 ion exchange resin was added to the solution to remove interfering cobalt(II) perchlorate ions presumably produced by the reduction of the initial Co(III) perchlorate. The solution was filtered, and the pH of the filtrate adjusted to 8. The reaction mixture was diluted in such a way that the combined concentration of pyridine acid and aldehyde would be equivalent to the molar concentration of the standard solutions. The ultraviolet spectra of the diluted reaction mixture were obtained and compared to those obtained for pure acid and aldehyde, and mixtures of acid and aldehyde. The results indicated for all cases that the oxidation of aldehyde to acid was greater than 80 percent complete.

TREATMENT OF DATA AND ERRORS

As will be shown in a later section of this work, the reaction between cobalt(III) ion and pyridine aldehydes follows pseudo first-order kinetics when the pyridine aldehyde concentration is in large excess. Under these conditions, then, one may write the rate law:

$$\frac{-d[Co(III)]}{dt} = k[Co(III)][PA] \simeq k'[Co(III)]$$

wherein $k' = k[PA]$

Hence $\frac{-d[Co(III)]}{[Co(III)]} = k'dt$

and, upon integration, one obtains

$$\ln[Co(III)] = -k't + C$$

where C is a constant of integration. At zero time,

$$C = \ln[Co(III)]_o$$

hence $\ln\frac{[Co(III)]}{[Co(III)]_o} = -k't$

Since the concentration of cobalt(III) was determined by spectrophotometric absorbance,

$$[Co(III)] = \frac{A}{Eb}$$

where A = absorbance

E = absorbancy index

b = cell length

therefore $\frac{[Co(III)]}{[Co(III)]_o} = \frac{A}{A_o}$

Hence $\frac{\ln A}{A_o} = -k't$

A plot of $\ln A/A_o$ vs time therefore would be expected to be linear with a slope equal to the value of k' but opposite in sign.

The pseudo first-order constants (k') were obtained at various concentrations of pyridine aldehyde. Since

$$k' = k[PA],$$

a plot of k' vs pyridine aldehyde concentration would be expected to be linear with a slope equal to the value of the second-order rate constant k. The slope of these lines was obtained by the method of least squares. The uncertainty in the least squares value of the second-order rate constant k was determined by obtaining the percent deviation between experimentally determined values of the pseudo first-order rate constant k' with those calculated from the expression for a straight line.

$$y = mx + b$$

In the equation y corresponds to k', m corresponds to the second-order rate constant k, x corresponds to pyridine aldehyde concentration, and b corresponds to the least squares intercept. Ideally the least squares intercept b should be zero. The small deviations from zero found for the intercepts are attributed to experimental error.

It became apparent during the course of this investigation that the rate of the reaction was markedly effected by hydrogen ion concentration. An inverse dependence was established. The second-order rate constant k was therefore determined to be of the form

$$k = k_1 + \frac{k_2}{[H^+]}.$$

Plots of k vs the hydrogen ion concentration yield straight lines (figures 1,2,3). The slopes and intercepts of these lines were determined by the method of least squares. The former were equal in value to k_2, the rate constant for the acid-dependent path, and the latter was equal in value to k_1, the rate constant for the acid-dependent path.

The values obtained for k_1 were small and showed no noticeable variation with temperature. It is therefore believed that these values may be the result of experimental error. In order to determine the constant k_2 for the acid-dependent path it is necessary to consider all reactions which may contribute to the values of k_2. The inverse dependence of the rate of reaction on the hydrogen ion concentration may be attributed to the following equilibrium.

Figure 1. Plots of k *vs* $[H^+]^{-1}$ at T = 4.80°C for the 2, 3, and 4-pyridine aldehydes.

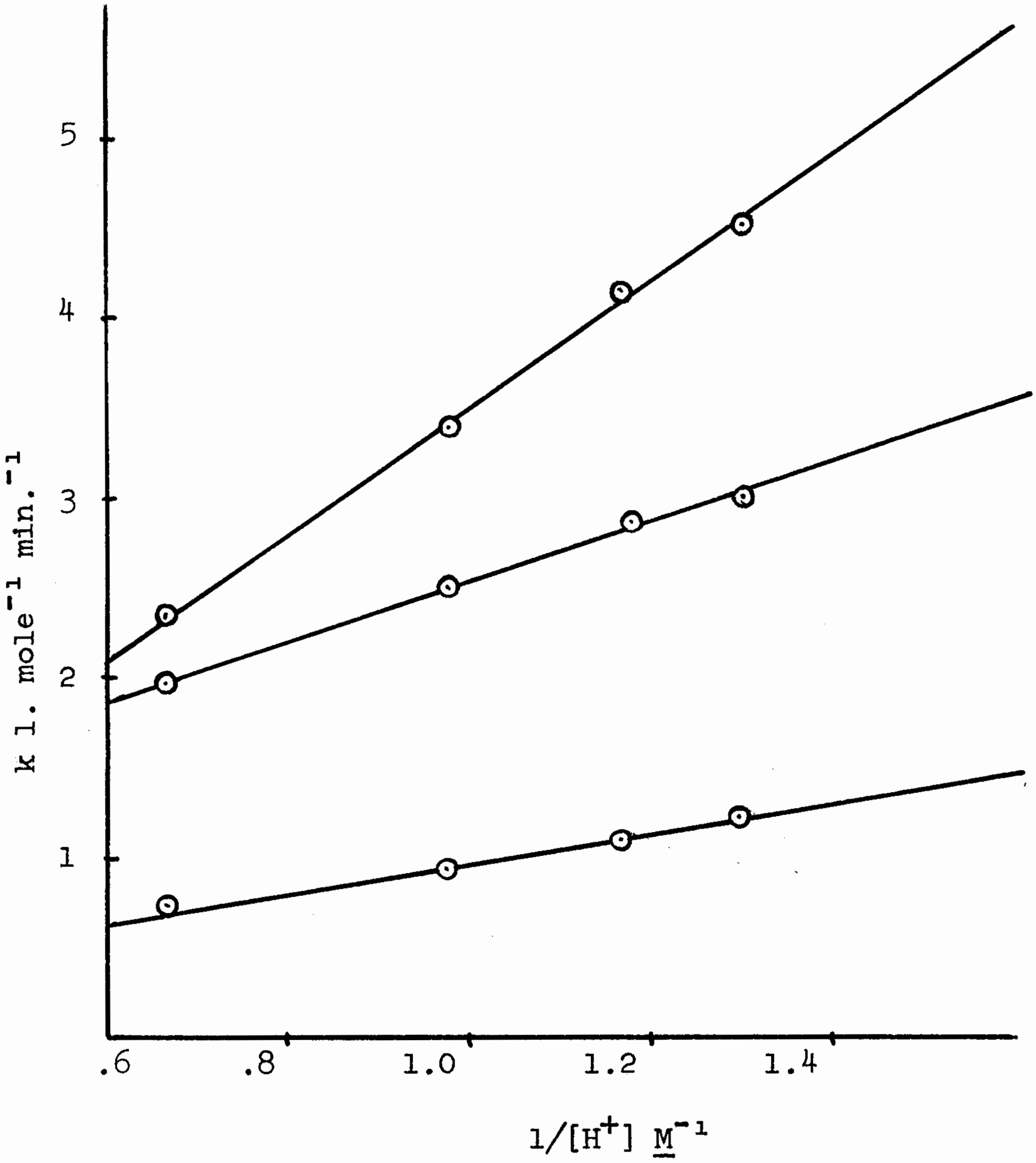


Figure 2. Plots of k vs $[H^+]^{-1}$ at T = 10.0°C for the 2, 3, and 4-pyridine aldehydes.

