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Formation And Kinetics Of Dissociation Of Some Pentaaquotrihalomethyl Chromium(Iii) Ions.

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FORMATION AND KINETICS OF DISSOCIATION OF SOME PENTAAQUOTRIHALOMETHYLCHROMIUM(III) IONS.

A Dissertation
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The Faculty of the Graduate School
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In Partial Fulfillment
of the Requirement for the Degree
Doctor of Philosophy

by
Sher Khan Malik
May 1973

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Dated

Formation and Kinetics of Dissociation of Some Pentaaquotrihalomethylchromium(III) Ions.

The present study was an investigation of the formation and kinetic stability of some complexes containing a chromium-carbon bond in an aqueous medium. An orange-brown pentaaquotrifluoromethylchromium(III) ion was obtained by the reduction of trifluoromethyl iodide with Cr(II) and is the most inert of any organochromium(III) complex known. The initial aquation rates of trifluoromethylchromium(III) ion were described by the differential rate law

$$-d\ln\,[(H_2O)_5CrCF_3{}^{2+}]/dt = k_o + k_1(H^+)$$

The products of the initial reaction were hexaaquochromium(III), carbon monoxide and HF. The values of k_o and k_1 at 45°C were 5.21×10^{-7} sec^{-1} and 9.38×10^{-7} M^{-1}sec^{-1} respectively. The activation parameters for the acid independent and acid dependent pathways were: $\Delta H^{\ddagger}_o = 19.7$ kcal/mole, $\Delta S^{\ddagger}_o = -27.4$ cal-deg^{-1}mole^{-1}; and $\Delta H^{\ddagger}_1 = 23.4$ kcal/mole and $\Delta S^{\ddagger}_1 = -12.9$ cal-deg^{-1}mole^{-1}.

The acceleration in the aquation with time was observed indicating autocatalysis by a product of the reaction. An intermediate, $(Cr(OH_2)_4FCrCF_3{}^{1+})$, was separated from the aquation reaction solution; this same ion was also formed immediately when fluoride ion was added to the $(H_2O)_5CrCF_3{}^{2+}$ ion in 0.05M perchloric acid. The added fluoride ion also increased the rate of aquation. Rapid formation of $(Cr(OH_2)_4FCrCF_3{}^{1+})$ ion was attributed to the strong labilizing effect of the trifluoromethyl ligand on water molecules in the inner coordination sphere of chromium(III).

A solvent-assisted mechanism for the aquation of pentaaquotrifluoromethylchromium(III) ion was proposed in which an activated complex was formed which dissociated in a concerted manner to give the products. Also, a reaction sequence was proposed for the complete aquation reaction which was consistent with the rate laws, the effect of added fluoride ion and the activation parameters.

Pink organochromium(III) species of 2+ charge was isolated in the reduction of carbon tetrachloride and carbon tetrabromide with chromium(II). The pink species have chromium:carbon:halide ratios of 1:1:1 and their uv-visible spectra showed unusually high absorbancy values in the 500 nm region. The pink organochromium(III) reacted very rapidly with oxygen. The products of dissociation were carbon monoxide, formic acid, formaldehyde, hexaaquochromium(III), chromium(II) and halide ions. The kinetics of aquation were studied, and initial rate coefficients and activation parameters were obtained. The identity of these organochromium(III) species was not established but most possible structures were proposed.

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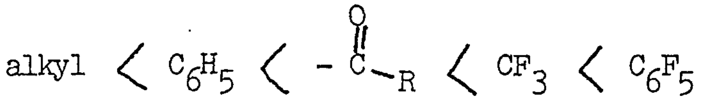
INTRODUCTION

Since the early 1950's, the chemistry of transition metal ions, in which the metal is bonded to carbon moities, has attracted a tremendous interest. Transition metal ions and their complexes have been used as catalysts in the preparation of many important organic and petroleum products. The structure of some of these organic derivatives of transition metals provide the basis for the tests of bonding theories.

Previously, the ligand-metal bond was described as being formed by the donation of a pair of electrons from the ligands to metal. But in some cases, such as unsaturated compounds, the ligand can donate more than two electrons to the metal atom to form a bond. In general, two types of bonding have been observed for organic ligands. In one case, a single carbon atom of the ligand is attached directly to the metal atom through a σ- bond. Organic radicals and one electron ligands fall in this type. The other type involves electron donation from the entire moity; in such cases, no apparent preferential bond between any single carbon atom and metal atom is formed which means these ligands are π- bonded.

Alkyl groups are among the common one-electron ligands which form a σ - bond to a transition metal. The alkyl ligand, $—CR_3$, R is hydrogen or halogen, can only be attached to the central metal atom by a σ- bond involving any number of available metal 'd' orbitals. The strength of this σ - bond has been discussed in terms of ionic and covalent contributions to the wave function (1,2) and the results suggests that the metal to carbon bond strength should increase with increasing effective electronegativity of the alkyl group. The general order of stability of the complexes containing a one-electron carbon ligands increases in the following order



$$\text{alkyl} < C_6H_5 < -\overset{O}{\overset{\|}{C}}-R < CF_3 < C_6F_5$$

The noticeable stavility of the compounds containing metals bonded to fluorinated carbon moities have been attributed (3,4) to metal-ligand π - bonding arising from donation of electrons from metal 'd' orbitals to the antibonding σ - orbitals on the ligands.

Recently, some work has been done with organochromium(III) complexes having chromium-carbon σ - bonds. These compounds are not stable but due to the substitution-inertness of chromium(III) (5) they can be studied.

The first known organochromium compound of chromium(III) containing a chromium-carbon σ - bond was isolated by Anet and Leblanc (6). They reported that the reduction of benzyl chloride by chromous perchlorate gave an organochromium ion structure $Cr(OH_2)_5CH_2Ph^{2+}$. Anet (7) reported that the product of reduction of chloroform by chromous perchlorate was dichloromethylchromium(III) ion which could be isolated by ion-exchange techniques. Recently, Dodd and Johnson (8) reported that the reduction of chloroform, bromoform and iodoform with chromous perchlorate gave air-stable dihalogenomethylchromium(III) ions. Also, reduction of dihalomethanes gave monohalogenomethylchromium(III) ions.

Other recent studies of organochromium(III) species have indicated that their dissociation can occur by different pathways, depending on the nature of the ligand. Benzylpentaaquochromium(III) ion (9) and 4-pyridomethylpentaaquochromium(III) ion (10) dissociates by homolytic cleavage of the chromium-carbon bond, while solvent-assisted hetrolytic cleavage appears to take place in organochromium species containing aliphatic ligands derived from simple alcohols and ethers (11).

The present work was undertaken in order to investigate the properties and kinetics of dissociation of some complexes containing a chromium-carbon σ- bond. These organochromium complexes were obtained by the reduction of trifluoromethyl iodide, carbon tetrachloride and carbon tetrabromide with chromium(II) perchlorate. Initial aquation rates for the pentaaquotrifluoromethylchromium(III) ion are described by a rate law containing two terms, one acid independent and the other acid dependent. The rate of aquation of this ion increased as the reaction progressed, indicating auto-catalysis by a product of the reaction. It was found that added fluoride ions also increased the aquation rates due to rapid formation of an intermediate, $(H_2O)_4FCrCF_3^{1+}$ which aquates more rapidly than $(H_2O)_5CrCF_3^{2+}$. Evidence was obtained that the presence of a Cr – C σ- bond has a very large activating effect on other coordinated ligands. A mechanism is proposed which best fits the observed rate law, products of dissociation, halide ion effect, and activation parameters.

Pink organochromium(III) species of 2+ charge were isolated in the reduction of carbon tetrachloride and tetrabromide with chromium(II). The pink species have chromium:carbon: halide ratios of 1:1:1 and their uv-visible spectra show unusually high absorbancy values in 500 nm region. The pink organochromium(III) species react very rapidly with oxygen, and their dissociation becomes accelerated as the reaction proceeds. Initial aquation rates for dissociation of the pink species were acid independent. The identity of these organochromium(III) species was not established but possible structures are proposed.

EXPERIMENTAL

A. Reagents

All the solutions were prepared from de-ionized distilled water. This water was distilled from an all-glass still, Model WFF94 (Belco Glass Inc.).

The following reagent-grade chemicals were used without further purification: trifluoromethyl iodide, trifluoromethyl bromide (PCR); carbon tetrachloride, sodium fluoride, sodium chloride, formaldehyde, sodium formate, silver nitrate, sodium hydroxide (Baker and Adamson); carbon tetrabromide (Aldrich Chemical); chromium metal (Fisher); 72% perchloric acid (Mallinckrodt); sodium carbonate (Matheson, Coleman and Bell); fluoride standard (Orion); lanthanum nitrate (Alfa Inorganics); Ascarite (Arthur H. Thomson); oxygen and nitrogen gases (Linde).

The oxygen gas present as impurity in nitrogen was absorbed by passing the nitrogen gas over a heated copper (I) oxide catalyst (BASF, R 3-11) tube (5 -6 ft. long).

Sodium Perchlorate solution

Sodium perchlorate solutions were prepared by reacting anhydrous sodium carbonate with perchloric acid. Perchloric acid was added slowly with constant stirring to solid sodium carbonate. The pH of the resulting sodium perchlorate solution was adjusted to 7.0 with perchloric acid or sodium carbonate. Stock solutions of 4.0M sodium perchlorate were prepared.

Formaldehyde solution

Formaldehyde solutions were prepared from 39% formaldehyde solution by dilution. The formaldehyde solutions were standardized by the bisulfite-iodine method (12).

Formic acid solution

Formic acid solutions were obtained by dissolving reagent-grade sodium formate in 1.0M and 0.1M (I = 1.0M) perchloric acid.

Ion-exchange resin

Ion-exchange separations were carried out by using a DOWEX 50W-X8, 200-400 mesh resin in hydrogen form. The resin was washed with 1.0M perchloric acid followed by distilled water prior to its use. The sodium form of the above cation-exchange column was prepared by displacing the hydrogen ions by washing the column with a saturated solution of sodium chloride. The sodium column was washed with distilled water until free of chloride ion.

B. Synthesis

Chromium(II) perchlorate solution

Solutions of chromium(II) perchlorate were prepared by the reaction of chromium metal and oxygen-free perchloric acid (13). The oxygen was removed from 0.5M perchloric acid by passing a stream of pure nitrogen gas through the solution for two hours prior to the addition of chromium metal. Teflon needles were used to pass the nitrogen because the use of stainless steel needles seemed to cause rapid decomposition of the chromium(II) solutions. The chromium metal was activated by breaking the metal into small pieces to expose fresh surfaces. The reaction vessel was sealed by tightening a rubber septum (sleeve-type) with a nichrome wire (diameter 0.025 cm). The hydrogen gas that developed in the vessel during the reaction between chromium and hydrogen ion was released periodically by poking the rubber septum with a hypodermic needle. The solution thus made was stored in the same vessel under positive pressure. All transfer operations were made under nitrogen atmosphere using hypodermic needles and teflon tubings. Solutions prepared in this manner were used within a week.

Pentaaquotrifluoromethylchromium(III) ion

50 ml of 0.5M chromium(II) perchlorate solution was introduced in an airtight oxygen-free reaction vessel. Trifluoromethyl iodide gas was bubbled through this solution. The reaction mixture was kept in the dark for 10-15 hours. Within this time, the solution became red, and appeared to be unchanged in two days, at room temperature, even in the presence of air. The solution was separated by ion-exchange chromatography, described below, to give a reddish-orange solution of the pentaaquotrifluoromethylchromium(III) ion.

Ion-exchange chromatography

Portions of the solutions as prepared above were absorbed on a cation-exchange column (10 x 2 cm) of DOWEX 50W-X8, 200-400 mesh, in hydrogen form. Iodide and any fluoride ion present were washed out with 0.1M perchloric acid which did not elute any species of charge 2+ or higher. One molar perchloric acid first eluted a reddish-orange color pentaaquotrifluoromethylchromium(III) ion followed by a very small portion green species whereas violet color hexaaquochromium(III) ion stayed on the column. Five molar perchloric acid eluted the violet hexaaquochromium(III) ion leaving a green binuclear chromium(III) species on the column. The reddish-orange pentaaquotrifluoromethylchromium(III) ion was collected in 1.0M perchloric acid and kept at 4°C. Under these conditions, very small (less than one percent) aquation takes place in a three month period. No experiments were conducted using any stock solution which had been stored more than a week.

Fluorotetraaquotrifluoromethylchromium(III) ion

This complex ion was prepared by the reaction of fluoride ion with pentaaquotrifluoromethylchromium(III) ion in 0.05M perchloric acid (I = 1.0M). Three equivalents of sodium fluoride were added to 5 ml of pentaaquotrifluoromethylchromium(III) ion in 0.05M perchloric acid, and resulting solution was stirred for 5 minutes at 25°C. A pink color solution resulted after this time. This solution was diluted 40 fold to lower ionic strength and then was absorbed on a cold cation-exchange column (10 x 2 cm) of DOWEX 50W-X8, 100-200 mesh, in sodium form. The temperature of the jacketed column was maintained near 0°C by circulating ice-cold water through it. The column was washed with 0.01M perchloric acid to remove the excess of fluoride ions, while no chromium(III) species were eluted. One tenth molar perchloric acid (I = 0.1M) eluted a pink color organochromium species believed to be $((H_2O)_4FCrCF_3{}^{1+})$, with 1^+ charge, leaving behind pentaaquotrifluoromethylchromium(III) ion on the column. This pink color organochromium(III) ion was collected and used immediately for various experiments. It aquates very rapidly and the solutions were never stored. The concentration of the complex ion obtained were in the range $4 \times 10^{-3} - 5 \times 10^{-4}$M.

Pentaaquomonochloroorganochromium(III) ion

Fifty ml of ice-cold 0.5M chromium(II) perchlorate solution was introduced to 10 ml of oxygen-free carbon tetrachloride kept at 0°C under nitrogen atmosphere; the mixture was stirred vigorously for one minute. A deep red solution was formed immediately which changed to a deep purple color in 3-5 minutes at 0°C. The purple color was stable for several days in nitrogen atmosphere but was rapidly turned green by air or by excess of chromous ion. Therefore, all the operations to process this purple solution were done under nitrogen atmosphere. The solution was passed through an ion-exchange column, as described below, to separate a deep pink organochromium ion which was quickly oxidized by oxygen.

Pentaaquomonobromoorganochromium(III) ion

Carbon tetrabromide (5 gm) was dissolved in 5 ml of acetone and the solution was made oxygen-free by bubbling nitrogen gas through it. The reaction vessel was maintained at 0°C by immersing in an ice-bath, and 40 ml of ice-cold 0.5M chromium(II) perchlorate was introduced under nitrogen atmosphere through teflon tubing. A deep red solution was formed almost immediately which changed to a pink color within one minute at 0°C. The pink color solution appeared to be unchanged for two days at 0°C but was rapidly destroyed by air and by excess of chromous ion, therefore all the operations were made under nitrogen atmosphere. The solution was separated by ion-exchange chromatography, described below, to give a deep pink solution which was very sensitive to oxygen.