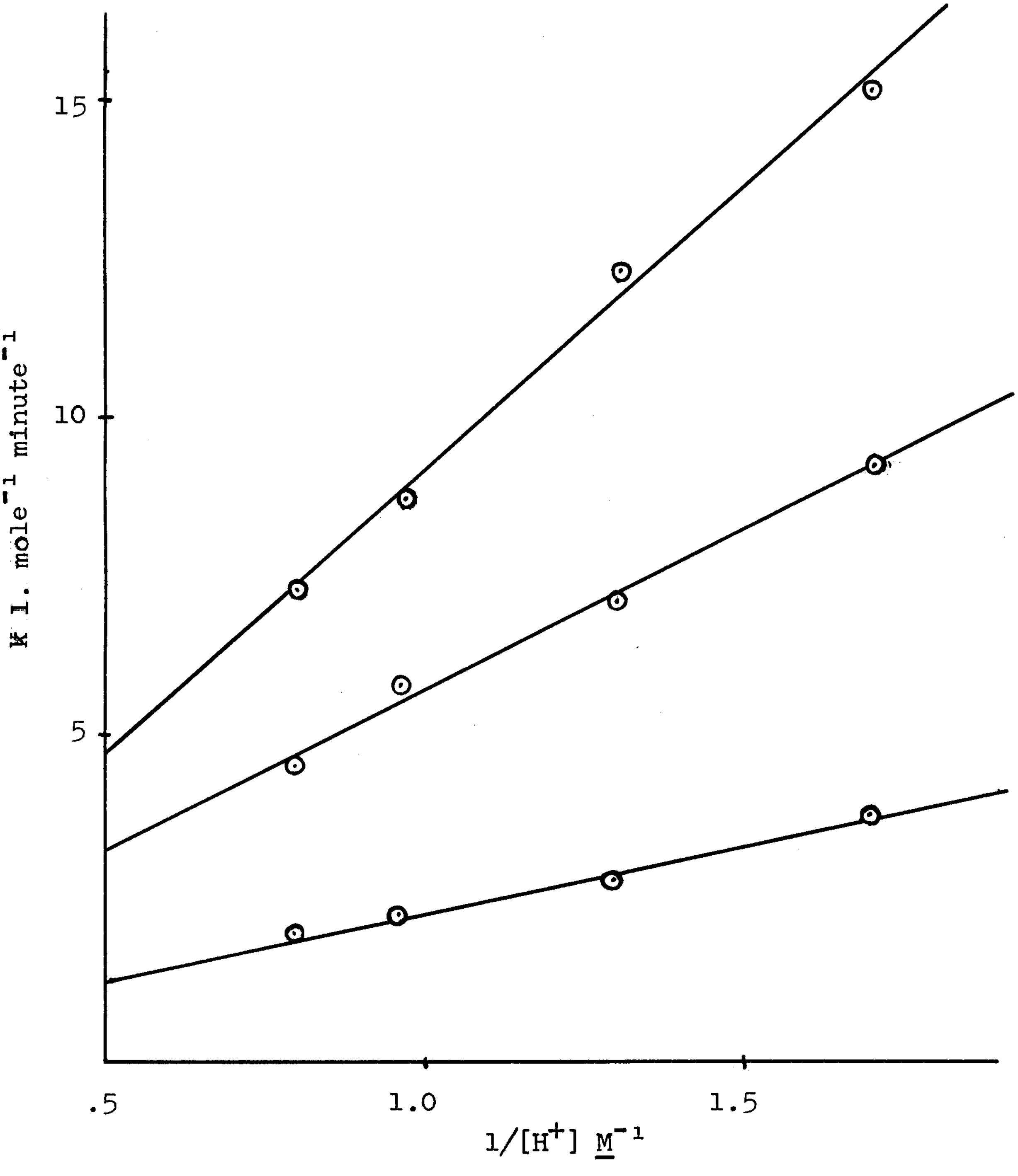
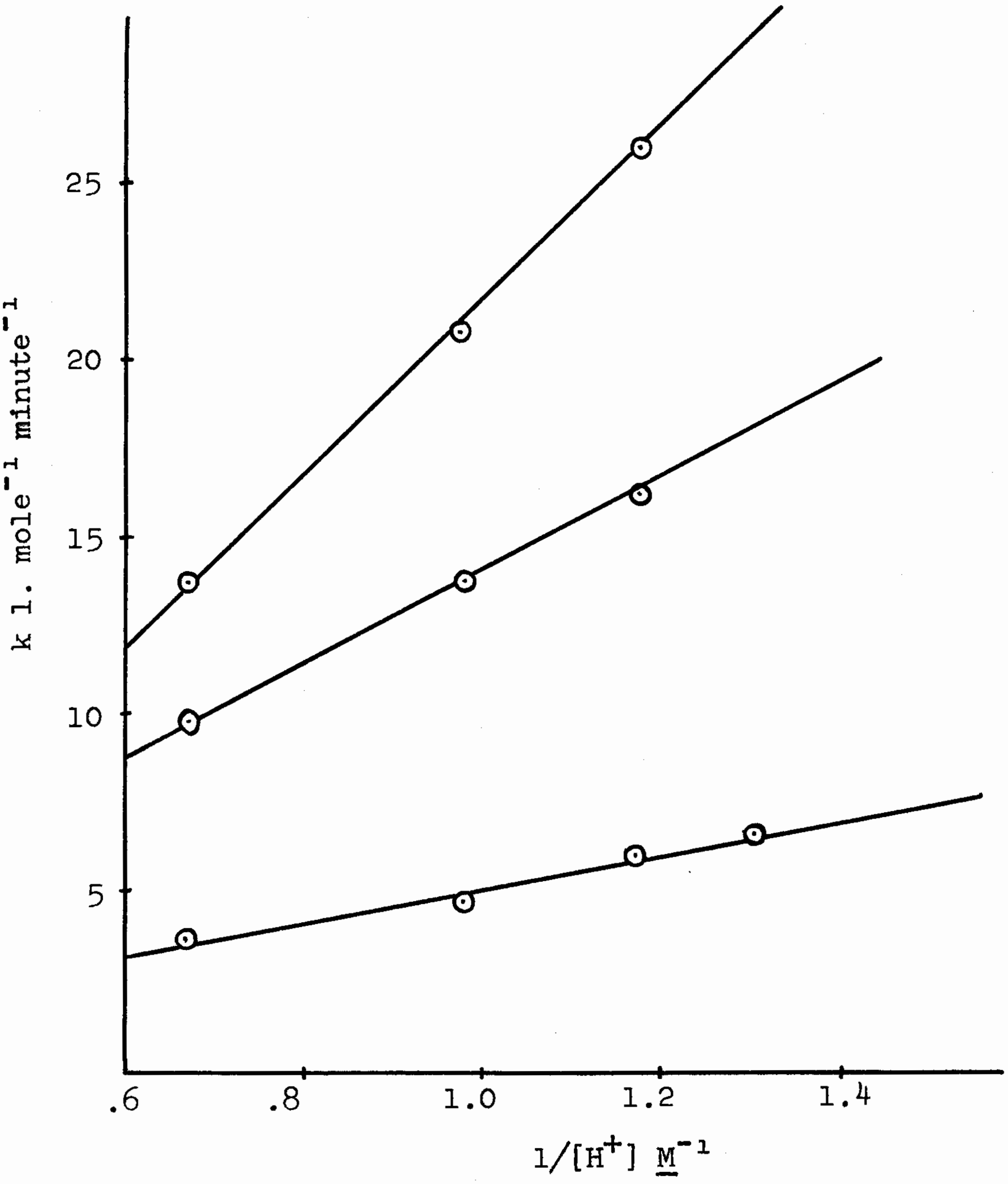


Figure 3. Plots of k *vs* $[H^+]^{-1}$ at t = 15.0°C for the 2, 3, and 4-pyridine aldehydes.



reaction between water and the hexaquocobalt(III) ion:

$$[Co(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Co(H_2O)_5OH]^{2+} + H_3O^+$$

The hydrolyzed species is presumably responsible for the acid-dependent path.

Hence Rate $= k_1[Co(H_2O)_6]^{3+}[PA] + k'_2[Co(H_2O)_5OH]^{+2}[PA]$

The inverse acidity dependence is not attributed to the degree of hydration of the pyridine aldehydes because their hydration is essentially complete within the pH range at which these reactions were carried out (20). The equilibrium constant for the hydrolysis reaction may be expressed as

$$k_h = \frac{[H^+][Co(H_2O)_5OH]^{2+}}{[Co(H_2O)_6]^{3+}}$$

Hence $[Co(H_2O)_5OH] = \dfrac{k_h[Co(H_2O)_6]}{[H^+]}$

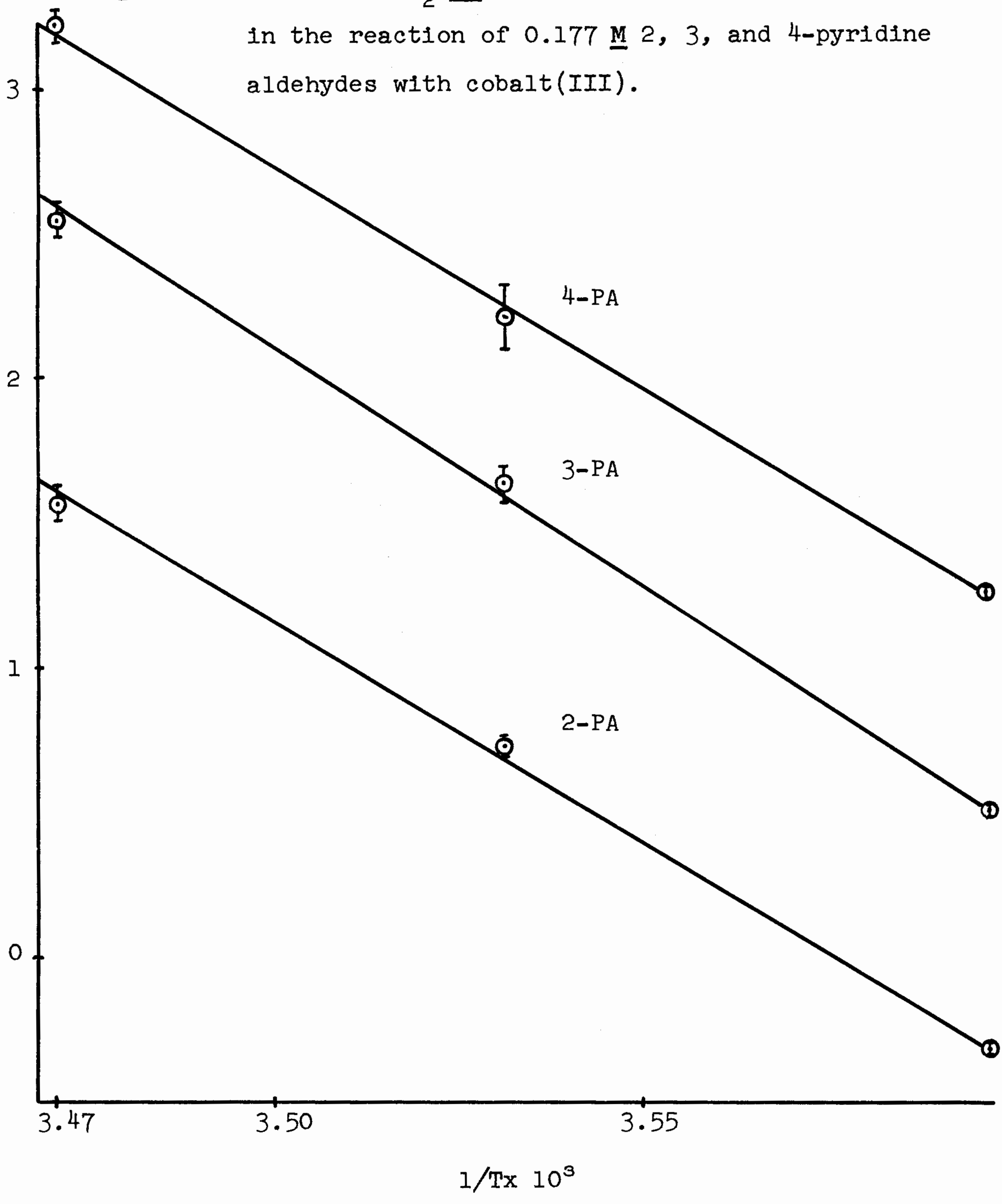
The rate expression may then be modified to

$$\text{Rate} = k_1[Co(H_2O)_6][PA] + \frac{k'_2k_h[Co(H_2O)_6]^{3+}[PA]}{[H^+]}$$

Therefore $k = k_1 + \dfrac{k'_2k_h}{[H^+]}$

Activation energies were obtained from plots of ln k_2 <u>vs</u> 1/T (figure 4). The slope of these plots is equal to $-E_{act}/R$ where E_{act} is the apparent activation energy for

Figure 4. Plot of ln k_2 vs 1/T for the acid-dependent path in the reaction of 0.177 M 2, 3, and 4-pyridine aldehydes with cobalt(III).



the acid-dependent step. This activation energy was converted into an enthalpy of activation by using the relation

$$\Delta H = E_{act} - Rt$$

The activation enthalpy obtained above is only an apparent enthalpy because k_2 is not a true specific rate constant. To obtain the true enthalpy of activation it was necessary to subtract the enthalpy of hydrolysis of the cobaltic species from the apparent enthalpy of activation.