Separation of monohalogenoorganochromium(III) ions

The ice-cold solutions containing the monohalogenoorganochromium(III) species, as prepared above, were diluted 5 fold and transferred under nitrogen atmosphere via teflon tubing onto an ice-cold, oxygen-free cation-exchange column (15 x 2 cm) of DOWEX 50W-X8, 100-200 mesh, in hydrogen form. The column was made oxygen-free by passing nitrogen gas through it for 3 hours prior to the transfer operations. The nitrogen gas trapped in the column was removed by shaking the column with deoxygenated distilled water under nitrogen atmosphere. The halide ions on the column were washed out with 0.1M perchloric acid which did not elute any chromium species. One molar perchloric acid first eluted the green halogenopentaaquochromium(III) ion followed by the pink organochromium species. The pink solutions were collected in oxygen-free bottles or optical cells. Five molar perchloric acid eluted the violet hexaaquochromium(III) ion leaving behind the green binuclear chromium(III) species on the column. The solutions thus collected were 10^{-3} - 10^{-4}M in concentration. These complex ions were used immediately in different experiments and were not stored.

Hexaaquochromium(III) ion

Hexaaquochromium(III) perchlorate was prepared by reduction of chromium trioxide with hydrogen peroxide in perchloric acid (14). The solution obtained was evaporated to obtain crystalline solid which was recrystallized from 0.1M perchloric acid. The ionic strength was adjusted to 1.0M with standardized solutions of perchloric acid and sodium perchlorate.

Fluoropentaaquochromium(III) ion

An acidic solution containing fluoropentaaquochromium as the only chromium- and fluoride- containing species was prepared by bringing together equimolar amounts of 2M chromium(III) perchlorate and 2M sodium fluoride solutions (15). The solution was boiled under reflux for 3 hours and cooled to 0°C, and the precipitated sodium perchlorate was removed. This solution was diluted 15 fold to reduce the ionic strength and then was passed on an cation-exchange column of DOWEX 50W-X8, 200-400 mesh in hydrogen form. The column was washed with 0.1M perchloric acid which eluted difluorochromium(III) ion impurities. Fluoropentaaquochromium(III) was separated by eluting the column with 1.0M perchloric acid whereas hexaaquochromium(III) remained on the column. Also, CrF^{2+} was obtained as a by-product in the aquation of pentaaquotrifluoromethylchromium(III) ion.

C. Analyses

Chromium(III)

The concentration of all the haloalkylchromium(III) ions, halochromium(III) ions in freshly prepared solutions and that of hexaaquochromium(III) ion were determined by the oxidation of chromium(III) to chromate ion (CrO_4^{2-}) with alkaline hydrogen peroxide. The alkaline solutions of hydrogen peroxide with chromium(III) were heated on a steam bath to drive off the excess of hydrogen peroxide. The light absorption of this solution was measured at 372 nm against a distilled water blank giving the total chromium concentration. The extinction coefficient of alkaline solution of chromate ion at this wavelength is $4.815 \times 10^{-3} M\ cm^{-1}$ (16).

Fluoride ion

The fluoride content of the product was analyzed by the method of pontentiometric titration using a fluoride ion activity electrode Model 94-09 (Orion). This method gives sharp end points in solutions which are above $10^{-3}M$ in fluoride and which do not contain more than 1% (based on total fluoride) of species which complex fluoride such as iron (III), aluminum or as in our case, trivalent chromium. The fluoride ion was present in the form of complexes of chromium(III), CrF^{2+}, and CrF_2^{1+} and HF or HF_2^- ion. The following steps were followed in total fluoride determination:

1. Standardization of lanthanum(III) nitrate solution - A 0.01M solution of lanthanum nitrate was prepared by dissolving 4.3 gm of "high purity" $La(NO_3)_3 6H_2O$ (Alfa Inorganics) in distilled water. Standard sodium fluoride solution (0.01M) was prepared by dilution of 0.1M standard sodium fluoride solution (Orion).

A 25 ml aliquot of this solution was pipetted into a polyethylene beaker and 50 ml of distilled water was added. The Lanthanum (III) nitrate solution was titrated against this 0.01M standard fluoride solution using the Corning Model 10 pH-meter with expanded scale in millivolts and the Specific Fluoride Ion Electrode. The solution was stirred throughout the entire titration using a magnetic stirrer. The end point was located by plotting, on a standard coordinate graph paper, ml of lanthanum nitrate solution added versus $\frac{(\Delta mv)}{(\Delta ml)}$. The highest point on the curve (Figure 1) was taken as end point.

2. Separation of chromium-complexed fluoride from free fluoride ion - The fluoride as F^-, HF or HF_2^- was separated from chromium(III) species by absorbing a known volume of the aquation product solution on a cation-exchange column of DOWEX 50W-X8, 200-400 mesh, in hydrogen form. The fluoride present as F^-, HF, or HF_2^- were eluted with 0.01M perchloric acid and collected in a polyethylene beaker. The chromium(III) species CrF_2^{1+}, CrF^{2+} and Cr^{3+}, were eluted with 0.1M, 1.0M and 5M perchloric acid respectively. These species were analyzed as chromate in alkaline hydrogen peroxide solution for total chromium. The amount of fluoride was calculated from the amount of difluorochromium(III) and fluorochromium(III) species.

3. Determination of free fluoride ion - The solution, containing free fluoride, was analyzed for total fluoride by adjusting the pH to ~ 6. With 0.1M sodium hydroxide and then titrating with a standardized 0.01M lanthanum(III) nitrate solution. The unknown fluoride molarity in the original sample was calculated from the equation:

$$M^x_F = \frac{V^x_{La} \; V^o_F}{V^o_{La} \; V^x_F} \; M^o_F \qquad (1)$$

where M^x_F = molarity of fluoride in unknown sample

M^o_F = molarity of NaF standard

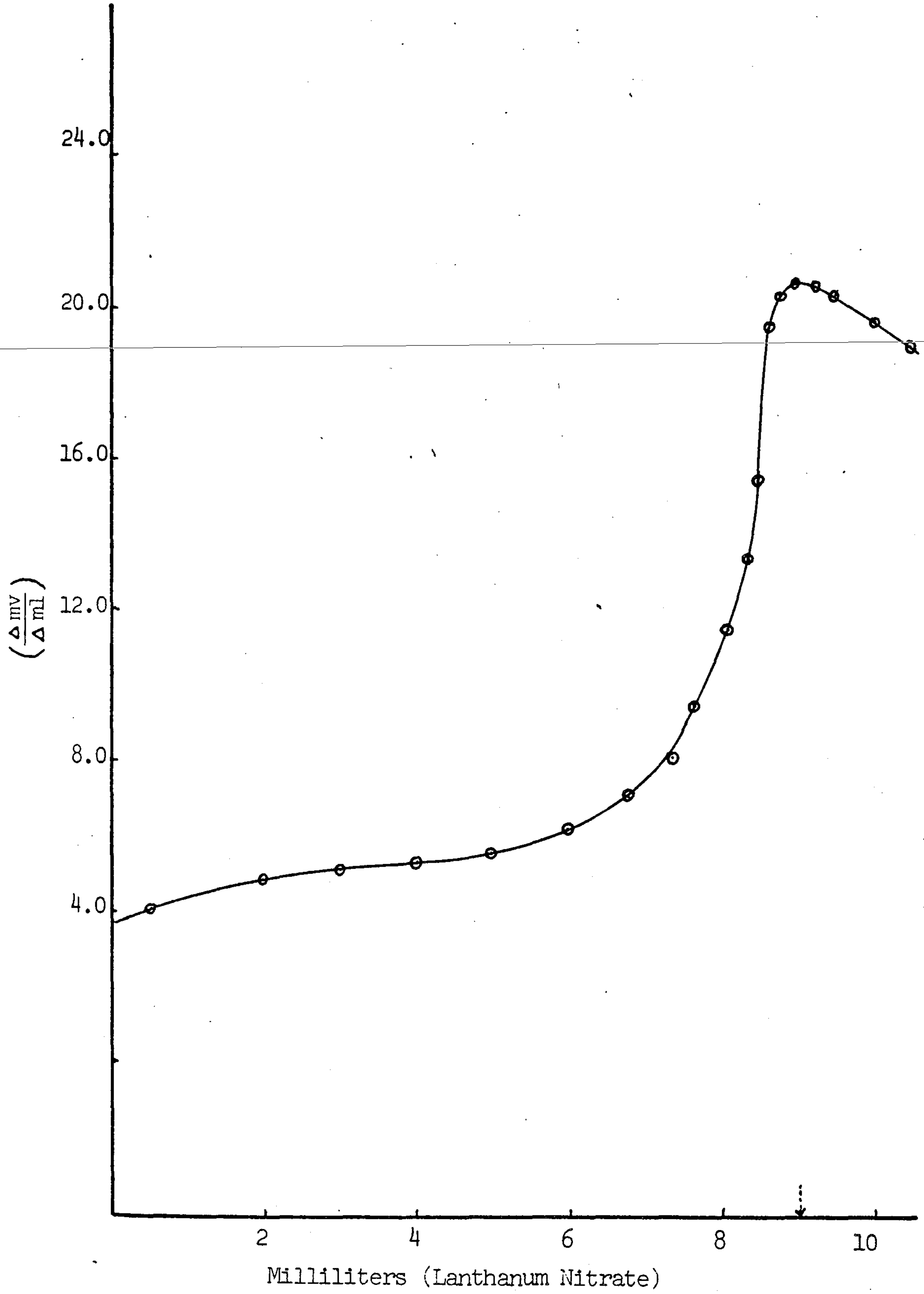


Figure 1: $\left(\frac{\Delta mv}{\Delta ml}\right)$ vs. Milliliters Lanthanum Nitrate for Standardization of $La(NO_3)_3$ against Fluoride Standard.

TABLE 1

STANDARDIZATION OF LANTHANUN NITRATE WITH SODIUM FLUORIDE.

Molarity of standard fluoride = 10^{-2}M.

Volume of standard Fluoride solution = 25 ml.

Run #1

ml. of $La(NO_3)_3$	millivolts	ml $La(NO_3)_3$	millivolts
00	-26.0		
1.0	-21.5	9.5	166.5
2.0	-16.6	10.0	170
3.0	-11.1	11.0	174.5
4.0	-5.0	12.0	177.5
4.5	- 1.8	13.0	179.5
5.0	+ 1.7	14.0	181.0
5.5	+ 5.8	15.0	182.1
5.8	+ 9.7	16.0	183.3
6.0	11.0		
6.4	16.0		
6.8	21.4		
7.0	24.8		
7.4	33.1		
7.8	45		
8.0	52.9		
8.2	67.1		
8.4	85.5		
8.65	142.0		
8.70	147.1		
8.8	153.0		
9.0	160.0		

TABLE 2

TITRATION OF FREE FLUORIDE WITH LANTHANUM NITRATE

Volume of the standard fluoride sample = 10 ml.

Molarity of standard Lanthanum nitrate = 10^{-2}M.

Run #1 ml of $La(NO_3)_3$	(+) millivolts	ml $La(NO_3)_3$	(+) millivolts
		22	78.5
00	+31	22.5	82.0
1	31.5	23.0	86.0
2	32.0	23.2	87.8
3	32.5	23.4	90
4	33.1	24.0	95.2
5	34.1	24.2	97.9
6	35.0	24.4	100
7	36.0	24.6	102
8	37.1	24.8	105
9	38.5	25.0	108
10	40	25.2	111.5
11.0	42	25.4	114
12	44	25.7	118.3
13	46	26.0	122.0
14	47.8	26.4	127.2
15	50.2	26.7	130
16	53	27.0	135
17	56.2	28.0	136.5
18	60	28.5	140.1
19	63.5	29.0	142
20	68	30	144
21	73	31	146
21.5	75.2	33	149
		37	153
		40	156

Table 2 continued.

Run #2

ml of La(NO_3)$_3$	(+) millivolts	ml La(NO_3)$_3$	millivolts
00	38	30	152.7
2	40	32	155
4	43	34	157
6	46	36	158.1
8	49	38	159.2
10	53	40	160.1
12	57	42	161
14	62	44	162
16	68	46	162.8
18	76	50	164.0
18.5	78.5		
19.0	81.0		
20	87.8		
21	96		
21.4	100.5		
22.0	108.5		
22.5	116.0		
23.0	123.0		
23.3	129.2		
23.6	132.4		
23.8	135.0		
24.0	136.8		
24.3	139.0		
24.6	140.5		
25.0	142		
26.0	145		
27.0	148		
28.0	150		

V_{La}^{x} = Unknown titration end-point volume

V_{La}^{o} = Standardization end-point volume

V_{F}^{x} = Volume of the unknown sample

V_{F}^{o} = Volume of NaF standard used in standardization titration.

Bromide and Chloride ions

Bromide and chloride were analyzed as silver halides.

$$Ag^{+} + X^{-} \longrightarrow AgX\downarrow \qquad (2)$$

The haloorganochromium species were allowed to aquate fully. An aliquote portion (200-300 ml) of the aquation product solutions were heated to boiling and small portions of 0.1M silver nitrate solution were added to this boiling solution with constant stirring. A slight excess of silver nitrate solution was added in order to ensure the complete precipitation of the halides as silver halide. Silver halide precipitates were kept in dark overnight and were filtered, washed with 0.01M nitric acid, dried and weighed to a constant weight. The ratio of chromium to halide was calculated from the amounts of total chromium and silver halide. The amounts of halides at the end of 10 half-lives and one week after full aquation agreed within ± 1%.

Carbon monoxide and carbon dioxide

Both carbon monoxide and carbon dioxide were determined as carbon dioxide by absorption on ascarite. Ascartie is solid sodium hydroxide coated on lead asbestos pieces. Carbon monoxide was converted to carbon dioxide by passing over a CuO catalyst heated to 950°C under a stream of nitrogen and oxygen gases and then was absorbed on ascarite.

$$CO + 1/2\ O_2 + CuO \xrightarrow{950^{\circ}C} CO_2 + CuO \qquad (3)$$

$$CO_2 + NaOH \longrightarrow NaHCO_3 \qquad (4)$$

The flow rate of the gases was maintained at 0.22 liters per hour. The apparatus is shown in Figure 2. Carbon dioxide present as impurity in nitrogen or oxygen was absorbed on the first ascarite tube. Then the flask containing the sample solution was swept and the gases were passed into an anhydrone tube which absorbed any water. The moisture free gas mixture was passed over a weighed ascarite tube which absorbed any carbon dioxide present in the sample. The gases were then passed over a copper oxide tube heated to 950°C to oxidize carbon monoxide to carbon dioxide (17). Again the gaseous mixture was passed over a second anhydrone tube to eliminate any moisture in the gases. Finally the gases were passed over another weighed ascarite tube #3 to absorb the carbon dioxide produced by combustion. The mixture of nitrogen and oxygen was finally lead into a gas flow meter to measure the flow rate. The amounts of carbon dioxide and carbon monoxide were calculated from the net gains in weights in ascarite tubes #2 and #3. The chromium to carbon ratio was calculated by the amount of total chromium and the total amount of all carbon present.

Formaldehyde

Formaldehyde was determined by the spectrophotometric method described by Bricker and Johnson (18). Formaldehyde gives a purple color when added to chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) in the presence of sulfuric acid. An aliquot (0.5 ml) of the chromotropic acid solution (2.5 gm in 25 ml) was added to 0.5 ml of the sample solution in a glass test tube. Then 5 ml of concentrated sulfuric acid was poured very slowly into the tube with constant stirring. The test tube was heated in boiling water

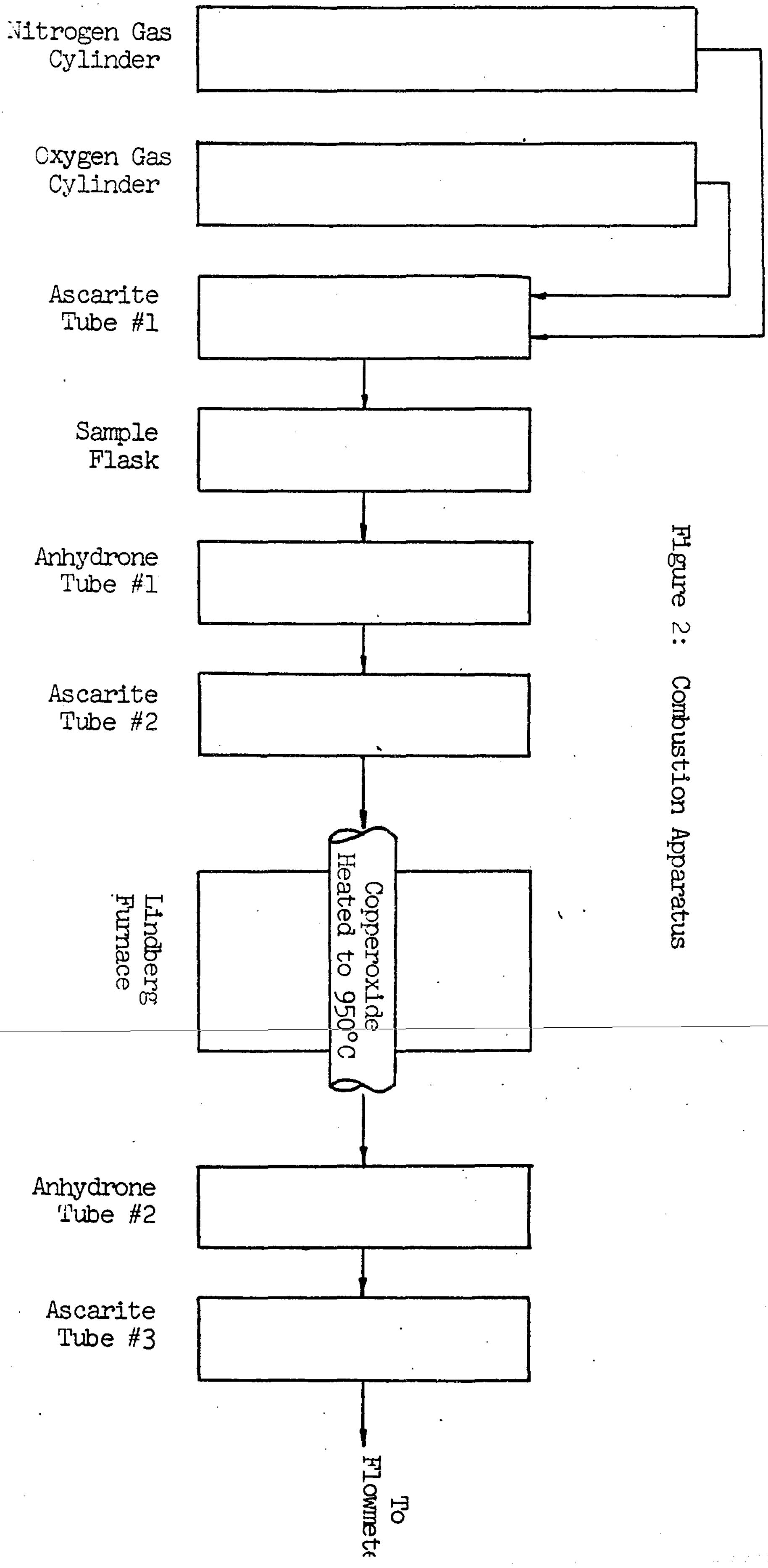


Figure 2: Combustion Apparatus

for 30 minutes. A purple color developed. The test tube was cooled to room temperature and the solution was diluted to 50 ml with distilled water. The absorbance of this purple color was read against a reagent blank at 570 nm. A Beer's law plot was obtained (Figure 3) by plotting Absorbance vs Concentration (micrograms per 0.5 ml) for five standard formaldehyde solutions. Formaldehyde solutions were standardized by socium bisulfite-iodine method (12). The amounts of formaldehyde were calculated from this plot for various product samples. This method gave good results for formaldehyde. The analysis was made with fresh Beer's law plots under the same conditions at the same time to minimize the changing absorbance in the stock chromotropic acid solutions. The chromium(III) species were removed from the product solutions prior to the formaldehyde analysis by absorbing these ions on a cation-exchange column (3 x 2 cm) of DOWEX 50W-X8, 200-400 mesh, in hydrogen form.

Formic Acid

Formic acid determined as formaldehyde by the method of Grant (19). This colorimetric method for the determination of 0.25 to 15 micrograms of formic acid in 0.5 ml of the solution is based on the reduction of formic acid to formaldehyde by means of magnesium with subsequent measurement of the formaldehyde by use of chromotropic acid. Since the product solutions contained both formaldehyde and formic acid, the formaldehyde was first removed by reaction with phenylhydrazine. The chromium(III) species were removed by passing the product solutions through a cation-exchange column of DOWEX 50W-X8, 200-400 mesh, in

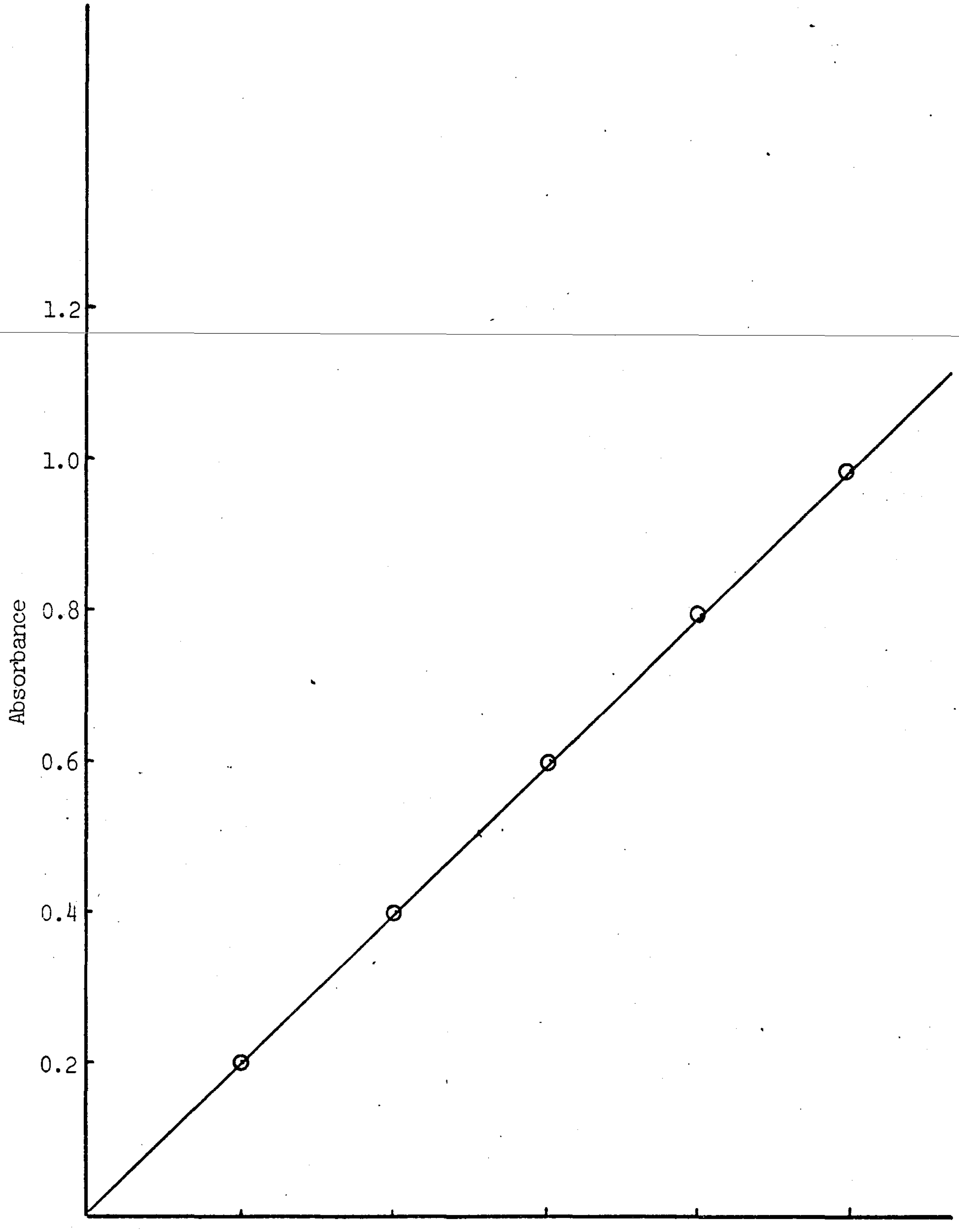


Figure 3: Beer's Law Plot for Formaldehyde (λ = 570 nm)

hydrogen form. A typical procedure is given below.

Eighty mg of magnesium ribbon were taken in separated test tubes which were then placed in an ice-bath and 0.5 ml of the sample solution containing formic acid was added to these test tubes. Then 0.5 ml of concentrated hydrochloric acid was added dropwise at a rate of one drop per 3 minutes. Freshly prepared chromotropic acid solution (0.5 ml) was added to each test tube followed by the addition of 5 ml of concentrated sulfuric acid. After 2 minutes, these test tubes were placed in boiling water bath and left there for 30 minutes. The test tubes were removed after 30 minutes and were cooled to room temperature. A heavy precipitate was formed which was centrifuged and dissolved in 2 ml of distilled water. This solution was diluted to 25 ml and the absorbance of purple color was measured against a reagent blank in a 5 cm cell at 570 nm. Beer's law plots (Figure 4) were obtained by plotting Absorbance vs. Concentration of formic acid (microgram per 0.5 ml). The amounts of formic acid in various product solutions was obtained from these plots. Standard formic acid solutions were prepared from primary standard sodium formate by dissolving in 1.0M perchloric acid.

Sodium perchlorate

An aliquot of solution containing sodium perchlorate was placed on a cation-exchange column of hydrogen form, DOWEX 50W-X8, 50-100 mesh, that previously had been washed free of excess of hydrogen ion. The acid replaced by sodium ions was collected and titrated with standard sodium hydroxide. The concentration of sodium perchlorate was calculated from the number of the acid equivalents collected.

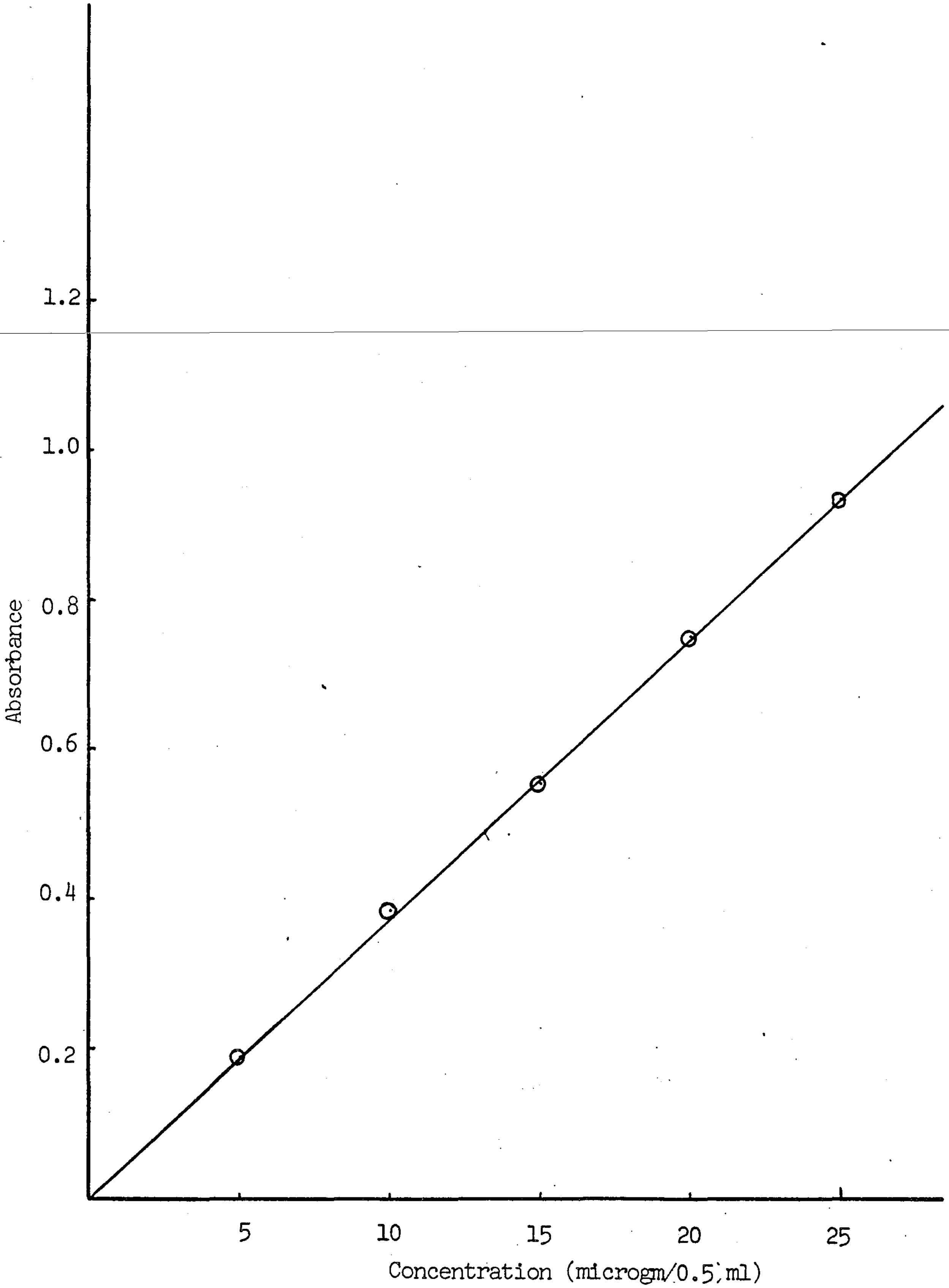


Figure 4: Beer's Law Plot for Formic Acid (λ = 570 nm)

D. Procedures

Spectral measurements were performed on a Cary spectrophotometer Model 14, Perkin-Elmer Model 202 or a Beckman spectrophotometer Motel DU which was equipped with special Gilford accessories. Sets of 1.00, 2.00, 5.00 and 10. cm quartz cell were used. The cells were cleaned and frequently checked for relative absorbance.