Sutcliff and Weber (16) determined values for the heat and enthropy of hydrolysis of the cobalt(III) perchlorate species at an ionic strength of 1.0 M to be 10 ± 2 kcal/mole and 25 ± 7 e.u., respectively. Sutcliff and Weber (21) subsequently reported that these values may be in error due to their discovery of the presence of dimeric species in solution. The value of 10 kcal/mole determined for the hydrolysis of cobaltic ion is comparable with values obtained for other ions of about the same size and charge (22). Shanker and DeSouze (22) calculated ΔS for the reaction

$$[Co(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Co(H_2O)_5OH]^{2+} + H_3{}^{+}O$$

using the empirical equation developed by Cobble (23). They found a value of 25 ± 5 cal/mole degree. This implies that the values reported by Sutcliff and Weber may not be in error by too large an amount. In the present study the values reported by Sutcliff and Weber were used with the assumption that the values do not vary with changes in ionic strength and temperature in the ranges studied. Because of the uncertainty in the values reported above, the activation energies calculated for the acid-dependent path will be in error by an undetermined amount.

The error in the activation energies was determined by the method of limiting slopes. This yielded the maximum and minimum slopes that could be obtained, and therefore also yielded the maximum and minimum activation energies obtainable from the data. These limits were used as the error in E_{act}.

The entropies of activation were calculated using the equation $\mathbf{k} = \frac{\mathbf{k}KT}{h} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^{\ddagger}}{RT}}$

which is derived from absolute rate theory. In the equation, $\mathbf{k}$ is the transmission coefficient and is generally set equal to 1.

k is the specific rate constant at temperature T degrees Kelvin

K is the Boltzman constant

h is Planck's constant

$\Delta H^{\ddagger}$ is the enthalpy of activation

ΔS^* is the entropy of activation

RESULTS

Order of the Reaction

Bawn and Jolley (13), Hargreaves and Sutcliff (2), and Waters et. al. (3-12) have studied the reactions of many different types of organic compounds with cobalt(III) perchlorate and have found these reactions to be first-order with respect to both cobalt(III) ion and the organic compound. In view of the foregoing, the reaction under present study would be expected to follow pseudo first-order kinetics as the reaction was followed under conditions where pyridine aldehyde of 15-150 fold excess was present in solution. That this is indeed the case can be seen by looking at figure - 5 wherein a plot of log A vs time is linear. This is true, of course, only for first-order conditions. The slope of these lines is equal to k', the pseudo first-order rate constant. From the pseudo first-order rate constant one can obtain the second-order rate constant k by dividing by the concentration of pyridine aldehyde. Tables 1, 2, and 3 contain experimental results obtained for reactions performed under pseudo first-order conditions at constant acid concentration.

The order of the reaction with respect to cobalt(III) perchlorate was determined by following the reaction under second-order conditions where there is not a large excess

Figure 5. Plot of absorbance vs time for 0.210 M 2-pyridine aldehyde 5.8×10^{-3} M cobalt(III) at 10.0°C.

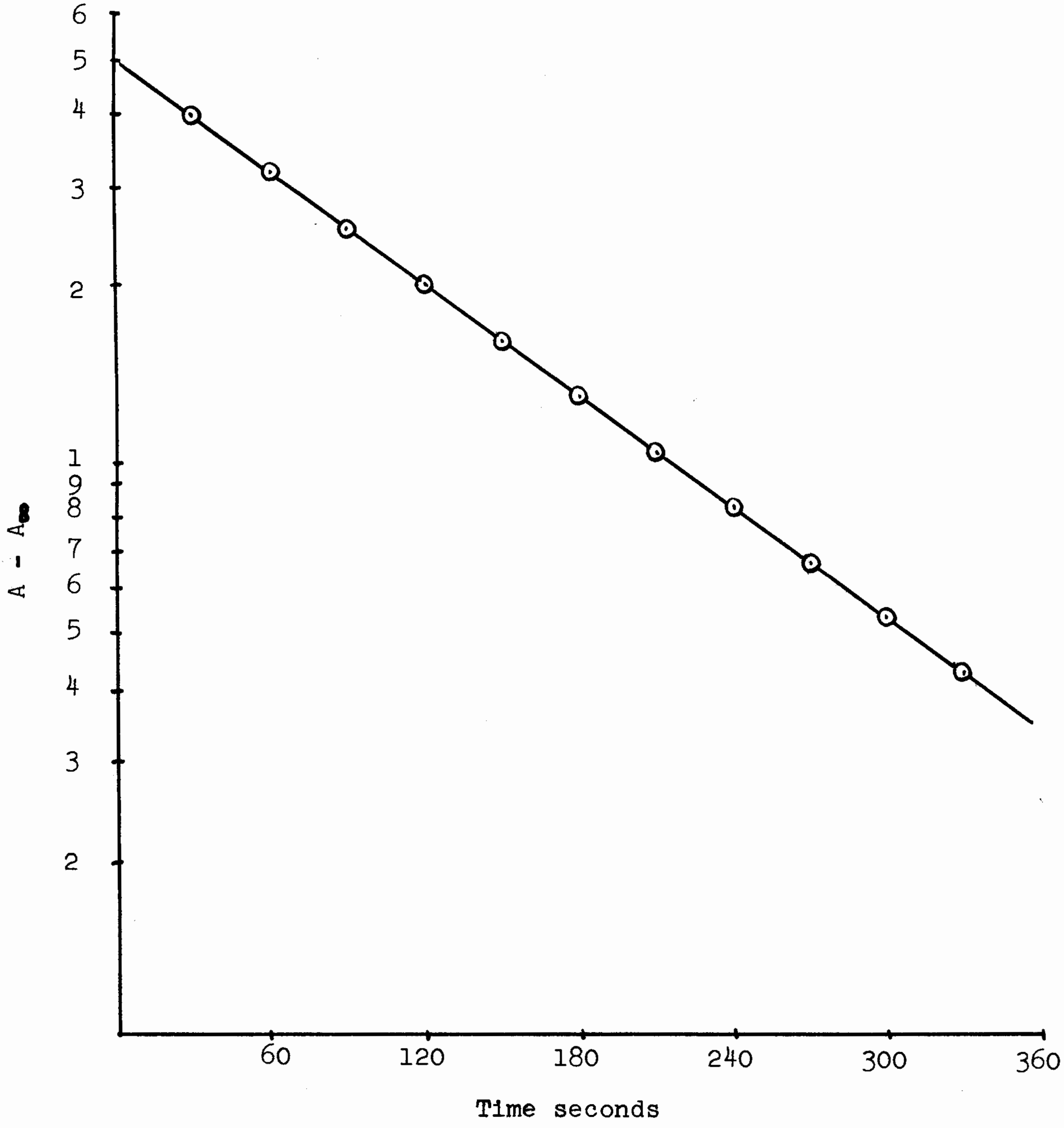


TABLE 1 Experimental data from the oxidation of 2-pyridine aldehyde by cobalt (III) in 1.025 M $HClO_4$.

t° C	[2-PA] M	[Co(III)] M	number of runs	k' mean	% dev. from mean	k' calc. from l. sq.	% dev. k' l. sq.	k l. sq.	intercept
14.9	0.144	.0092	2	0.775	1.3	0.711	8.3	5.30	-.052
14.9	0.175	.0092	3	0.913	2.4	0.876	4.1	5.30	
14.9	0.210	.0056	2	1.09	0.5	1.06	3.6	5.30	
14.9	0.286	.0051	2	1.44	0	1.46	1.4	5.30	
14.9	0.350	.0045	2	1.76	0.9	1.80	2.2	5.30	
14.9	0.420	.0055	2	2.04	0.5	2.17	6.0	5.30	
14.9	0.573	.0050	3	2.94	4.3	2.98	1.3	5.30	
14.9	0.700	.0044	3	3.78	4.8	3.66	3.2	5.30	
10.0	0.144	.0048	2	0.326	0	0.300	8.0	2.26	-.027
10.0	0.175	.0052	2	0.364	1.6	0.370	1.4	2.26	
10.0	0.210	.0048	2	0.457	1.1	0.450	1.5	2.26	
10.0	0.286	.0044	2	0.612	0.2	0.621	1.4	2.26	
10.0	0.350	.0048	2	0.743	1.2	0.766	3.0	2.26	
10.0	0.420	.0058	2	0.887	0.4	0.924	4.0	2.26	
10.0	0.573	.0054	2	1.26	0	1.27	0.8	2.26	
10.0	0.700	.0050	5	1.57	1.3	1.56	0.6	2.26	
5.3	0.210	.0064	2	0.188	2.1	0.200	6.0	0.93	-.005
5.3	0.286	.0060	2	0.246	0	0.271	9.2	0.93	
5.3	0.350	.0052	2	0.335	1.5	0.330	1.5	0.93	
5.3	0.420	.0064	2	0.385	1.3	0.396	2.8	0.93	
5.3	0.573	.0057	3	0.526	0.8	0.538	2.2	0.93	
5.3	0.700	.0066	2	0.640	0	0.656	2.4	0.93	

TABLE 2 Experimental data from the oxidation of 3-pyridine aldehyde by cobalt (III) in 1.025 M HClO$_4$.