Determination of Isosbestic for Hexaaquochromium(III) Ion and Fluoropentaaquochromium(III) Ion.

The solutions of hexaaquochromium(III) and fluoropentaaquochromium(III) were prepared as described earlier. The concentration of these stock solutions was determined as chromate in alkaline solutions of hydrogen peroxide. These stock solutions were further diluted such that the resulting solutions of hexaaquochromium(III) and fluoropentaaquochromium(III) were at the same concentrations (1.870×10^{-2}M) in 1.0M perchloric acid. The visible spectra for these species were obtained on the same paper under the same conditions and in 5.0 cm cell lengths. The spectra are given in Figure 5.

E. Kinetic Measurements

Pentaaquotrifluoromethylchromium(III) ion.

The aquation of this complex ion was followed by measuring the change in absorbance. Oxygen-free solutions were kept in plastic bottles which were painted black. Aliquots of the reaction mixtures were transferred periodically from these flasks under nitrogen atmosphere to spectophotometer cells and the reaction was quenched by rapid

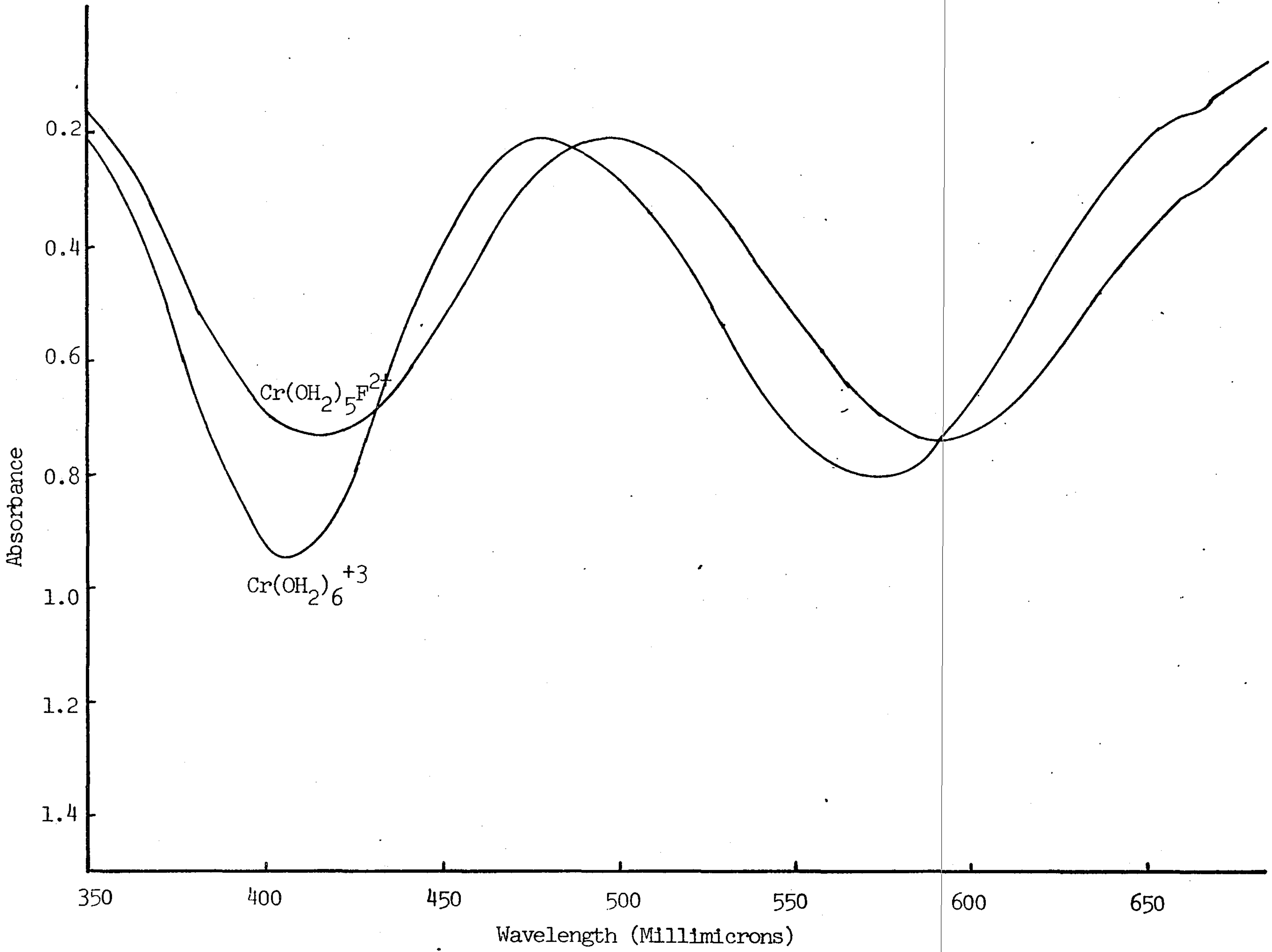


Figure 5: Isosbestic Points of Hexaaquochromium(III) and Fluoropentaaquochromium(III) Ions.

cooling to room temperature or below by inserting the cell in ice cold water. The absorbance of the solutions was measured with the Beckman Model DU. Thermostating was accurate within ± 0.1°C in all the experiments. The concentrations of the complex ions in the solutions were such that the maximum absorbance in a 2 cm cell was ∿ 1 absorbance unit. These measurements were carried out at 380 nm, 446 nm, 486 nm, and 500 nm. The maxima for trifluoromethylchromium(III) are 390 nm and 500 nm; and 486 nm is the isosbestic point for hexaaquochromium(III) and fluoropentaaquochromium(III) ions. Plots of $\ln(A_t-A_\infty)$ against time "t" were obtained (Figure 6). Where A_t and A_∞ are the absorbance of the solution at a chosen time "t" and at an infinite time. The values for the rate coefficients were obtained by linear least-square analysis of $\ln(A_t-A_\infty)$ vs. "t" data.

Pentaaquomonohalogenoorganochromium(III) ions

The aquation of monochloroorganochromium(III) ion was followed at 350 nm, 406 nm and 536 nm whereas that of monobromoorganochromium(III) ion was followed at 360 nm, 406 nm and 538 nm. These complexes react rapidly with oxygen, therefore, the aquations were carried out under nitrogen atmosphere. Aliquots of the reaction mixtures were transferred periodically into the deoxygenated optical cells under nitrogen stream through a deareated syringe equipped with a filtering disk. The open end of the plastic syringe (5 cc) was sealed with a rubber septum. The septum was tightened with nichrome wire (0.025 cm diameter). The syringe was equipped with stainless steel needles and a teflon tubing. The rubber septum end of the syringe was used for the transfer of the

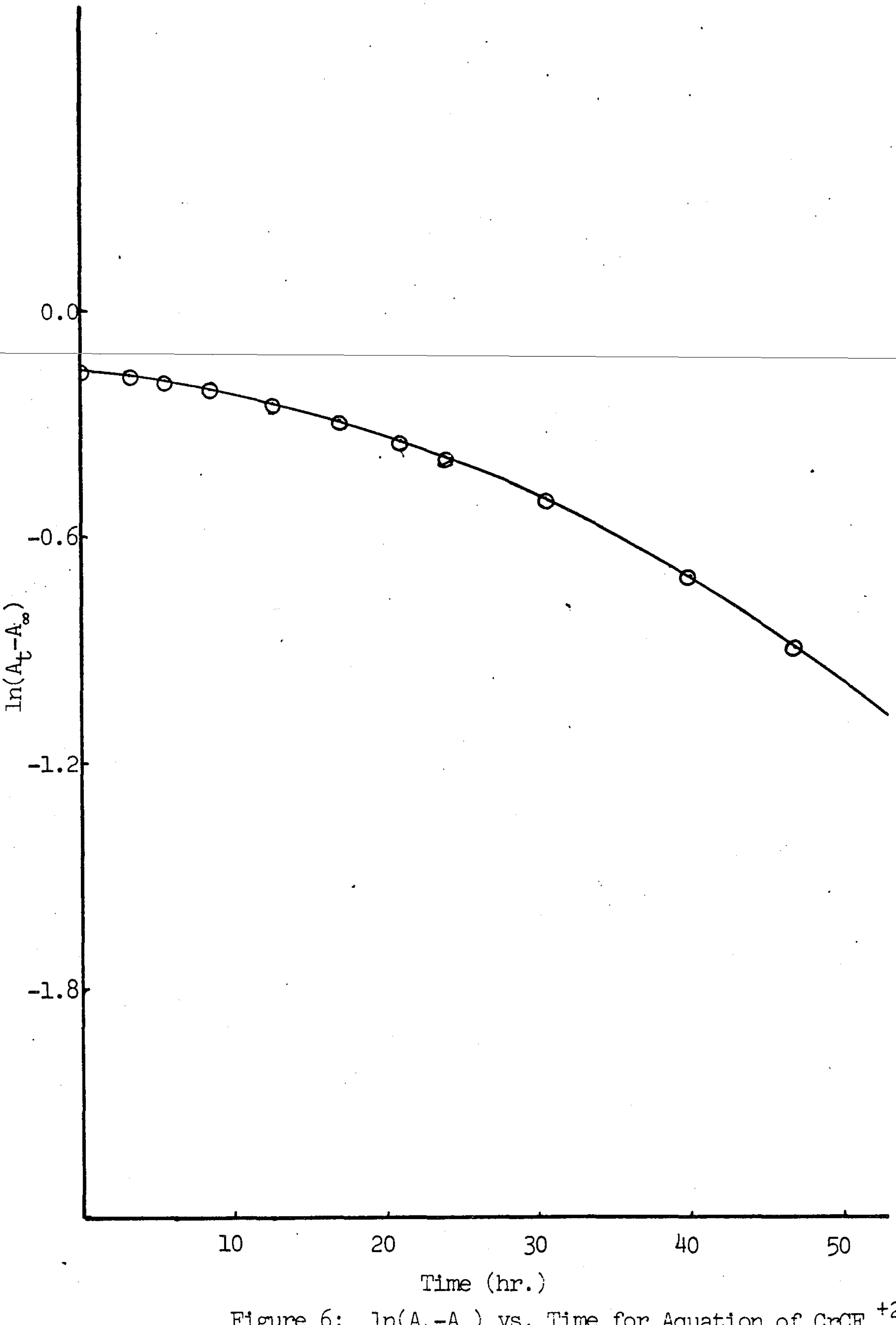


Figure 6: $\ln(A_t-A_\infty)$ vs. Time for Aquation of $CrCF_3^{+2}$ Ion at 55.2°C and 0.1M $HClO_4$ (λ = 500 nm).

sample solution under nitrogen atmosphere. The needle end of the syringe lead to the oxygen-free spectrophotometer cell. This arrangement was necessary due to the development of solid particles in the complex solutions with time which interferred with the absorbance measurements. Great care was taken in all the transfer operations to avoid any oxygen coming in contact with these solutions.

Measurements of the fluoropentaaquochromium(III) ion in aquation and anation reactions.

The amounts of the fluoropentaaquochromium(III) ion formed in the aquation of the pentaaquotrifluoromethylchromium(III) ion and in the reaction of hexaaquochromium(III) ion with sodium fluoride was followed with time at 55.2°C. Aliquot portions of the reaction mixtures were withdrawn periodically from the reaction vessels and were absorbed on a cation-exchange column in hydrogen form. Chromium(III) species, CrF_2^{1+}, CrF^{2+} and Cr^{3+}, were separated by eluting the column with 0.1M (I = 0.1M), 1.0M and 3M, perchloric acid solutions. These were analyzed as total chromium described earlier.

Constant temperature bath.

The temperature of the reacting solutions was controlled by immersing the reaction vessel in a water bath. The temperature of the bath was kept constant within ± 0.1°C with a thermistemperature controllers Model 71 (Yellow Springs Instruments Co.) which were equipped with both heating and cooling devices.

RESULTS

A. Pentaaquotrifluoromethylchromium(III) ion.

UV-Visible Spectrum

The visible spectrum of the $(H_2O)_5CrCF_3^{+2}$, Figure 7, in perchloric acid solutions of all ionic strengths shows absorption maxima at 500 nm (E, $40M^{-1}cm^{-1}$) and 380 nm (E, $67M^{-1}cm^{-1}$) and a minimum at 444 nm (E, $26M^{-1}cm^{-1}$). There is a small shoulder at 620 nm. The UV spectrum, Figure 8, is unaffected in perchloric acid solutions of different ionic strengths and has a maximum at 216 nm (E, $3737M^{-1}cm^{-1}$) and a minimum at 202 nm (E, $2697M^{-1}cm^{-1}$). The molar absorbancy indices values obtained by using Cary Model 14 and Perkin-Elmer Model 202 Spectrophotometers agreed within $\pm$ 0.5%.

Composition

The composition of pentaaquotrifluoromethylchromium(III) ion was established as follows. Chromium was determined spectrophotometrically as chromate. The free fluoride concentration, after complete aquation of $CrCF_3^{+2}$, was determined by potentiometric titration with lanthanum(III) using a fluoride ion activity electrode and the chromium complexed fluoride by the method of ion-exchange chromatography. Carbon was present as carbon monoxide in the products and was identified by mass spectrometry and quantitated by converting to carbon dioxide and then absorbing it as ascarite. Chromium to carbon and chromium to fluoride ratios were found to be 1:0.96 and 1:2.97 respectively. These results are summarized in Table 3.

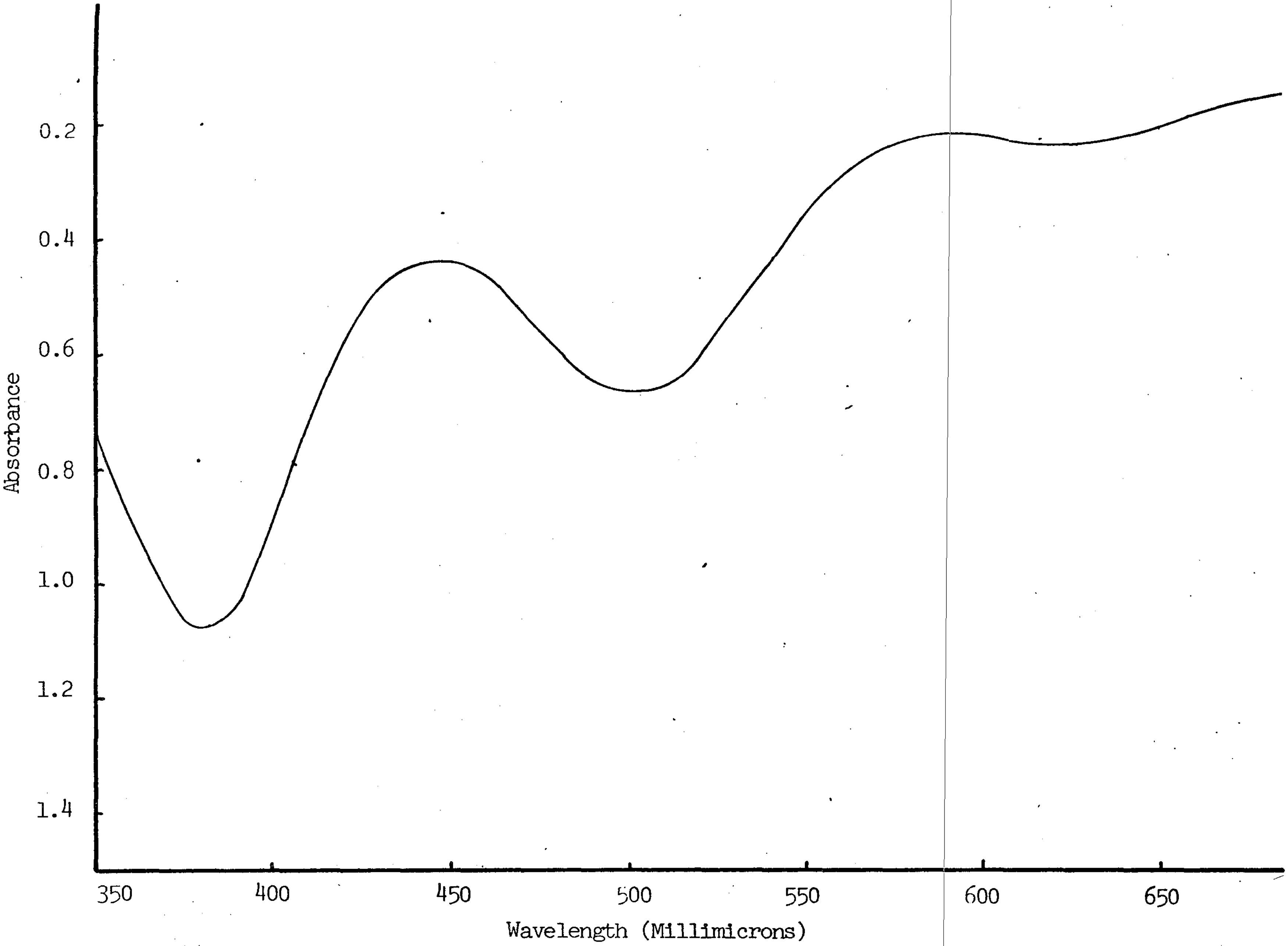


Figure 7: Visible Spectrum of $CrCF_3^{2+}$ Ion in 1.0M $HClO_4$.

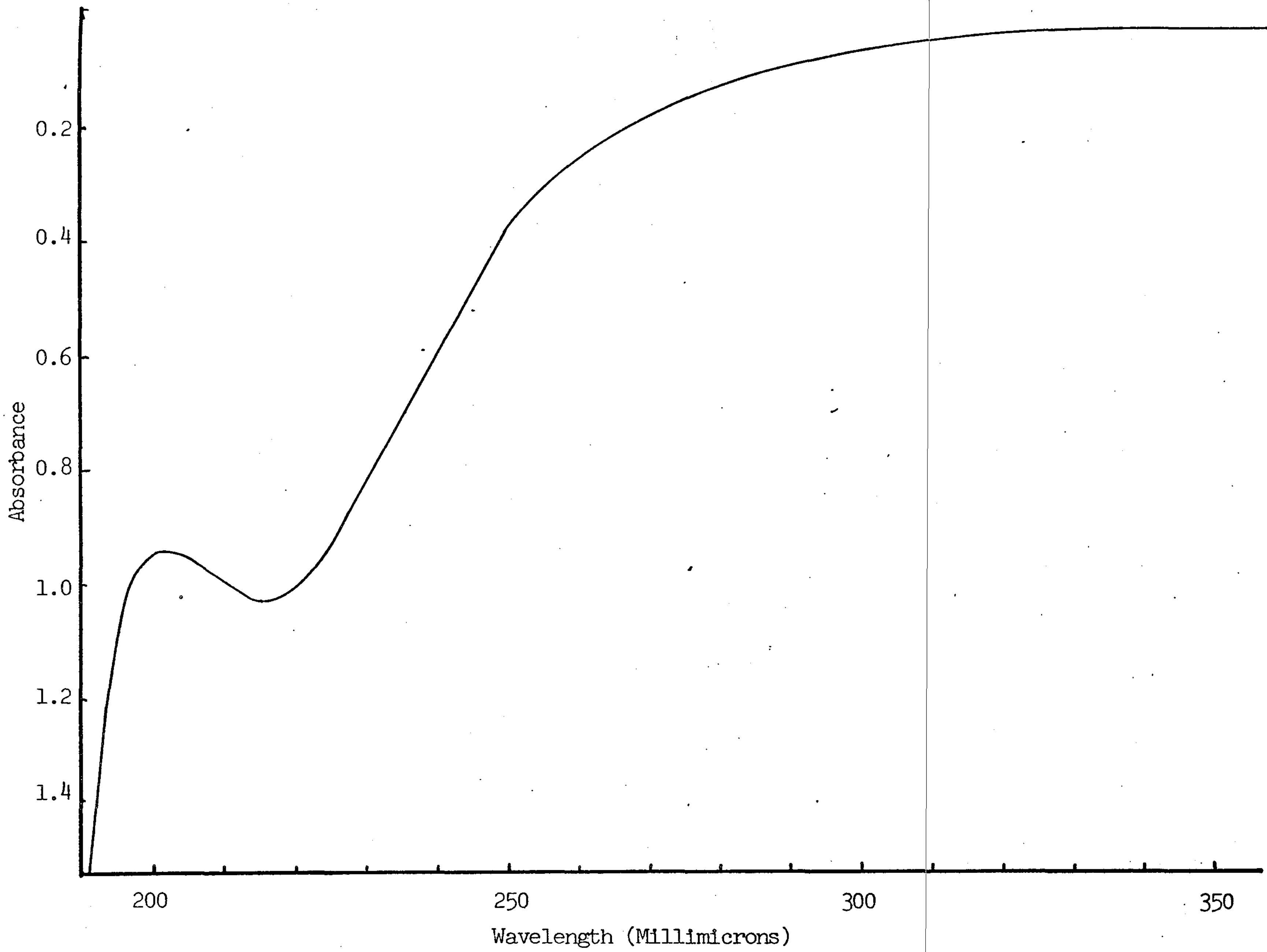


Figure 8: UV Spectrum of $CrCF_3^{2+}$ Ion in 1.0M $HClO_4$.

TABLE 3

AQUATION PRODUCTS FOR THE AQUATION OF $CrCF_3^{+2}$ ION IN THE ABSENCE OF OXYGEN

Total Moles of Chromium	Moles of Carbon monoxide as carbon dioxide	Moles of[a] Fluoride	$Cr:C:F^-$ Ratio
3.72×10^{-4}	3.58×10^{-4}	11.08×10^{-4}	1.00:0.95:2.98
3.52×10^{-4}	3.38×10^{-4}	10.37×10^{-4}	1.00:0.96:2.95
3.62×10^{-4}	3.55×10^{-4}	10.83×10^{-4}	1.00:0.98:2.98

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[a] Sum of $[F^-]$, $[CrF_3^{2+}]$ and $2[CrF_2^{1+}]$.

The visible spectrum of the complex ion in perchloric acid solution shows an absorption maxima at 380 nm. All the octahedral chromium complexes containing a chromium-carbon sigma bond do show a maximum in this region, although position of this maximum for $CrCF_3^{+2}$ was at lower wavelength as compared to the maxima of other chromium complexes. The behavior of this ion on the ion-exchange column is similar to that of fluoropentaaquochromium(III) and pentaaquodichloromethylchromium(III) ions and is compatible with a 2^+ charge. From the above information, the complex ion can be written as $[(H_2O)_5CrCF_3^{2+}]$.

Aquation of pentaaquotrifluoromethylchromium(III) ion.

Chromium(III) products

The $CrCF_3^{2+}$ ion, in the absence of oxygen, gave hexaaquochromium(III), fluoropentaaquochromium(III) and difluorotetraaquochromium(III) species as the only chromium(III) complexes. These complexes were identified by their behavior on an ion-exchange column and by their uv-visible spectra. The amounts of $Cr(OH_2)_6^{3+}$, CrF^{2+} and CrF_2^{1+} formed during the aquation reaction of $CrCF_3^{2+}$ ion at 55.2°C were followed with time, and were found to be different at different concentrations of perchloric acid. In separate experiments, the rates of anation of solutions of hexaaquochromium(III) and fluoride were determined by following the appearance of the products. Aliquot portions of the complex $CrCF_3^{2+}$ solution and the anation mixtures were withdrawn periodically from solutions thermostated at 55.2°C and under nitrogen atmosphere. These aliquots were absorbed on a cation-exchange column of DOWEX 50W-X8, 200-400 mesh, in sodium ion form. The columns were eluted with 0.1M, 1.0M and 3M perchloric acid solutions to collect 1+, 2+ and 3+ charged chromium(III) species respectively. It was observed that when the sample from the $CrCF_3^{2+}$ ion solution was eluted with 0.1M perchloric acid (I = 0.1M), a pink color solution was collected showing that this chromium(III) species has a 1+ charge. This pink solution was first observed after twelve hours in 0.05M perchloric acid at 55.2°C. The compositions of the $CrCF_3^{2+}$ aquation solution and of the anation reaction mixture as function of time are summarized in Table 4.

Kinetics

The aquation of $CrCF_3^{2+}$ ion was followed by measuring the absorbance changes with time at 486 nm, the isosbestic point for hexaaquochromium(III) and fluorochromium(III) ions and also at the two maxima in the visible region, i.e. 380 nm and 500 nm. The absorbance vs. time data is summarized in Table 5 to Table 7.

The initial concentrations of the complex ion were in the range $5 \times 10^{-3} - 5 \times 10^{-4}$M. The plots of $\ln(A_t - A_\infty)$ vs. time were obtained (Figure 9). With increasing time, these plots showed curvature; the rate becoming faster as the reaction proceeded. Therefore, the initial rate coefficients were obtained by analyzing the data at the very beginning of the reaction. The rate coefficients were found to be independent of wavelength. At a particular hydrogen ion concentration, the reaction initially obeyed the first-order rate law

$$\frac{-d[CrCF_3^{2+}]}{dt} = k_{obs}[CrCF_3^{2+}] \qquad (5)$$

The initial rate coefficients as function of temperature and hydrogen ion concentration, were obtained by using a linear least-

TABLE 4a

CHROMIUM(III) PRODUCTS VS TIME DURING THE AQUATION OF $CrCF_3^{2+}$ ION.

Temperature = 55.2°C

0.05 $HClO_4$ $[CrCF_3^{2+}] = 1.15 \times 10^{-2}$M

0.95 $NaClO_4$

Time (hr)	[a] % 1+ [b] charge complex	% [b] $CrCF_3^{2+}$	% [b] CrF^{2+}	% [b] Cr^{3+}
24	trace	70.8	18.3	10.8
45	13.8	34.1	35.1	17.0
72	19.7	15.4	48.2	16.8
144	20.3		61.9	17.8
	15.3		60.4	24.3

[a] It is believed that the 1+ charge complex is a mixture of $FCrCF_3^{1+}$ and CrF_2^{1+}.

[b] reported as % of total chromium.

TABLE 4b

CHROMIUM(III) PRODUCTS VS TIME DURING THE REACTION OF FLUORIDE WITH HEXAAQUOCHROMIUM(III) ION.

Temperature = 55.2°C

0.05 $HClO_4$	Moles of $Cr(OH_2)_6^{3+}$ = 1.27×10^{-4}
0.95 $NaClO_4$	Moles of F^- ion = 3.81×10^{-4}

Time (hr)	% CrF_2^{1+} [a]	% CrF^{2+} [a]	% Cr^{+3} [a]
24		5.0	95.0
50		7.0	93.0
72	0.4	12.0	87.6
142	3.0	19.0	78.0

[a] Reported as % of total Cr.

TABLE 5

ABSORBANCE VS. TIME FOR THE AQUATION OF PENTAAQUOTRIFLUOROMETHYL CHROMIUM (III) ION.

(a) Temperature = 35°C   0.1M $HClO_4$ 0.9M $NaClO_4$ Cell length = 2 cm.

Time (days)	Absorbance λ(nm) 380	500
00	0.966	0.576
1	0.956	0.570
4	0.910	0.537
6	0.887	0.522
10	0.833	0.489
13	0.784	0.459
17	0.724	0.421
23	0.608	0.340
31	0.478	0.267
45	0.306	0.153
66	0.192	0.085
∞	0.180	0.078

(b) Temperature = 35°C   1.0M $HClO_4$ Cell length = 2 cm.

Time (days)	Absorbance λ(nm) 380	500
00	0.724	0.429
0.25	0.715	0.421
1.92	0.686	0.404
4	0.654	0.387
6	0.621	0.363
8	0.584	0.338
10	0.551	0.321
12	0.514	0.297

TABLE 5 (b) continued.

Time (days)	Absorbance λ(nm) 380	500
14	0.487	0.282
17	0.437	0.246
20	0.393	0.219
23	0.346	0.191
26	0.316	0.173
30	0.279	0.153
34	0.249	0.137
38	0.232	0.126
42	0.208	0.108
48	0.186	0.099
61	0.149	0.072
∞	0.115	0.050

TABLE 5-1

ABSORBANCE VS. TIME FOR THE AQUATION OF PENTAAQUOTRIFLUOROMETHYL CHROMIUM (III) ION.

(a) Temperature = 45°C   0.1M $HClO_4$ Cell length = 2 cm.
0.9M $NaClO_4$

Time (days)	Absorbance λ(nm) 380	500
Run #1		
00	0.850	0.507
1	0.826	0.489
2	0.794	0.469
3	0.742	0.434
5	0.665	0.388
9	0.465	0.263
12	0.337	0.188
14	0.286	0.152
17	0.227	0.117

TABLE 5-1(a) Run #1 continued.

Time (days)	Absorbance λ(nm) 380	 500
20	0.194	0.095
24	0.169	0.081
28	0.164	0.076
32	0.153	0.067
∞	0.152	0.065

Run #2

Time (hrs.)	Absorbance λ(nm) 446	 486
00	0.707	1.322
25	0.684	1.259
49	0.668	1.199
72	0.624	1.088
96	0.586	0.962
120	0.546	0.838
∞	0.340	0.156

(b) Temperature = 45°C

$0.2M\ HClO_4$
$0.6M\ NaClO_4$

Cell length = 2 cm.

Time (days)	Absorbance (nm) 380	 500
00	0.975	0.578
3	0.831	0.493
5	0.702	0.417
7	0.562	0.327

TABLE 5-1(b) continued.

Time (days)	Absorbance λ(nm) 380	500
9	0.445	0.254
12	0.301	0.167
16	0.204	0.105
19	0.176	0.090
∞	0.131	0.056

(c) Temperature = 45°C $0.4M\ HClO_4$ Cell length = 2 cm.
$0.6M\ NaClO_4$

Time (days)	Absorbance λ(nm) 380	500
00	0.781	0.461
2	0.705	0.414
5	0.565	0.325
7	0.473	0.268
9	0.395	0.220
14	0.243	0.128
18	0.179	0.094
21	0.155	0.079
∞	0.105	0.045

TABLE 5-1continued.

(d) Temperature = 45°C $0.6M\ HClO_4$ $0.4M\ NaClO_4$ Cell length = 2 cm.