t° C	[2-PA] M	[Co(III)] M	number of runs	k' mean	% dev. from mean	k' calc. from l. sq	% dev. k' l. sq.	k l. sq.	intercept
5.0	0.177	.0053	3	0.430	1.3	0.433	0.7	2.65	-.036
5.0	0.212	.0047	3	0.523	1.3	0.526	0.6	2.65	
5.0	0.290	.0054	3	0.740	2.6	0.732	1.1	2.65	
5.0	0.354	.0043	3	0.916	2.2	0.902	1.5	2.65	
5.0	0.425	.0054	3	1.08	2.7	1.09	0.9	2.65	
10.0	0.0885	.0068	3	0.535	0	0.501	6.4	5.74	-.007
10.0	0.133	.0048	6	0.750	2.0	0.756	0.8	5.74	
10.0	0.177	.0068	2	1.08	0	1.01	6.5	5.74	
10.0	0.266	.0053	3	1.53	4.4	1.53	0.7	5.74	
10.0	0.318	.0052	3	1.79	1.7	1.79	1.7	5.74	
10.0	0.354	.0068	3	2.04	2.0	2.02	1.0	5.74	
10.0	0.531	.0052	3	3.07	0.3	3.04	1.0	5.74	
14.8	0.0885	.0063	3	1.15	0	1.19	3.4	13.6	-.000
14.8	0.133	.0062	3	1.96	3.0	1.80	8.2	13.6	
14.8	0.177	.0062	3	2.36	1.7	2.40	1.7	13.6	
14.8	0.266	.0061	4	3.48	4.7	3.61	3.6	13.6	
14.8	0.354	.0063	4	4.80	4.0	4.80	0.0	13.6	
14.8	0.531	.0062	3	7.34	2.1	7.21	1.8	13.6	
14.8	0.708	.0068	3	9.58	1.2	9.62	0.4	13.6	

TABLE 3 Experimental rate constants for the oxidation of 4-pyridine aldehyde by cobalt(III) in 1.025 M $HClO_4$.

t° C	[4-PA] M	[Co(III)] M	number of runs	k' mean	% dev. from mean	k' calc from l. sq.	% dev. k' l. sq.	k l. sq.	inter-cept
10.0	0.708	.00566	2	6.12	1	6.16	0.7	8.65	.039
10.0	0.579	.00592	2	5.07	1.6	5.05	0.4	8.65	
10.0	0.426	.00	2	3.67	1.1	3.72	1.4	8.65	
10.0	0.323	.00490	3	2.71	1.5	2.83	4.3	8.65	
10.0	0.264	.00545	3	2.33	3.9	2.32	0.4	8.65	
10.0	0.194	.00582	2	1.73	0	1.72	0.6	8.65	
10.0	0.177	.00	3	1.53	1.3	1.57	2.6	8.65	
10.0	0.146	.00530	3	1.28	3.9	1.30	1.5	8.65	
15.0	0.106	.00620	2	2.02	1.0	2.19	7.8	20.90	-.021
15.0	0.145	.00570	2	2.85	0	3.01	5.3	20.90	
15.0	0.177	.00540	2	3.62	2.3	3.70	2.2	20.90	
15.0	0.212	.00620	2	4.38	0	4.41	0.7	20.90	
15.0	0.290	.00570	2	6.52	0	6.04	7.4	20.90	
15.0	0.354	.00550	2	7.76	1.8	7.38	4.9	20.90	
15.0	0.425	.00575	2	8.67	.4	8.86	2.2	20.90	
15.0	0.579	.00560	2	11.85	2.9	12.08	1.8	20.90	
5.0	0.145	.00557	2	.509	.4	0.522	2.5	3.70	-.014
5.0	0.177	.00537	2	.60	0	0.641	6.4	3.70	
5.0	0.212	.00540	2	.753	.4	0.770	2.2	3.70	
5.0	0.290	.00582	2	1.09	1.8	1.05	3.7	3.70	
5.0	0.354	.00562	2	1.36	0	1.30	4.4	3.70	
5.0	0.425	.00645	2	1.59	3.2	1.56	1.9	3.70	
5.0	0.579	.00600	2	2.08	.5	2.13	2.4	3.70	
5.0	0.708	.00550	2	2.60	.8	2.61	.4	3.70	

of pyridine aldehyde. A reaction obeying second-order kinetics should follow the equation

$$kt = 1/a\text{-}b \; \frac{\ln b(a-x/2)}{a(b-x)}$$

Under these conditions a plot of $\frac{\ln b(a-x/2)}{a(b-x)}$ vs t where a = the initial conc. of pyridine aldehyde, b = the initial conc. of Co(III) perchlorate, x = the decrease in Co(III) perchlorate at time t, (a-x/2) = conc. of pyridine aldehyde at time t, and (b-x) = the conc. of Co(III) perchlorate at time t , should yield a straight line.

Because the oxidation of aldehyde to acid is a two electron process, 2 molecules of Co(III) perchlorate are required for every molecule of pyridine aldehyde oxidized. Figure 6 shows the results obtained for the reaction of pyridine aldehyde and Co(III) perchlorate under second-order conditions. The linearity obtained demonstrates the reaction to be second-order overall.

The data allows calculation of second-order rate constants for these reactions. Table 4 shows these constants to be in fair agreement with the second-order rate constants calculated from the pseudo first-order rate constant.

The large variation in the rate constants determined for the reaction under second-order conditions is believed

Figure 6 Plot of logb/a $\frac{(a-x)}{(b-x)}$ vs time for 0.0151 M 3-pyridine aldehyde in 0.00378 M cobalt(III) at 9.9° C.

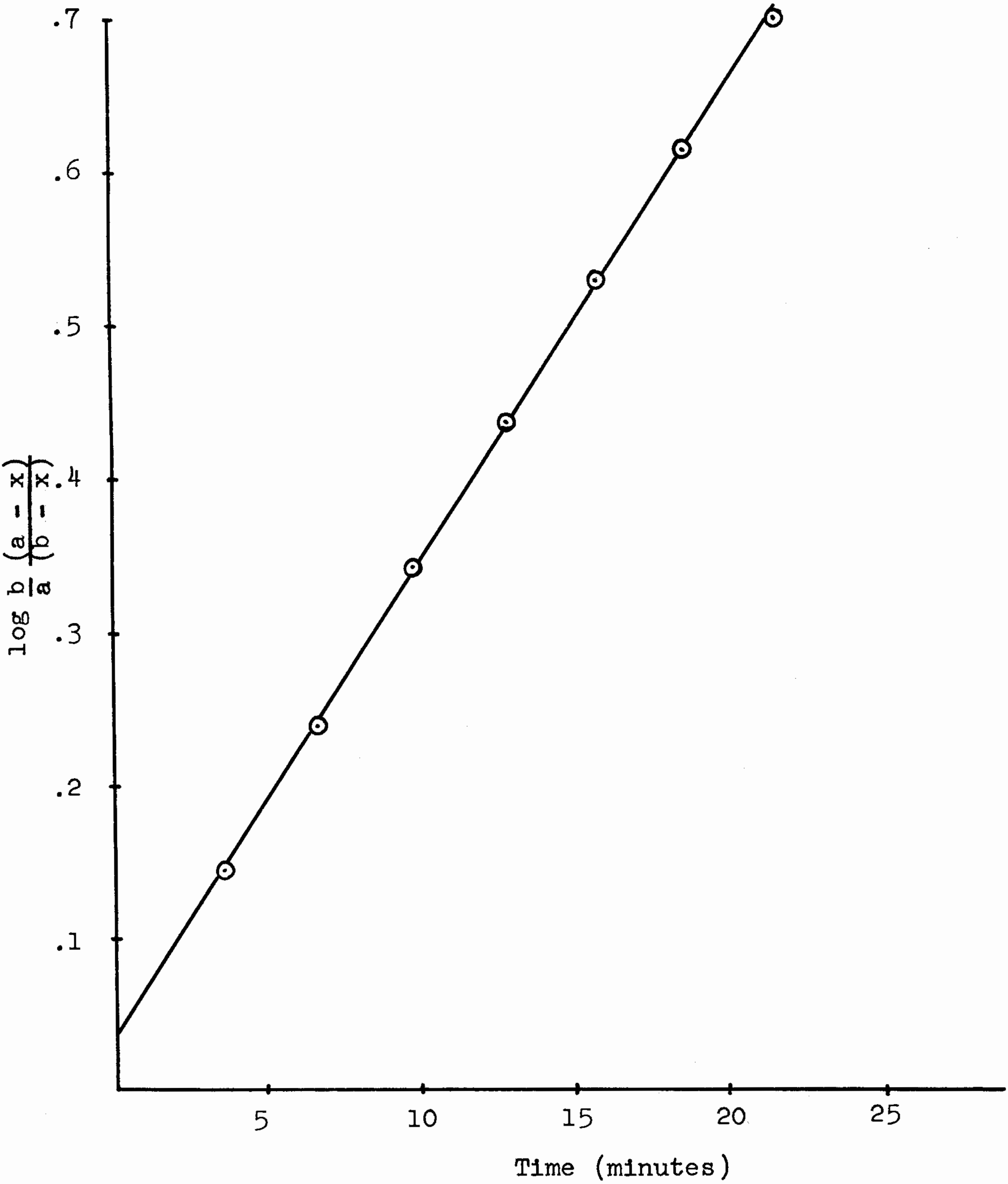


TABLE 4 Comparison of rate constants obtained via second-order and pseudo first order kinetics.

compound	original [Co(III)]	ratio [PA] to [Co(III)]	t° C	2nd order k	% deviation	1st order k
2-PA	0.00328	4	14.9	5.45	2.7	5.30
2-PA	0.00365	4	14.9	4.96	6.4	5.30
2-PA	0.00550	2	14.9	5.27	0.6	5.30
3-PA	0.00378	4	10.0	6.32	9.2	5.74
3-PA	0.00565	2	10.0	6.03	4.9	5.74
3-PA	0.00401	4	10.0	6.46	11.2	5.74

to be due to the difficulty of obtaining a true initial absorbance reading. The initial absorbance had to be estimated as the solution was being diluted by the addition of pyridine aldehyde. Because of this, estimation of an accurate initial absorbance was impossible. It can be seen from the second-order rate equation that a small error in the initial absorbance will result in large errors in the determined rate constant.