Time (days)	Absorbance λ(nm) 380	500
00	0.994	0.589
2	0.868	0.511
4	0.735	0.426
6	0.594	0.340
9	0.431	0.235
11	0.346	0.185
14	0.252	0.131
17	0.206	0.104
∞	0.162	0.070

(e) Temperature = 45°C $0.8M\ HClO_4$ $0.2M\ NaClO_4$ Cell length = 2 cm.

Time (days)	Absorbance λ(nm) 380	500
00	1.002	0.588
2	0.859	0.501
4	0.706	0.407
6	0.558	0.314
10	0.347	0.185
13	0.298	0.133
∞	0.150	0.062

TABLE 5-1continued.

(f) Temperature = 45°C 1.0M $HClO_4$ Cell length = 2 cm.

Run #1 Time (days)	Absorbance	
	λ(nm) 380	500
00	0.724	0.426
1	0.668	0.390
2	0.603	0.352
3	0.525	0.301
4	0.472	0.268
5	0.422	0.236
6	0.378	0.210
7	0.338	0.185
8	0.302	0.163
9	0.277	0.150
10	0.244	0.130
11	0.220	0.116
12	0.205	0.107
13	0.189	0.096
14	0.176	0.089
15	0.167	0.083
16	0.157	0.079
18	0.147	0.071
19	0.140	0.060
21	0.133	0.063
∞	0.124	0.058

TABLE 5-1(f) continued.

Run #2 Time (hrs.)	Absorbance λ(nm) 446	 486
00	0.523	0.976
25	0.476	0.866
49	0.454	0.782
72	0.411	0.679
96	0.379	0.576
120	0.347	0.401
∞	0.254	0.118

Run #3 Time (days)	Absorbance λ(nm) 380	 500
00	0.871	0.513
1	0.794	0.462
4	0.585	0.329
5	0.518	0.288
7	0.408	0.220
9	0.321	0.167
11	0.265	0.136
15	0.198	0.094
18	0.178	0.084
21	0.167	0.075
26	0.154	0.065
∞	0.151	0.060

TABLE 6

ABSORBANCE VS. TIME FOR THE AQUATION OF PENTAAQUOTRIFLUOROMETHYL CHROMIUM (III) ION.

(a) Temperature = 55.2°C $0.1M\ HClO_4$ $0.9M\ NaClO_4$ Cell length = 2 cm.

Run #1

Time (hrs.)	Absorbance λ(nm) 380	500
00	1.561	0.927
3.25	1.535	0.918
6	1.512	0.903
13	1.412	0.855
17	1.368	0.818
21	1.311	0.783
24	1.257	0.754
30.5	1.126	0.680
40	0.978	0.571
47	0.842	0.485
54	0.738	0.424
65	0.559	0.306
79.5	0.404	0.210
91	0.321	0.156
114	0.232	0.104
∞	0.187	0.078

Run #2

Time (hrs.)	Absorbance λ(nm) 446	486
00	0.652	1.199
4	0.646	1.160
9	0.626	1.108
18.25	0.569	0.961
24	0.541	0.856

TABLE 6 (a) Run #2 continued.

Time (hrs.)	Absorbance (nm) 446	486
27	0.521	0.794
33	0.488	0.671
44	0.410	0.467
50	0.381	0.378
57	0.347	0.295
72	0.273	0.192
∞	0.273	0.109

Run #3

Time (hrs.)	Absorbance (nm) 446	486
00	0.388	0.684
2	0.386	0.674
4	0.382	0.660
6	0.380	0.649
10	0.372	0.631
∞	0.197	0.109

TABLE 6 continued.

(b) Temperature = 55.2°C

0.1M $HClO_4$ $[(H_2O)_5CrCF_3{}^{2+}] = 1.33 \times 10^{-2}M$

0.9M $NaClO_4$ $[F^-] = 1.33 \times 10^{-2}M$ Cell length = 2 cm.

Time	Absorbance	
(hrs.)	(nm) 446	486
00	0.584	1.055
1.5	0.575	1.008
4.0	0.554	0.929
7.25	0.509	0.812
9.25	0.487	0.750
12	0.448	0.660
19	0.373	0.461
26	0.324	0.318
43	0.258	0.150
∞	0.242	0.140

(c) Temperature = 55.2°C

0.1M $HClO_4$ $[H_2O)_5CrCF_3{}^{2+}] = 9.55 \times 10^{-3}M$

0.9M $NaClO_4$ $[Cl^-] = 9.55 \times 10^{-2}M$ Cell length = 2 cm.

Time	Absorbance	
(hrs.)	(nm) 380	500
00	1.341	0.791
3.25	1.309	0.774
6.5	1.300	0.758
13.5	1.214	0.725
17	1.172	0.698
21	1.117	0.663
24	1.079	0.635

TABLE 6 (c) continued.

Time	Absorbance	
(hrs.)	(nm) 380	500
31	0.970	0.574
40	0.817	0.482
47	0.702	0.414
54	0.615	0.354
65	0.487	0.271
79.5	0.355	0.186
91	0.291	0.145
113	0.208	0.094
∞	0.163	0.069

(d) Temperature = 55.2°C
0.1M $HClO_4$
0.9M $NaClO_4$
$[Al^{3+}]$ = 0.1M
Cell length = 2 cm.

Time	Absorbance
(hrs.)	(nm) 486
00	0.766
1.75	0.621
3.75	0.588
7.50	0.416
12.33	0.396
∞	0.130

Table 6-e continued.

Temperature = 55.2°C
0.1M $HClO_4$ $[CrCF_3^{2+}] = 6.28 \times 10^{-3}M$ Cell
0.9M $NaClO_4$ $[Fluoride] = 12.57 \times 10^{-3}M$ Length = 2 cm.

Time	Absorbance
(min)	(nm) 380
00	0.845
30	0.828
60	0.815
90	0.804
120	0.787
150	0.778
180	0.766
∞	0.118

Table 6-e continued.

Temperature = 55.2°C
0.1M $HClO_4$ $[CrCF_3^{2+}] = 6.28 \times 10^{-3}M$ Cell
0.9M $NaClO_4$ $[Fluoride] = 15.71 \times 10^{-3}M$ Length = 2 cm.

Time	Absorbance
(min)	(nm) 380
00	0.840
40	0.814
60	0.806
90	0.788
120	0.771
150	0.760
180	0.748
∞	0.116

Table 6-e continued.

Temperature = 55.2°C
0.1M $HClO_4$ | $[CrCF_3^{2+}]$ = 6.28 x 10^{-3}M | Cell length = 2 cm.
0.9M $NaClO_4$ | [Fluoride] = 15.81 x 10^{-3}M

Time (min)	Absorbance (nm) 380
00	0.821
30	0.795
60	0.776
90	0.756
120	0.737
150	0.718
180	0.700
∞	0.113

Table 6-e continued.

Temperature = 55.2°C
0.1M $HClO_4$ | $[CrCF_3^{2+}]$ = 6.28 x 10^{-3}M | Cell length = 2 cm.
0.9M $NaClO_4$ | [Fluoride] = 25.13 x 10^{-3}M

Time (min)	Absorbance (nm) 380
00	0.607
10	0.579
20	0.551
38	0.518
60	0.468
70	0.452
90	0.418
∞	0.110

TABLE 6 continued.

(e) Temperature = 55.2°C $0.2M\ HClO_4$, $0.8M\ NaClO_4$ Cell length = 2 cm.

Run #1

Time	Absorbance	
(hrs.)	λ(nm) 446	486
00	0.833	1.524
2	0.828	1.502
4	0.822	1.478
6	0.814	1.446
8	0.805	1.422
10	0.790	1.386
12	0.782	1.362
∞	0.380	0.165

Run #2

Time	Absorbance	
(hrs.)	λ(nm) 446	486
00	0.471	0.838
2	0.467	0.828
4	0.464	0.812
6	0.461	0.801
8	0.457	0.791
10	0.446	0.773
∞	0.233	0.124

TABLE 6 continued.

(f) Temperature = 55.2°C $0.4M\ HClO_4$ $0.6M\ NaClO_4$ Cell length = 2 cm.

Run #1

Time (hrs.)	Absorbance λ(nm) 446	486
00	0.628	1.157
2	0.623	1.137
4	0.618	1.121
6	0.615	1.098
8	0.610	1.070
10	0.597	1.042
12	0.576	0.989
∞	0.286	0.132

Run #2

Time (hrs.)	Absorbance λ(nm) 446	486
00	0.460	0.820
2	0.455	0.804
4	0.448	0.782
6	0.442	0.767
8	0.437	0.751
10	0.430	0.736
∞	0.221	0.118

TABLE 6 continued.

(g) Temperature = 55.2°C $0.6M\ HClO_4$ $0.4M\ NaClO_4$ Cell length = 2 cm.

Run #1

Time (hrs.)	Absorbance λ(nm) 446	486
00	0.700	1.273
2	0.691	1.244
4	0.681	1.221
6	0.672	1.208
8	0.664	1.162
10	0.654	1.130
12	0.647	1.095
∞	0.324	0.148

Run #2

Time (hrs.)	Absorbance λ(nm) 446	486
00	0.521	0.922
2.17	0.514	0.904
4	0.509	0.886
6	0.500	0.864
8	0.492	0.844
10	0.483	0.823
∞	0.248	0.128

TABLE 6 continued.

(h) Temperature = 55.2°C   0.8M $HClO_4$ 0.2M $NaClO_4$ Cell length = 2 cm.

Run #1 Time (hrs.)	Absorbance λ(nm) 446	 486
00	0.622	1.128
2	0.614	1.102
4	0.604	1.074
6	0.594	1.042
8	0.584	1.015
10	0.572	0.979
12	0.562	0.948
∞	0.280	0.130

Run #2 Time (hrs.)	Absorbance λ(nm) 446	 486
00	0.580	1.034
1.83	0.575	1.016
4	0.562	0.977
6	0.552	0.948
8	0.540	0.921
10	0.533	0.894
∞	0.280	0.144

TABLE 6 continued.

(i) Temperature = 55.2°C 1.0M $HClO_4$ Cell length = 2 cm.

Run #1 Time (hrs.)	Absorbance λ(nm) 380	 500
00	1.200	0.695
2	1.171	0.674
5	1.117	0.644
8	1.071	0.615
11	1.022	0.583
20	0.861	0.490
24	0.794	0.442
28	0.731	0.406
33	0.658	0.364
37	0.597	0.327
46	0.492	0.256
53	0.417	0.210
77	0.265	0.120
∞	0.168	0.062

Run #2 Time (hrs.)	Absorbance λ(nm) 446	 486
00	0.769	1.382
4	0.726	1.275
9.25	0.678	1.151
19	0.579	0.871
24	0.524	0.722
27	0.502	0.668
33	0.457	0.528
44	0.391	0.346

TABLE 6 (i) Run #2 continued.

Time (hrs.)	Absorbance λ(nm) 446	486
50	0.376	0.282
57	0.354	0.224
71	0.335	0.163
∞	0.304	0.116

Run #3

Time (hrs.)	Absorbance λ(nm) 446	486
00	0.698	1.253
2	0.685	1.211
4	0.674	1.171
6	0.665	1.140
8	0.646	1.095
10	0.630	1.051
∞	0.324	0.156

TABLE 6 continued.

(j) Temperature = 55.2°C

1.0M $HClO_4$ $[(H_2O)_5CrCF_3{}^{2+}] = 1.01 \times 10^{-2}M$ Cell length = 2 cm.

$[F\ ] = 2.02 \times 10^{-2}M$

Time	Absorbance	
(hrs.)	(nm) 446	486
00	0.429	0.804
3.8	0.393	0.690
7	0.356	0.594
10	0.334	0.519
13	0.315	0.415
16	0.297	0.403
18.8	0.275	0.351
25	0.238	0.251
32.3	0.218	0.189
49	0.190	0.111
60.5	0.181	0.087
∞	0.177	0.068

TABLE 7

ABSORBANCE VS. TIME FOR THE AQUATION OF PENTAAQUOTRIFLUOROMETHYL CHROMIUM (III) ION.

(a) Temperature = 64.8°C

$0.1M\ HClO_4$

$0.9M\ NaClO_4$

Cell length = 2 cm.

Run #1

Time (minutes)	Absorbance λ(nm) 486
00	0.665
30	0.655
60	0.648
80	0.645
120	0.636
150	0.633
180	0.625
210	0.618
∞	0.102

Run #2

Time (minutes)	Absorbance λ(nm) 486
00	0.665
30	0.658
60	0.653
90	0.648
120	0.643
155	0.638
180	0.634
∞	0.102

TABLE 7 (a) continued.

Run #3

Time (hrs.)	Absorbance λ(nm) 486
00	1.056
4.01	0.948
8.01	0.811
11	0.678
12	0.640
21.20	0.346
22.50	0.288
23.75	0.261
25	0.242
27	0.214
31	0.180
34.67	0.161
∞	0.144

Run #4

Time (hrs.)	Absorbance λ(nm) 486
00	1.069
1	1.041
5.01	0.935
8.70	0.811
11.50	0.691
12.25	0.654
21.50	0.363
22.75	0.322
24.16	0.285
25.36	0.263
27.14	0.233
31.25	0.193
35.00	0.172
∞	0.150

TABLE 7 continued.

(b) Temperature = 64.8°C　　$0.2M\ HClO_4$, $0.8M\ NaClO_4$　　Cell length = 2 cm.

Run #1

Time (minutes)	Absorbance λ(nm) 486
00	0.664
30	0.658
60	0.651
90	0.644
120	0.638
150	0.634
180	0.625
∞	0.099

Run #2

Time (minutes)	Absorbance λ(nm) 486
00	0.668
30	0.663
60	0.658
90	0.650
120	0.642
150	0.629
180	0.628
∞	0.100

TABLE 7 continued.

(c) Temperature = 64.8°C $0.4M\ HClO_4$ $0.6M\ NaClO_4$ Cell length = 2 cm.

Run #1

Time (minutes)	Absorbance λ(nm) 486
00	0.654
30	0.636
65	0.631
90	0.622
120	0.611
150	0.604
180	0.596
∞	0.091

Run #2

Time (minutes)	Absorbance λ(nm) 486
00	0.636
30	0.625
60	0.617
90	0.608
120	0.600
150	0.591
180	0.584
∞	0.092

TABLE 7 continued.

(d) Temperature = 64.8°C   0.6M $HClO_4$ Cell length = 2 cm.
0.4M $NaClO_4$

Run #1

Time (minutes)	Absorbance λ(nm) 486
00	0.535
30	0.531
50	0.520
90	0.516
120	0.508
150	0.498
180	0.492
∞	0.088

Run #2

Time (minutes)	Absorbance λ(nm) 486
00	0.542
30	0.534
60	0.524
90	0.516
120	0.507
150	0.498
180	0.488
∞	0.087

TABLE 7 continued.

(e) Temperature = 64.8°C 　 $0.8M\ HClO_4$ $0.2M\ NaClO_4$ 　 Cell length = 2 cm.

Run #1

Time (minutes)	Absorbance λ(nm) 486
00	0.553
30	0.542
60	0.532
90	0.523
120	0.516
150	0.505
180	0.497
∞	0.087

Run #2

Time (minutes)	Absorbance λ(nm) 486
00	0.553
30	0.543
60	0.534
90	0.524
120	0.513
150	0.504
180	0.496
∞	0.083

TABLE 7 continued.