Effect of Ionic Strength

The effect of ionic strength on the rate of reaction was determined by comparing the rate constants obtained from solutions that differed only in $LiClO_4$ content. Rate constants were determined for solutions at specific concentrations of pyridine aldehyde, perchloric acid, and Cobalt (III) Perchlorate. Solutions of identical concentrations of pyridine aldehyde, Perchloric acid and Cobalt(III) perchlorate which also contained various amounts of $LiClO_4$ were prepared and their rate constants determined. As can be seen from Table 5 the rate constants obtained under both conditions were identical within experimental error. It was therefore concluded that ionic strength effects are neglible within the range of concentration that these oxidation reactions were studied. Waters and Cooper (5) in their study of the oxidation of _m_ and _p_-nitrobenzaldehyde

TABLE 5 Ionic strength effects. The last two colums compare the second-order rate constants k* and k obtained in the presence and abscence of lithium perchlorate, respectively.

t° C	compound	[PA]	[$HClO_4$]	[$LiClO_4$]	total ionic strength	k'	k*	k
10.0	2-PA	.177	1.025	.354	1.556	.400	2.26	2.13
10.0	2-PA	.118	1.025	.472	1.615	.280	2.37	2.26
10.0	3-PA	.177	1.025	.354	1.556	1.08	6.10	6.11
10.0	3-PA	.118	1.025	.472	1.615	.694	5.88	5.74
10.0	4-PA	.177	1.025	.531	1.733	1.54	8.70	8.83
10.0	4-PA	.145	1.025	.434	1.636	1.22	8.41	8.67
10.0	4-PA	.177	.592	.654	1.423	2.69	15.20	15.25
10.0	4-PA	.177	.762	.483	1.422	2.17	12.26	12.43

by Cobalt(III) perchlorate also found that the reaction was unaffected by variations in ionic strength.

Effect of Hydrogen Ion

Due to the fact that no ionic strength effect was observed, hydrogen ion dependence studies were not carried out at constant ionic strength.

TABLE 6 Values of the slopes ($\underline{k}_2$) and intercepts (k_1) obtained from the k vs H plots.

compound	t° C	k_1 $\underline{M}^{-1}$ min.$^{-1}$	K_2 min.$^{-1}$
2-PA	4.8 ± .05	0.25	0.736
2-PA	10.0 ± .05	0.24	2.09
2-PA	15.0 ± .05	0.32	4.79
3-PA	4.8 ± .05	0.91	1.65
3-PA	10.0 ± .05	0.65	5.11
3-PA	15.0 ± .05	0.88	13.21
4-PA	4.8 ± .05	-0.04	3.54
4-PA	10.0 ± .05	0.11	9.08
4-PA	15.0 ± .05	-3.16	24.8

The hydrogen ion dependence study was accomplished by maintaining a constant pyridine aldehyde concentration and varying the hydrogen ion concentration. From the pseudo first-order rate constant k' that was obtained, k was calculated and plotted vs $1/[H^+]$. The least squares slopes and intercepts obtained are listed in Table 6.

Enthalpies and Entropies of Activation

The enthalpies and entropies of activation were calculated as indicated in the section on Treatment of Data and Errors. The apparent enthalpies and entropies of activation for the acid-dependent path are shown in Table 7 and the enthalpies and entropies of activation corrected for the hydrolysis of the Cobalt(III) ion are shown in Table 9. Enthalpies and entropies of activation were not calculated for the acid-independent path because the intercepts were found to be small and temperature independent. These results indicate that either there is no acid-independent path or, if an acid-independent path does exist, it is smaller than experimental error and therefore the temperature dependence would not be apparent. Assuming that the data indicating the acid-independent path to be small or non-existant is valid, the apparent enthalpies and entropies of activation may be calculated from the data obtained for reactions performed at constant acid strength. In the absence of an acid-independent path the rate equation becomes

$$\text{Rate} = k_2/H\ [PA][Co(III)] = k[PA][Co(III)]$$

when k is the second-order rate constant that was calculated

TABLE 7 Apparent enthalpies and entropies of activation for the acid-dependent path in the oxidation of 0.177 M, 2, 3, and 4-pyridine aldehydes by cobalt (III).

compound	t° C	$\Delta H^{\ddagger}$ kcal/mole	ΔS^{*} cal/deg mole
2-PA	15.0	29.6 ± 1.9	39.0 ± 6.5
3-PA	15.0	32.6 ± 2.6	51.4 ± 9.0
4-PA	15.0	29.6 ± 2.6	42.1 ± 9.0
2-PA	25.0	29.6 ± 1.9	39.3 ± 6.5
3-PA	25.0	32.6 ± 2.6	51.6 ± 9.0
4-PA	25.0	29.6 ± 2.6	42.4 ± 9.0

TABLE 8 Apparent enthalpies and entropies of activation for the oxidation of the 2, 3, and 4-pyridine aldehydes by cobalt(III) in 1.025 M $HClO_4$.

compound	t° C	$\Delta H^{\ddagger}$ kcal/mole	ΔS^{*} cal/deg mole
2-PA	15.0	28.8 ± 1.6	36.4 ± 5.6
3-PA	15.0	26.0 ± 2.4	28.5 ± 8.3
4-PA	15.0	27.6 ± 4.1	35.0 ±14.7
2-PA	25.0	28.8 ± 1.6	36.7 ± 5.3
3-PA	25.0	26.0 ± 2.4	28.7 ± 8.1
4-PA	25.0	27.6 ± 4.1	35.2 ±14.0

TABLE 9 Enthalpies and entropies of activation for the acid-dependent path in the oxidation of 0.177 M 2, 3, and 4-pyridine aldehydes by cobalt(III).

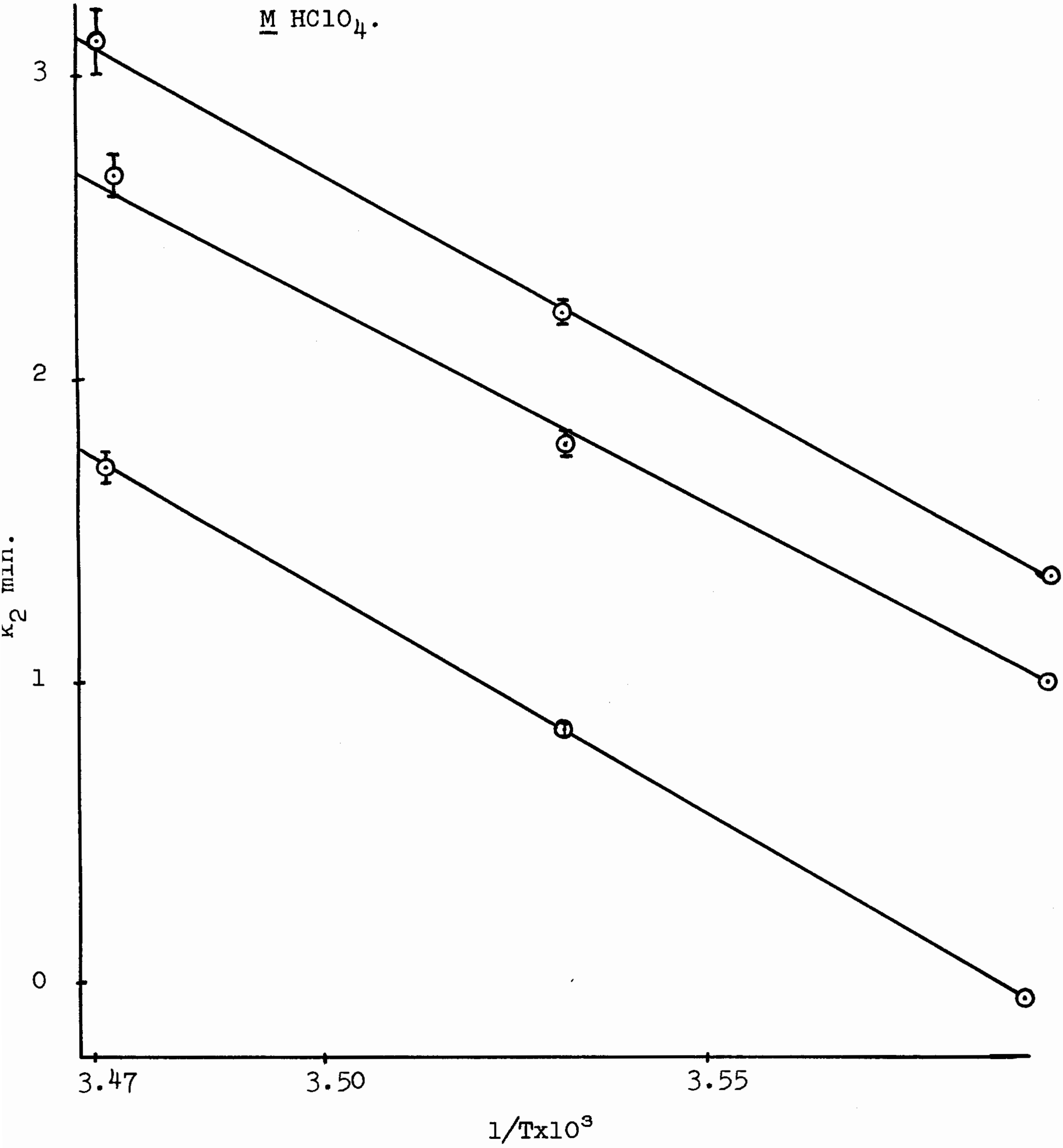
compound	t° C	$\Delta H^{\ddagger}$ kcal/mole	ΔS^{*} cal/deg mole
2-PA	15.0	19.6 ± 3.9	- 19 ± 13
3-PA	15.0	22.6 ± 4.6	- 8 ± 16
4-PA	15.0	19.6 ± 4.6	- 18 ± 14
2-PA	25.0	19.6 ± 3.9	- 19 ± 13
3-PA	25.0	22.6 ± 4.6	- 7 ± 16
4-PA	25.0	19.6 ± 4.6	- 16 ± 14

TABLE 10 Enthalpies and entropies of activation for the oxidation of the 2, 3, and 4-pyridine aldehydes by cobalt(III) in 1.025 M $HClO_4$.

compound	t° C	$\Delta H^{\ddagger}$ kcal/mole	ΔS^{*} cal/deg mole
2-PA	15.0	18.8 ± 3.6	- 23 ± 11
3-PA	15.0	16.0 ± 4.4	- 31 ± 14
4-PA	15.0	17.6 ± 6.1	- 25 ± 20
2-PA	25.0	18.8 ± 3.6	- 22 ± 11
3-PA	25.0	16.0 ± 4.4	- 30 ± 14
4-PA	25.0	17.6 ± 6.1	- 23 ± 20

from pseudo first-order kinetics given in Tables 1, 2, and 3, p. 29 , 30, 31. The rate constant k may then be converted to the acid-dependent rate constant k_2 by multiplying each rate constant k by the acid concentration at which that rate constant was determined. From the Arrhenius plots of $\ln k_2$ vs $1/T$ the apparent energy of activation may be calculated (figure 7), and from this the enthalpies and entropies of activation obtained. The procedure described above was used to determine apparent enthalpies and entropies of activation for the oxidation reactions followed at constant acid concentration. The values obtained for the apparent activation enthalpies and entropies are shown in Table 8, and the enthalpies and entropies of activation corrected for the hydrolysis are shown in Table 10.

Figure 7 Plot of $\ln k_2$ vs $1/T$ for the reaction of the 2, 3, and 4-pyridine aldehydes with cobalt(III) in 1.025 M $HClO_4$.



DISCUSSION

Enthalpies and Entropies of Activation

The general rate equation for the oxidation of the pyridine aldehydes by cobalt(III) has the form

$$\text{RATE} = \left[k_2/[H^+][Co(III)][PA]\right]$$

where k_2 is the acid-dependent rate constant for the reaction. In the discussion on the determination of enthalpies and entropies of activation in the preceeding section it was stated that an apparent activation energy was calculated for the 2, 3, and 4-pyridine aldehydes for reactions at constant acid strength using the assumption that an acid-independent path did not exist. The fact that the acid-independent constants k_1 (Table 6, p.37) determined from a plot of the second-order rate constants k vs $1/[H^+]$ show no noticealbe variation with temperature tends to support this view. Comparison of the enthalpies and entropies of activation of the pyridine aldehydes lends further support to this assumption. The enthalpies and entropies of activation determined for the 2, and 4-pyridine aldehydes are in agreement within experimental error. This agreement would not have been expected if an acid-independent path were present.

The considerable disagreement for the two sets of data on activation enthalpies and entropies of the 3-pyridine aldehydes was not entirely unexpected. The Arrhenious plot, obtained for 3-pyridine aldehyde at constant acid strength (figure 7, p.42) shows that the correct slope of the line is in considerable doubt. Part of the uncertainty in the k values used for the Arrhenious plots is due to the experimental procedure employed for following the reaction of the 3-pyridine aldehydes. The reactions were initiated by adding 1 ml. pyridine aldehyde solution 1.025 M in $HClO_4$ to 2 ml. cobalt(III) solution 1.025 M in $HClO_4$ which was placed in the cell compartment of the spectrophotometer. The temperature of the cell compartment was between 1 and 2 degrees warmer than the temperature in the water bath used to cool the cell compartment. The syringe which was used to inject the pyridine aldehyde solution was allowed to equilibrate in the water bath. The resultant temperature upon addition of pyridine aldehyde was calculated from the volume of the aldehyde added, the volume of cobalt(III) solution in the compartment, and the respective temperatures of cell and water bath. Although the data obtained at various concentrations and temperatures showed fairly good reproducability, the uncertainty in the actual temperature of the reacting species negated the value of data produced. Meaningful comparisons of activation energies and entropies for the 3-pyridine aldehydes must therefore await the obtainment of additional data.

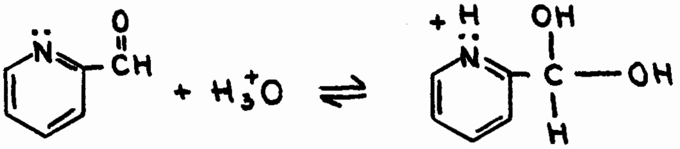
Effect of Hydrogen Ion

From Table (5, p.36) it is apparent that the rate of reaction of the pyridine aldehydes was not affected noticeably by the presence of $LiClO_4$ ion in solution in the ionic strength range in which these reactions were followed. Cooper and Waters (5) in their study of the oxidation of *m*-nitrobenzaldehyde by Co(III) found the rate of oxidation of aldehyde to be independent of ionic strength in the range 0.93 to 3.50 *M*. If one considers the possible mechanisms through which the oxidation can occur, it is observed that changes in ionic strength would not be expected to appreciably affect the rate of oxidation.

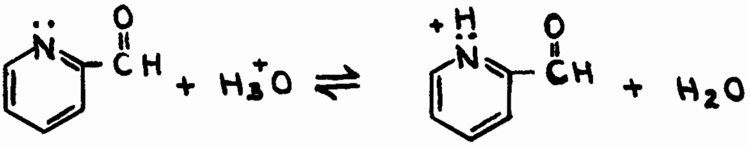
Reaction Mechanisms

The following mechanisms are seen as possible routes for the oxidation process. The mechansims are demonstrated using 2-pyridine aldehyde as reducing agent.

In acid solution the pyridine aldehydes exist in either the hydrated or non-hydrated forms labeled I and II below (20).



I



II

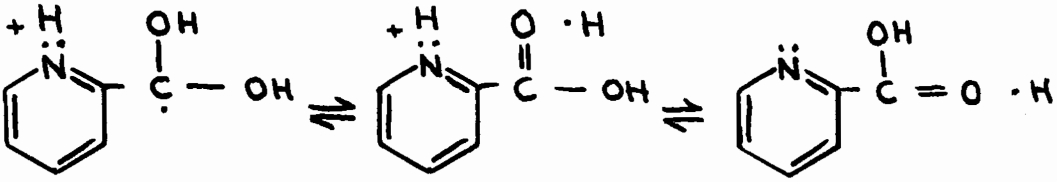
The following equilibrium reaction has been shown to exist for the cobalt(III) species.

$$[Co(H_2O)_6]^{3+} \rightleftharpoons HO-Co(H_2O)_5 + H^+$$

III IV

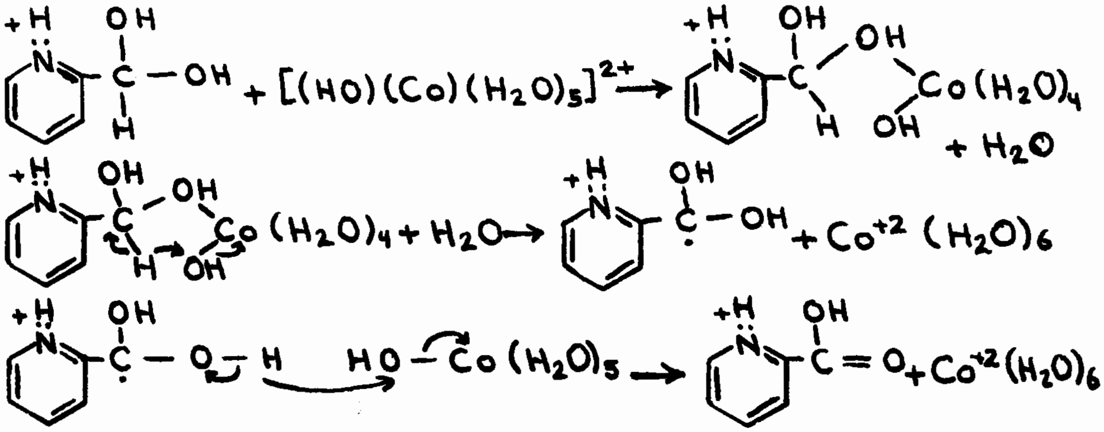
The inverse acidity effect observed for reactions of this type implies that species IV is the oxidant in the reaction with pyridine aldehyde.

In solutions of high acid strength (1.0 M) it has been shown that the pyridine aldehydes exist essentially 100 percent in the hydrated form (20). It must therefore be concluded that the hydrated form of the aldehyde is the most likely species to be involved in the reaction mechanism. Consideration of resonance stabilization effects lends further support to the view that the hydrated species is the reactive species. For the hydrated form of aldehyde the following resonance structures involving the free radical can be drawn.

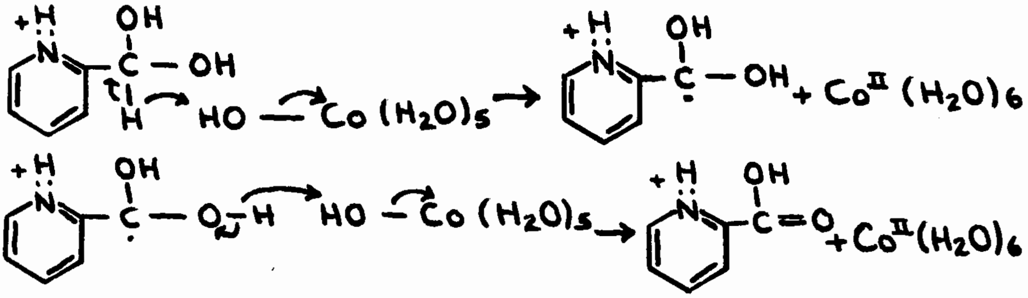


Similar resonance stabilization is not possible for the non-hydrated pyridine aldehydes.

A. For the hydrated form of aldehyde possible reaction mechanisms for the rate determining step are:

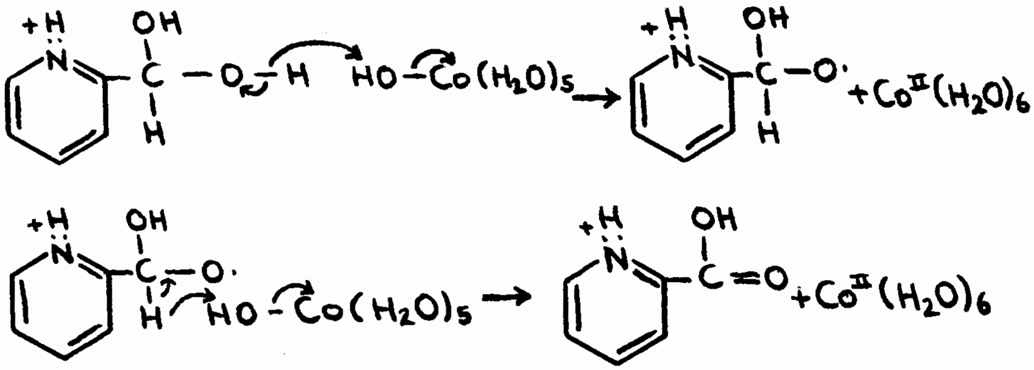
1.


The mechanism described above is an "inner sphere" or bridged mechanism and involves formation of a cobalt-aldehyde complex prior to abstraction of the hydrogen atom. The rate determining step of the mechanism involves abstraction of the aldehydic hydrogen atom by the Cobalt(III) hydroxyl ligand with simultaneous transfer of an electron from the hydroxyl ligand to Cobalt(III). In a second step a hydrogen atom situated on a hydroxyl group of the hydrated aldehyde is abstracted by the cobaltic hydroxyl ligand with simultaneous transfer of an electron from the hydroxyl ion to Cobalt(III).

2.