(f) Temperature = 64.8°C 1.0M $HClO_4$ Cell length = 2 cm.

Run #1

Time (minutes)	Absorbance λ(nm) 486
00	1.211
15	1.202
45	1.181
75	1.157
105	1.138
135	1.114
170	1.074
195	1.053
225	1.030
∞	0.142

Run #2

Time (minutes)	Absorbance λ(nm) 486
00	1.214
30	1.185
60	1.161
90	1.135
120	1.113
150	1.087
180	1.062
∞	0.143

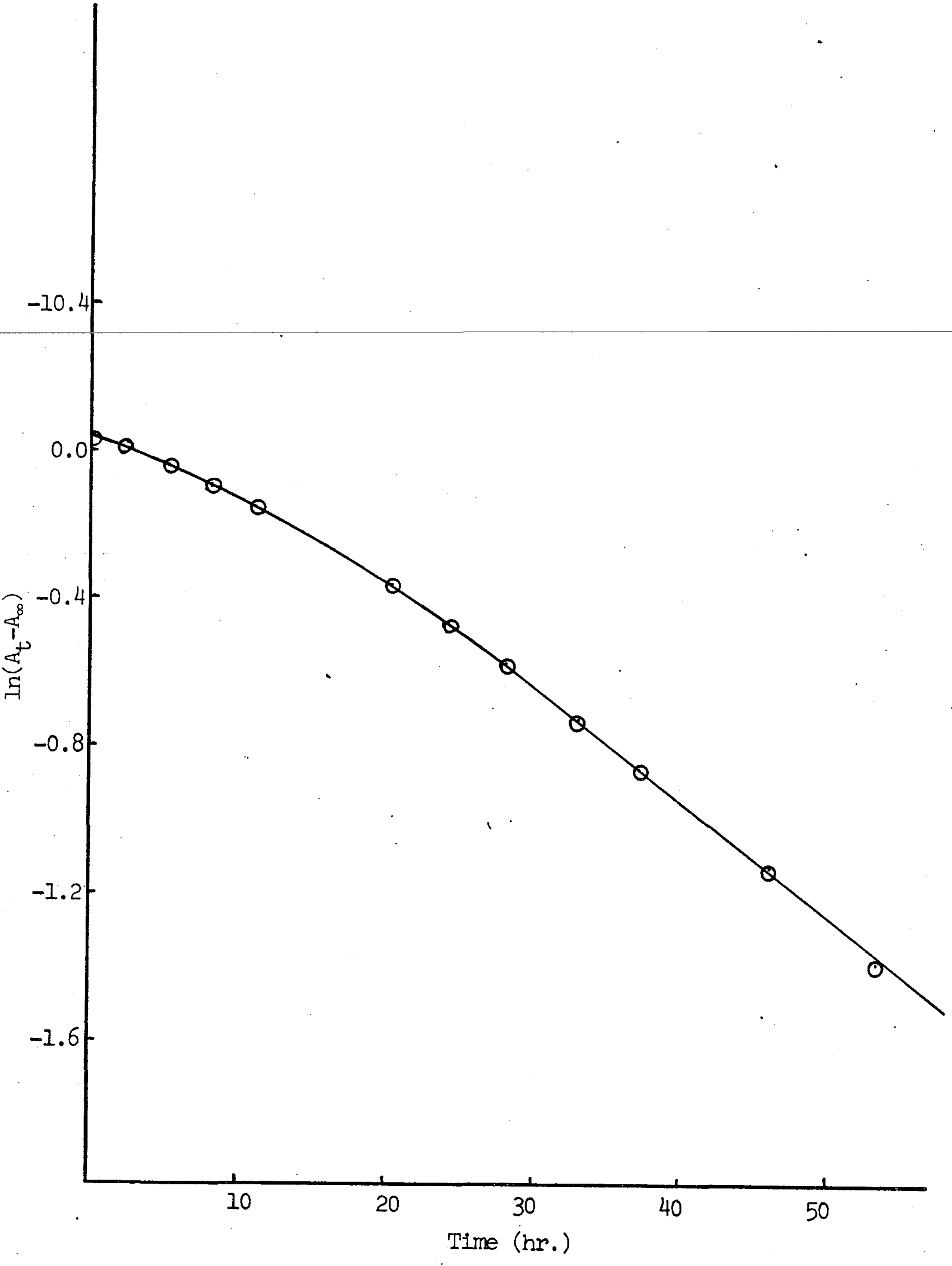


Figure 9-b: $\ln(A_t-A_\infty)$ vs. Time for the Aquation of $CrCF_3^{+2}$ Ion at 55.2°C and 1.0M $HClO_4$ (λ = 380 nm)

square program on the computer for $\ln(A_t-A_\infty)$ vs. time and are summarized in Table 8. The change in the hydrogen ion concentration during a run was negligible since it was in large excess. The pseudo-first-order rate coefficients were dependent on hydrogen ion concentration and linear dependence was obtained in the plots of k_{obs} vs. hydrogen ion concentration (Figure 10). The plots show that there is a multi-term rate law with $k_{obs} = k_o + k_1[H^+]$. The values of k_o and $k_1[H^+]$ as function of temperature are given in Table 9, where k_o is the rate coefficient with no hydrogen ion dependence and $k_1[H^+]$ is hydrogen ion dependent.

Aquation of ($CrCF_3^{2+}$) in the presence of halide ions.

Aquation Products.

The aquation products of $CrCF_3^{2+}$ at 55.2°C in the presence of added fluoride ions were separated by ion-exchange chromatography and were found to contain considerable amounts of fluorochromium(III) and difluorochromium(III) ions. It was noticed that the addition of fluoride ion to solutions of $CrCF_3^{2+}$ in 0.01M perchloric acid (I = 1.0M) gave a pinkish-red solution immediately. A pink chromium complex of charge 1+ was separated from the reaction mixture by an ion-exchange procedure.

Kinetics

The aquation of $CrCF_3^{2+}$ ion was followed at 380 nm, 446 nm and 486 nm in the presence of added fluoride ion at 55.2°C under nitrogen atmosphere. The absorbance of the complex ion solution with added fluoride ion was measured periodically. The values for rate coefficients

TABLE 8

INITIAL RATE COEFFICIENTS FOR THE AQUATION OF $[(H_2O)_5CrCF_3{}^{2+}]$ ION AS FUNCTION OF TEMPERATURE AND (H^+) ION CONCENTRATION.[a]

$$\frac{-d[CrCF_3{}^{2+}]}{dt} = k_{obs}[CrCF_3{}^{2+}]$$

Temp. = H^+	35° x 10^7 sec	45° x 10^6sec	55.2° x 10^6sec	64.8° x 10^6sec
0.1	2.26	0.61	1.90 ± 0.10	6.30 ± 0.20
0.2		0.91	2.40 ± 0.5	7.18 ± 0.15
0.4		0.91	3.40 ± 0.15	9.08 ± 0.16
0.6		1.09	3.75 ± 0.05	10.50 ± 0.30
0.8		1.27	4.90 ± 0.10	12.01 ± 0.20
1.0	5.25	1.46	5.54 ± 0.15	13.75 ± 0.15

[a] Ionic strength was maintained constant at 1.0M with solutions of $NaClO_4$ and $HClO_4$.

TABLE 9

HYDROGEN ION DEPENDENT AND INDEPENDENT INITIAL RATE COEFFICIENTS FOR AQUATION OF $CrCF_3^{2+}$ AS FUNCTION OF TEMPERATURE.

Temperature °C	k_o x 10^6sec	$k_1(H^+)$ x 10^6M sec
45	0.52	0.94
55.2	1.54	4.06
64.8	5.59	8.16

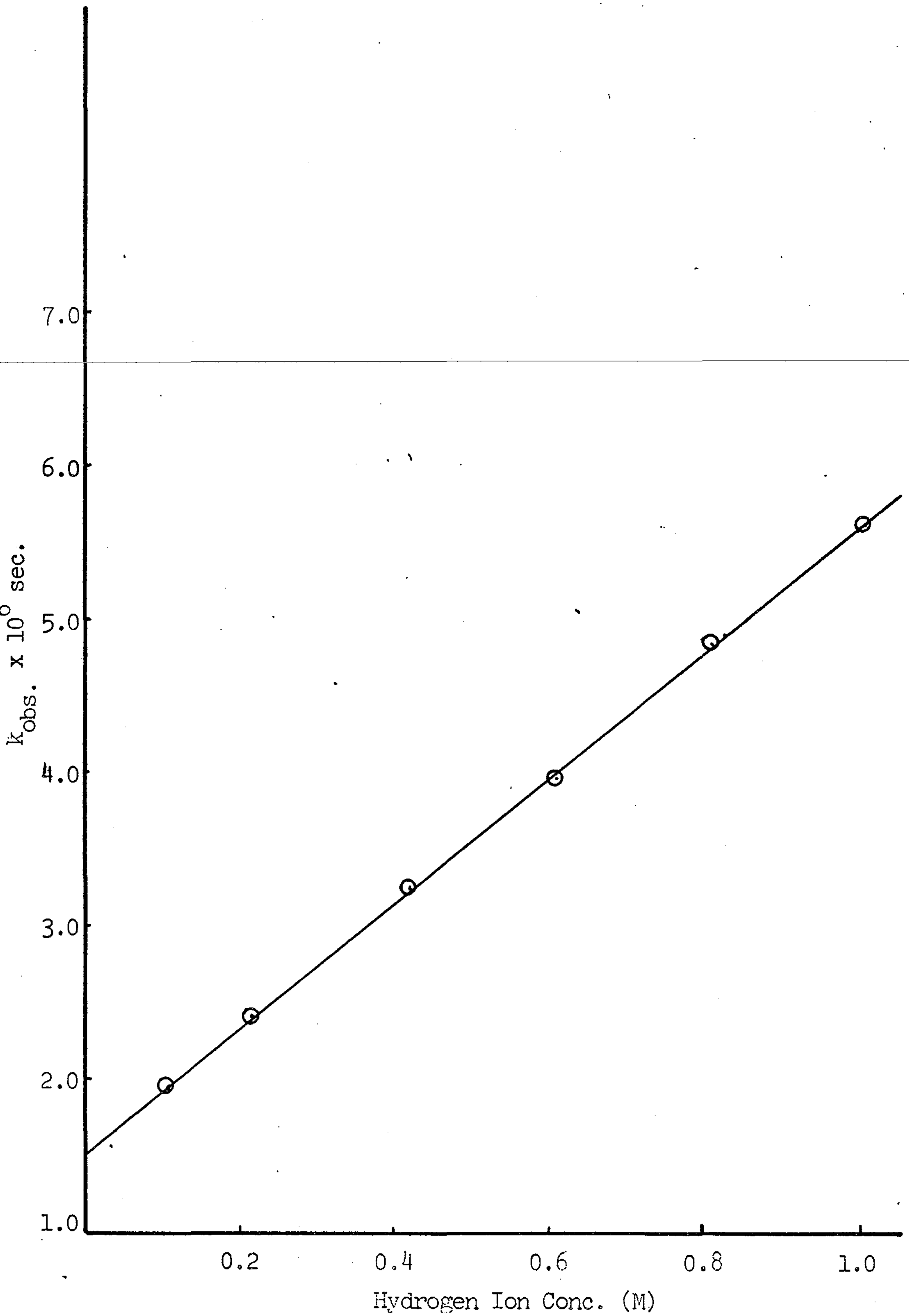


Figure 10: $k_{obs.}$ vs. $[H^+]$ at 55.2°C for $CrCF_3^{2+}$

were obtained by computer using a linear least-square program for $\ln(A_t - A_{\infty})$ vs. time. A constant ionic strength of 1.0M was maintained by the addition of sodium perchlorate solution. It was observed that the initial rate coefficients increased with the increase in fluoride ion concentration. The rate coefficients are summarized in Table 10.

When excess of chloride ion (10 times the concentration of the complex ion) was added to the $CrCF_3^{2+}$ solution in 0.1M perchloric acid, it slightly increased the reaction rate. The value for the rate coefficient was $2.1 \times 10^{-6}\text{sec}^{-1}$ as compared to $1.85 \times 10^{-6}\text{sec}^{-1}$ with no chloride.

It was also observed that azide and thiocyanate ions reacted very rapidly with $CrCF_3^{2+}$ to give pink color solutions. This pink color disappeared upon addition of excess of hydrogen ion.

Effect of fluoride ion on other complexes containing chromium-carbon bonds.

Fluoride ion showed a marked effect on other organochromium complexes. When added to pentaaquodichloromethylchromium(III) and pentaaquomonohalomethylchromium(III) species, it reacted very rapidly with these species to give deep pink solutions in acid medium. These pink charge 1+ complexes of chromium were separated from the reaction mixtures by ion-exchange procedures. The pink chromium complexes with F^- ion aquated rapidly giving fluoropentaaquochromium(III) and difluorotetraaquochromium(III) ions.

TABLE 10

INITIAL RATE COEFFICIENTS FOR THE AQUATION OF $CrCF_3^{2+}$ ION WITH ADDED FLUORIDE.

Temperature = 55.2°C

0.1M $HClO_4$

0.9M $NaClO_4$

$[CrCF_3^{2+}]$ (M)	$[F^-]$ (M)	$k_{obs} \times 10^6 sec$
1.33×10^{-2}	1.33×10^{-2}	8.10
6.28×10^{-3}	1.26×10^{-2}	10.90
6.28×10^{-3}	1.57×10^{-2}	12.10
6.28×10^{-3}	1.89×10^{-2}	18.40
6.28×10^{-3}	3.42×10^{-2}	72.00
1.01×10^{-2}	2.02×10^{-2}	13.58 [a]

[a] 1.0M $HClO_4$

B. Fluorotetraaquotrifluoromethylchromium(III) ion

UV-visible spectrum

A visible spectrum of this complex ion, Figure 11, shows maxima at 510 nm (E, $31M^{-1}cm^{-1}$) and at 385 nm (E, $35M^{-1}cm^{-1}$). The UV spectrum has a maximum at 214 nm (E, $2686M^{-1}cm^{-1}$) and a minimum at 201 nm (E,$2226M^{-1}cm^{-1}$) Figure 12.

Composition

The product analysis showed that chromium to carbon ratio was 1.00:0.99. Chromium was determined as chromate whereas carbon was determined as carbon dioxide. Fluoride was present as difluorochromium(III), fluorochromium(III) as well as HF. Chromium to fluoride ratio was found to be 1.00:3.85. The results are summarized in Table 11. The behavior of this ion on the ion-exchange column is similar to that of difluorochromium(III) and is compatible with a charge of 1+.

It shows large absorption maxima at 385 nm in perchloric acid which is in accord with the spectra of many complexes of chromium having a chromium-carbon sigma bond. Therefore, the complex can be represented as $[(H_2O)_4FCrCF_3{}^{1+}]$.