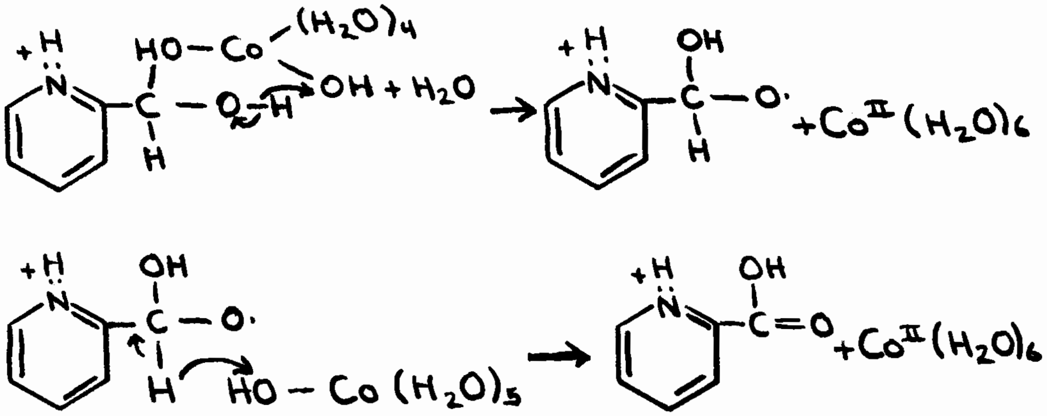
Mechanism 2 is described as an "outer sphere" mechanism and differs from one by the fact that no prior formation of a cobalt-aldehyde complex is required for abstraction of the hydrogen atom to occur.

3.



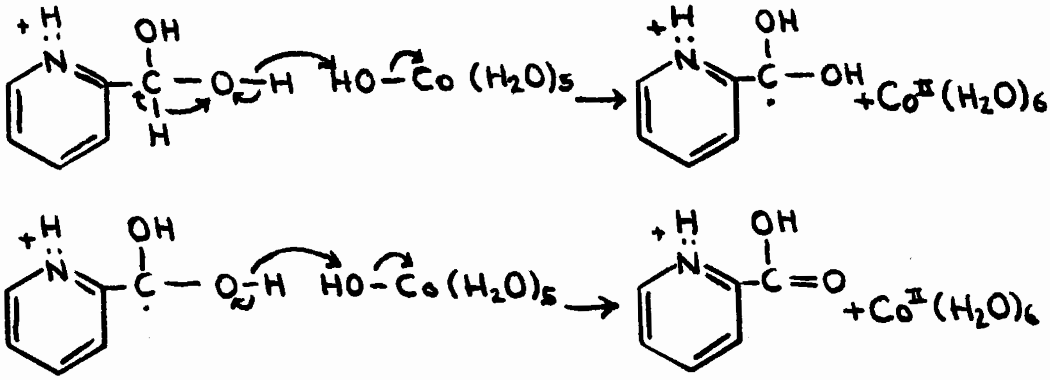
In this instance the hydrogen atom stiuated on the oxygen atom is abstracted rather than the hydrogen atom bonded to carbon. The mechanism corresponds to the outer sphere mechanism shown in 2.

4.



Mechanism 4 corresponds to "inner sphere" mechansim 1. As in mechanism 3, the hydrogen atom situated on the oxygen atom is abstracted.

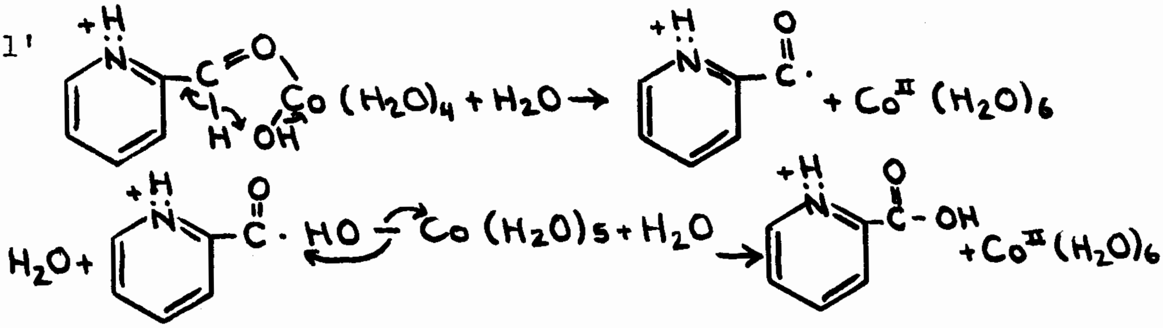
5.



In the above mechanism there is a shift of the hydrogen atom bonded to carbon to the oxygen atom simultaneous to the abstraction of hydrogen atom from oxygen.

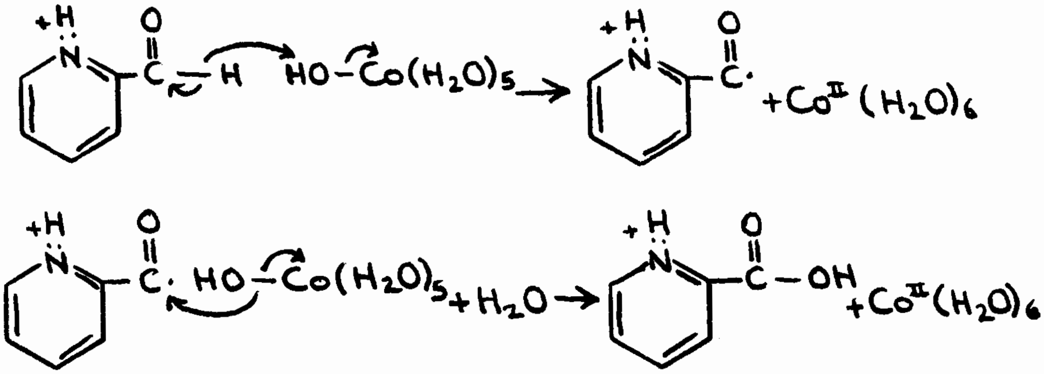
B. For the non-hydrated form of aldehyde possible reaction mechanisms for the rate determining step are:

1'



The mechanism described above corresponds to the "inner sphere" mechanism proposed for the hydrated species of aldehyde.

2'



This mechanism corresponds to the "outer sphere" mechanism proposed for the hydrated species of aldehyde.

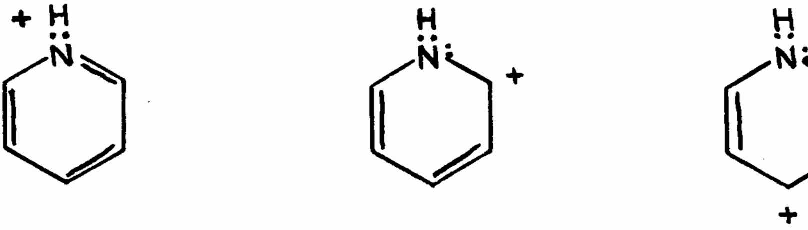
One can observe that charge is neither created nor destroyed in the rate determining step of any of the proposed reaction mechanisms. Because of this, one would not expect the reaction to be subject to either ion catalysis or inhibition. It is to be noted, however, that both reacting species are positively charged. In acid solutions the pyridine aldehydes are protonated. Because of this, the reaction mechanisms that have been discussed are ion-radical mechanisms. In general factors which stabilize ions also stabilize free radicals.

Resonance, Inductive, and Complexation Effects

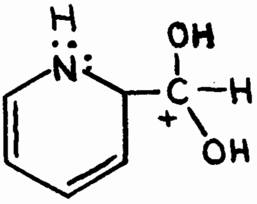
There are three main effects that must be considered in the prediction of the relative rates of oxidation of the pyridine aldehydes: resonance effects, inductive effects, and complexation effects. These will be considered in turn.

Resonance effects

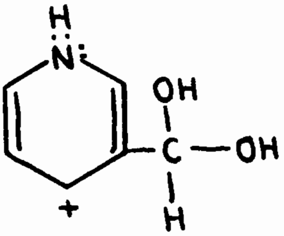
If one considers the possible resonance structures using the protonated pyridine molecule for reference, it would appear that 3-pyridine aldehyde should undergo oxidation most readily if the mechanism involves abstraction of a C-H ion in the rate-determining step.



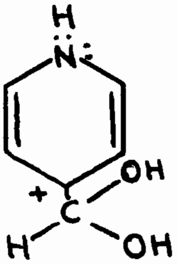
This is to be expected as both the 2 and 4-pyridine aldehydes exhibit resonance structures in which charge is centered on the carbon atom from which the hydrogen atom is being abstracted. One would expect the electrons on the carbon bearing the positive charge to be more tightly held thereby increasing the difficulty of hydrogen atom abstraction.



2-pyridine aldehyde

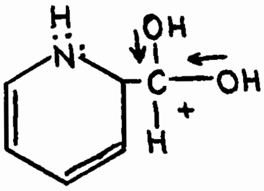


3-pyridine aldehyde

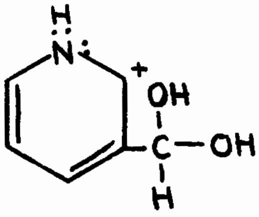


4-pyridine aldehyde

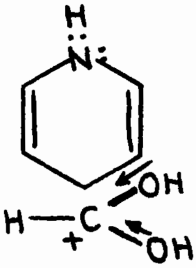
Similar effects will be observed if the rate determining step involved abstraction of the O-H hydrogen atom. One draws the possible resonance structures as before placing the hydrated form of the aldehyde in positions 2, 3, and 4.



2-PA



3-PA



4-PA

In this instance the positive charge situated on carbons 2 and 4 of the pyridine ring would cause electron density to flow from the oxygen atom to the positively charged carbon atom. This decrease in electron density around the oxygen atom would increase the affinity of xoygen for electrons, thereby making abstraction of a hydrogen atom more difficult.

Inductive effects

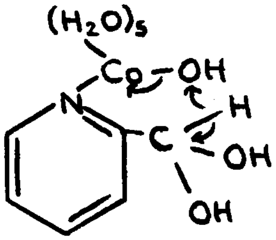
On the basis of inductive effects one would expect the reactivity sequence to be 4-pyridine aldehyde > 3-pyridine aldehyde > 2-pyridine aldehyde. This is because the ability of the positive charge on the nitrogen atom to inhibit abstraction of the aldehydic hydrogen atom is lessened as distance between positively charged species and reactive species is increased, i.e., one would expect electron density to be drawn from the ring to neutralize the positive charge situated on the nitrogen atom. The electron density change will be greatest on those atoms nearest the site of positive charge. This is the basis for assigning reactivity as described above.

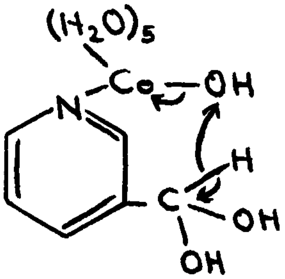
Complexation effects

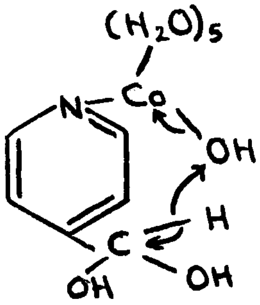
Two effects are considered in the event that complexation occurs between the nitrogen atom and the reactive cobaltic species.

1. complex formation between the nitrogen atom and the cobaltic species occurs and the resulting complex is involved in the rate determining step.

In the earlier discussion on possible reaction mechanisms no mention was made of any mechanism that involved complex formation between the nitrogen atom and the cobaltic species. The reasons for excluding mechanisms of this type from consideration will become obvious later. If one considers reactions involving complexes of the type shown below, consideration of steric effects would indicate that the relative reactivity of the complexes should follow the

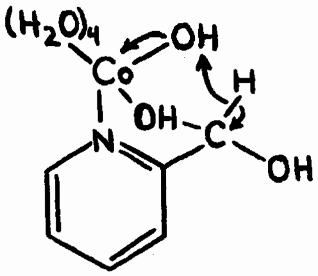






order 2-pyridine aldehyde > 3-pyridine aldehyde > 4-pyridine aldehyde. The assignment of the relative reactivities in the above manner is due to the fact that the 2-pyridine aldehyde complex involves a 6-membered reaction parameter whereas the 3, and 4-pyridine aldehydes contain 7 and 8 membered reaction systems, respectively. In organic species steric considerations favor reaction processes involving 6-membered systems.

2. Cobalt-nitrogen-oxygen complexes are formed.



In the figure shown above cobalt is complexed to both nitrogen and oxygen. Structural considerations indicate that complexes of this type are reasonable only for the 2-pyridine aldehydes. Therefore these complexes could not account for the oxidation reactions of the 3 and 4-pyridine aldehydes.

The expected results of resonance effects, inductive effects, and complexation effects on the relative rates of oxidation of the pyridine aldehydes by cobalt(III) perchlorate in $HClO_4$ solution were described in the last section.

In the present discussion experimental results are reported and compared to the results that would be expected if the various effects described previously were involved in the mechanism of reaction.

Experimental results showed the relative reactivity to be 4-pyridine aldehyde > 3-pyridine aldehyde > 2-pyridine aldehyde. 4-pyridine aldehyde was found to react approximatly 1 1/2 times more rapidly than 3-pyridine aldehyde under similar reaction conditions and 3-pyridine aldehyde was found to react 2 1/2 times more rapidly than 2-pyridine aldehyde.

Complexation effects

In the discussion on cobalt-nitrogen complexes two conclusions were drawn.

1. For complexes involving cobalt and nitrogen the reactivity should follow the order 2-pyridine aldehyde > 3-pyridine aldehyde > 4-pyridine aldehyde.
2. For complexes involving cobalt-nitrogen and oxygen only 2-pyridine aldehyde would be expected to undergo oxidation readily.

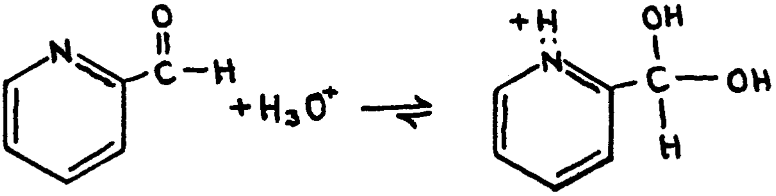
Neither of these predictions can account for the observed results. Therefore complexes of this type are not expected to contribute significantly to the reaction rate. It should also be stated that formation of a cobalt nitrogen complex requires that hydrogen ion be displaced. Since hydrogen ion is present in vastly greater quantities, the amount of cobalt-nitrogen complex that would be expected to form would be quite small.

Resonance effects

It was concluded from the discussion on resonance effects that reactivity should follow the sequence 2-pyridine aldehyde > 3-pyridine aldehyde > 4-pyridine aldehyde. This is opposite to the reactivity sequence observed and it must therefore be concluded that resonance contribution to oxidation reactions of this type are relatively small. This result should not be surprising as the importance of resonance effects is directly related to the stability of the resonance structures that can be drawn. Structures in which a positive charge is placed on a carbon atom that is already electron deficient are not expected to be very stable. Because of this resonance stabilization is assumed to be small and therefore resonance effects should be small.

Inductive effects

In the discussion on inductive effects it was concluded that the order of reaction should follow the sequence 4-pyridine aldehyde   3-pyridine aldehyde   2-pyridine aldehyde. This is, of course, precisely the results observed experimentally. The fact that 2-pyridine aldehyde is proportionally much slower to 3-pyridine aldehyde than 3-pyridine aldehyde is to 4-pyridine aldehyde in oxidation rate lends further support to the view that reaction rate is governed by inductive effects. It would be expected that 2-pyridine aldehyde would be inhibited proportionatly greater than 3-pyridine aldehyde and 4-pyridine aldehyde as inductive effects decrease with distance. It is therefore concluded that the relative reaction rates for the 2, 3, and 4-pyridine aldehydes are determined primarily by inductive effects. This is, the major factor in determining the relative rate of reaction of the 2, 3, and 4-pyridine aldehydes is their proximity to the protonated nitrogen atom of the pyridine ring. In an earlier section seven possible reaction mechanisms were listed. It is not possible to exclude any of these mechanisms from the experimental results obtained in this work. However, some conclusions can be drawn about the relative probability of these mechanisms. It has been previously determined (20) that the pyridine aldehydes are essentually 100 percent hydrated in solutions of 1 M acidity. It is therefore concluded that mechanisms involving the hydrated form of aldehyde as intermediates in the oxidation reaction are the most likely. The non-hydrated form of aldehyde can not be excluded as a possible intermediate, however, as the equilibrium is extremely rapid)27).



Probable Reaction Mechanisms

Of the five mechanisms described for the hydrated species of aldehyde the three mechanisms involving abstraction of the O-H hydrogen atom are believed to be less probable as consideration of bond energies reveals O-H bond strength to be 111 kcal/mole as compared to 99 kcal/mole for the C-H bond. On this basis it would be expected that the C-H hydrogen atom would be abstracted more readily than the O-H hydrogen atom. It may be that the question of O-H vs C-H hydrogen atom abstractions can be resolved by consideration of deuterium isotope effects.

If the C-H bond is involved in the rate determining step, the rate of reaction should be markedly decreased when C-O is substituted. If the O-H hydrogen atom is involved, the rate of reaction should not be significantly altered.

Of the two mechanisms remaining, mechanism one which involves prior formation of a cobalt aldehyde complex appears to be more logical. For abstraction of a hydrogen atom to occur. Proper orientation must be attained between the cobaltic species and the hydrogen atom. The formation of a cobalt(III) oxygen complex as precurser to the reaction would enable the molecule to be in the reaction vicinity for a much greater time than would be possible for random meetings of Cobalt(III) ion and aldehyde. Because of this, the probability of reaction would be enhanced for the species involving the complexed form of aldehyde.

APPENDIX

TABLE 11 Rate constants obtained from the oxidation of 0.177 M 2, 3, and 4-pyridine aldehydes by cobalt (III) at 10.0 C.

compound	[$HClO_4$]	k' ave.	% dev. k'	k	$1/[H^+]$
2-PA	0.592	0.685	2.0	3.87	1.689
2-PA	0.762	0.496	0	2.82	1.312
2-PA	1.025	0.404	1.0	2.28	0.975
2-PA	1.247	0.353	2.3	1.99	0.802
3-PA	0.592	1.65	3.0	9.32	1.689
3-PA	0.762	1.28	0.8	7.23	1.312
3-PA	1.025	1.03	2.9	5.82	0.975
3-PA	1.247	0.822	1.5	4.64	0.802
4-PA	0.592	2.70	5	15.25	1.689
4-PA	0.762	2.20	1.4	12.43	1.312
4-PA	1.025	1.56	2.0	8.81	0.975
4-PA	1.247	1.30	2.3	7.34	0.802

TABLE 12 Rate constants obtained from the oxidation of 0.177 M 2, 3, 4-pyridine aldehydes by cobalt(III) at 4.8° C.

compound	[$HClO_4$]	k'	% dev. k'	k	$1/[H^+]$
2-PA	0.769	0.219	0.5	1.24	1.300
2-PA	0.854	0.199	1.5	1.12	1.171
2-PA	1.025	0.165	1.8	0.932	0.975
2-PA	1.505	0.136	0	0.768	0.664
3-PA	0.769	0.536	4.1	3.03	1.300
3-PA	0.854	0.488	1.6	2.76	1.171
3-PA	1.025	0.450	2.2	2.54	0.975
3-PA	1.505	0.348	0	1.97	0.664
4-PA	0.769	0.802	0.8	4.53	1.300
4-PA	0.854	0.738	2.8	4.17	1.171
4-PA	1.025	0.596	0	3.37	0.975
4-PA	1.505	0.411	0.7	2.32	0.664

TABLE 13 Rate constants obtained from the oxidation of 0.177 M 2, 3, and 4-pyridine aldehydes by cobalt(III) at 15.0° C.

compound	$[HClO_4]$	k'	% dev. k'	k	$1/[H^+]$
2-PA	0.769	1.16	4	6.55	1.300
2-PA	0.854	1.07	2.8	6.04	1.171
2-PA	1.025	0.863	0	4.88	0.975
2-PA	1.505	0.636	0	3.59	0.664
3-PA	0.854	2.86	1.4	16.16	1.171
3-PA	1.025	2.40	0	13.56	0.975
3-PA	1.505	1.71	0	9.66	0.664
4-PA	0.854	4.57	1.0	25.82	1.171
4-PA	1.025	3.64	1.0	20.56	0.975
4-PA	1.505	2.39	1.2	13.50	0.664

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