Equilibrium Constant

The pink color of $FCrCF_3{}^{1+}$ started to change to pinkish red on standing in acidic solutions. The pink color disappeared on addition of 1.0M perchloric acid but reappeared when more fluoride ion was added to it. These observations were taken as evidence that there exists an equilibrium between parent complex, $CrCF_3{}^{2+}$ and the intermediate

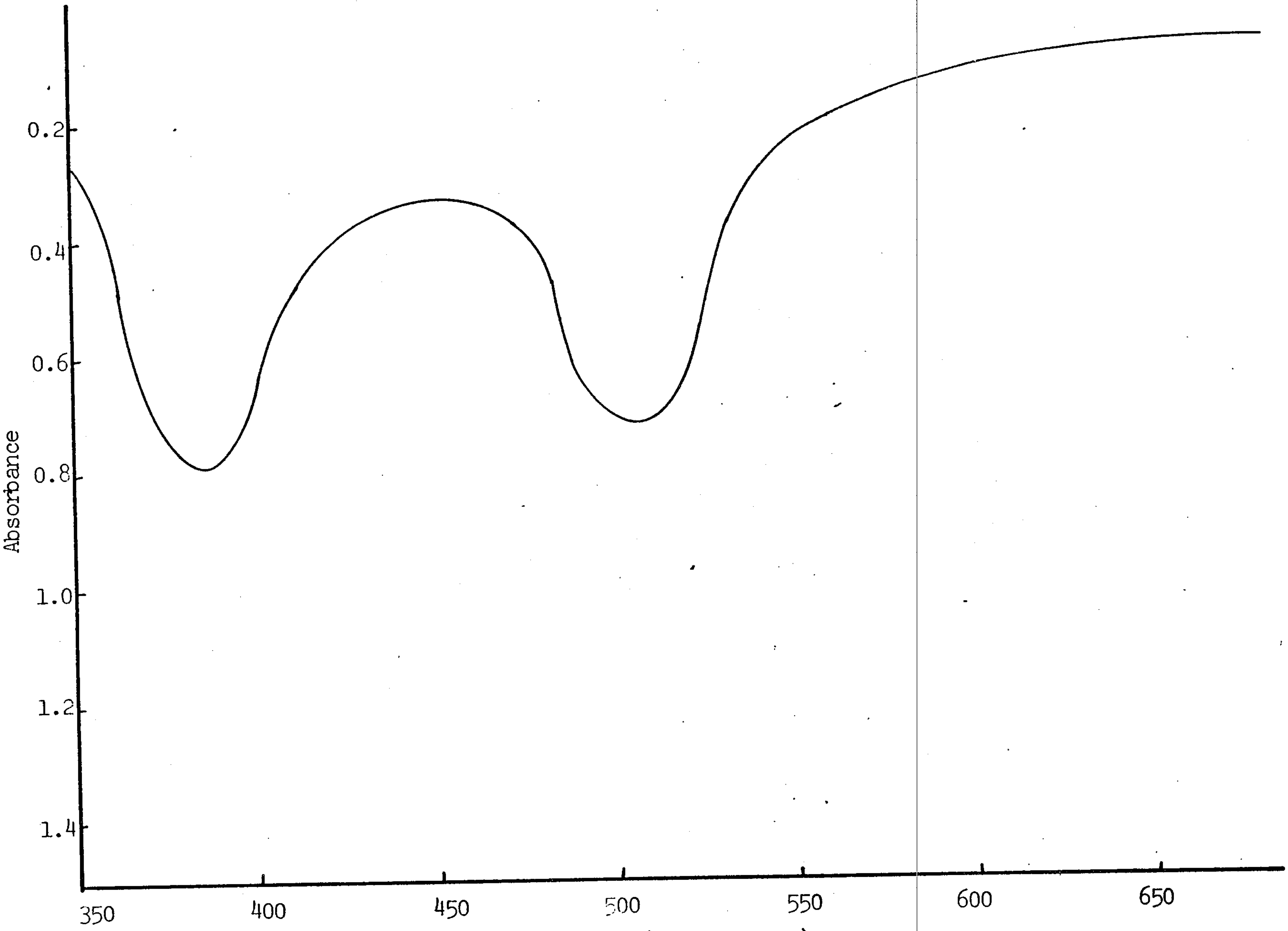


Figure 11: Visible Spectrum for $FCrCF_3^{1+}$ Ion in 0.10M $HClO_4$

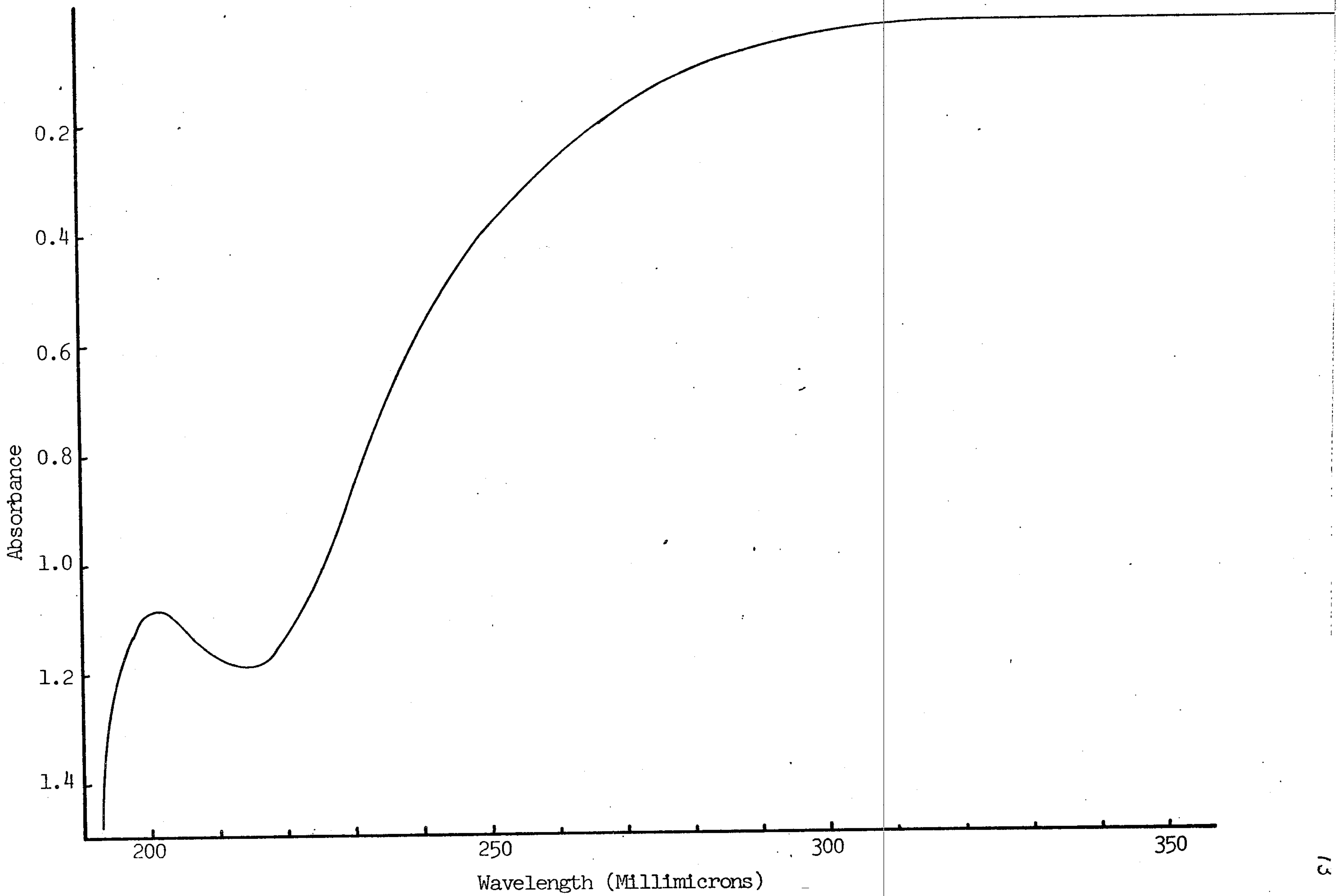


Figure 12: UV Spectrum of $FCrCF_3^{1+}$ Ion in 0.01M $HClO_4$

TABLE 11

PRODUCT ANALYSIS FOR THE AQUATION OF $FCrCF_3^{1+}$ ION

Total Moles of Chromium	Moles of Carbon monoxide as carbon dioxide	Moles of Fluoride [a]	$Cr:C:F^-$ Ratio
4.27×10^{-4}	4.23×10^{-4}	11.08×10^{-4}	1.00:0.99:3.86
4.20×10^{-4}	4.18×10^{-4}	16.10×10^{-4}	1.00:1.00:3.83
2.72×10^{-5}	2.69×10^{-5}	10.79×10^{-5}	1.00:0.99:3.96

[a] Sum of $[F^-]$, $[CrF^{2+}]$ and $2[CrF_2^{1+}]$.

$FCrCF_3^{1+}$. This equilibrium is shown as $CrCF_3^{2+} + HF \rightleftharpoons FCrCF_3^{1+} + H^+$
The equilibrium quotient, Q, for this reaction is given by

$$Q = \frac{[FCrCF_3^{1+}][H^+]}{[CrCF_3^{2+}][HF]} \qquad (6)$$

In order to determine Q, the $CrCF_3^{2+}$ ion was allowed to react with added fluoride ion in 0.1M perchloric acid. The change in absorbance at 380 nm and 500 nm was followed to a constant absorbance (equilibrium).

At equilibrium, the concentration of $CrCF_3^{2+}$ ion was obtained by using the relationship

$$\tilde{a}[C_{CrCF_3^{2+}}] = a_o[CrCF_3^{2+}] + a_1[FCrCF_3^{1+}]$$

where $C_{CrCF_3^{2+}}$ = initial concentration of $CrCF_3^{2+}$ ion
$[CrCF_3^{2+}]$ = equilibrium concentration of $CrCF_3^{2+}$ ion
$[FCrCF_3^{1+}]$ = equilibrium concentration of $FCrCF_3^{1+}$ ion

$\tilde{a}$ was obtained from the absorbance at equilibrium and $C_{CrCF_3^{2+}}$. a_o and a_1 are the molar absorbance indices for the $CrCF_3^{2+}$ and $FCrCF_3^{1+}$ species which were determined as described earlier. The equilibrium concentration of $FCrCF_3^{1+}$ was then, the difference in the initial and equilibrium concentrations of $CrCF_3^{2+}$ ion, $C_{CrCF_3^{2+}} - [CrCF_3^{2+}]$. Hydrogen fluoride concentration was calculated from the added fluoride minus the fluoride present in $FCrCF_3^{1+}$ and hydrogen ion concentration was obtained from its initial concentration and hydrogen complexed with fluoride to give HF assuming that all of the F^- was protonated. The values for Q were obtained by substituting the equilibrium concentrations in the expression (6) and are summarized in Table 12.

TABLE 12

EQUILIBRIUM QUOTIENT VALUES FOR

$$(H_2O)_5CrCF_3^{2+} + HF \rightleftharpoons (H_2O)_4FCrCF_3^{1+} + H^+$$

$$Q = \frac{[(H_2O)_4FCrCF_3^{1+}][H^+]}{[(H_2O)_5CrCF_3^{2+}][HF]}$$

Temperature = 25°C

0.1M $HClO_4$

0.9M $NaClO_4$

[a] $[H^+]$ M x 10^2	$[CrCF_3^{2+}]$ M x 10^3	[HF] M x 10^2	$[FCrCF_3]$ M x 10^3	Q
6.13	3.82	3.87	1.76	0.73
3.62	2.44	6.38	3.14	0.79
6.42	4.32	3.58	1.96	0.80
7.01	4.80	2.99	1.48	0.72
5.82	4.04	4.18	2.24	0.76
13.10	2.21	26.90	3.24	0.72 [b]

[a] Equilibrium concentrations. The $CrCF_3^{2+}$ concentration was determined from equilibrium values of molar absorbancy indices and $FCrCF_3^{1+}$ concentration was obtained from the initial and equilibrium concentrations of $CrCF_3^{2+}$. Hydrogen fluoride was obtained from the added fluoride and $FCrCF_3^{1+}$ concentrations and hydrogen ion concentration was obtained from its initial concentration and HF.

[b] 0.4M $HClO_4$ (I = 1.0M)

Activation Parameters

All rate coefficients were treated simultaneously for all hydrogen ion concentration and temperatures according to the expression

$$k_{obs} = \frac{kt}{h} \sum_i (H^+)^i \; e^{\Delta S^{\ddagger}/R} \; e^{-\Delta H^{\ddagger}/RT} \qquad (7)$$

where $i = 0$ for k_o and $i = 1$ for $k_1(H^+)$.

k_{obs} = observed rate coefficient

k = Boltzman constant

T = Temperature (°K)

h = Plank's constant

$\Delta S^{\ddagger}$ = Entropy of activation

$\Delta H^{\ddagger}$ = Enthalpy of activation

R = Gas constant

The values of the enthalpies and entropies of activation were calculated using a computer and a linear least-square program. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for $CrCF_3^{2+}$ and $FCrCF_3^{1+}$ ions are given in Table 13.

TABLE 13

ACTIVATION PARAMETERS FOR PENTAAQUOTRIFLUOROMETHYLCHROMIUM(III) ION.

Rate Coefficient	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ cal/deg-mole
$k_o(\text{sec}^{-1})$	19.1	-27.4 ± 0.33
$k_1(H^+)(M^{-1}\text{sec}^{-1})$	23.4	-12.7 ± 0.50

C. Monohalogenoorganochromium(III) ions.

Characterization

Ultraviolet-visible Spectrum

The visible spectrum of pentaaquomonochloroorganochromium(III) ion, Figure 13, shows maxima at 536 nm (E, $154M^{-1}cm^{-1}$) and 350 nm (E, $180M^{-1}cm^{-1}$) and a minimum at 450 nm (E, $46M^{-1}cm^{-1}$). The UV spectrum, Figure 14, shows maxima at 324 nm (E, $800M^{-1}cm^{-1}$), 241 nm (E, $2826M^{-1}cm^{-1}$) and 237 nm (E, $2615M^{-1}cm^{-1}$) and a minimum at 224 nm (E, $1450M^{-1}cm^{-1}$).

Pentaaquomonobromoorganochromium(III) ion shows maxima at 538 nm (E, $129M^{-1}cm^{-1}$) and 360 nm (E, $160M^{-1}cm^{-1}$), and a minimum at 454 nm (E, $47M^{-1}cm^{-1}$), Figure 15. The UV spectrum of this ion shows maxima at 324 nm (E, $823M^{-1}cm^{-1}$), 242 nm (E, $2850M^{-1}cm^{-1}$) and 239 nm (E, $2688M^{-1}cm^{-1}$) and a minimum at 225 nm (E, $1528M^{-1}cm^{-1}$), Figure 16.

The molar absorbancy indices for these ions (given in parentheses above) were determined from the freshly prepared solutions. The spectrum was obtained by using the Perkin-Elmer Model 202 and the total chromium was analyzed as chromate ion.

Reaction with oxygen

Oxygen reacts rapidly with these complexes yielding carbon dioxide, hexaaquochromium(III) and halide ions. Chromium(III) was determined as chromate. Carbon was present as carbon dioxide and was determined by absorbing over ascarite whereas the halide ions were determined gravimetrically as silver halides. The results are summarized in Table 14.

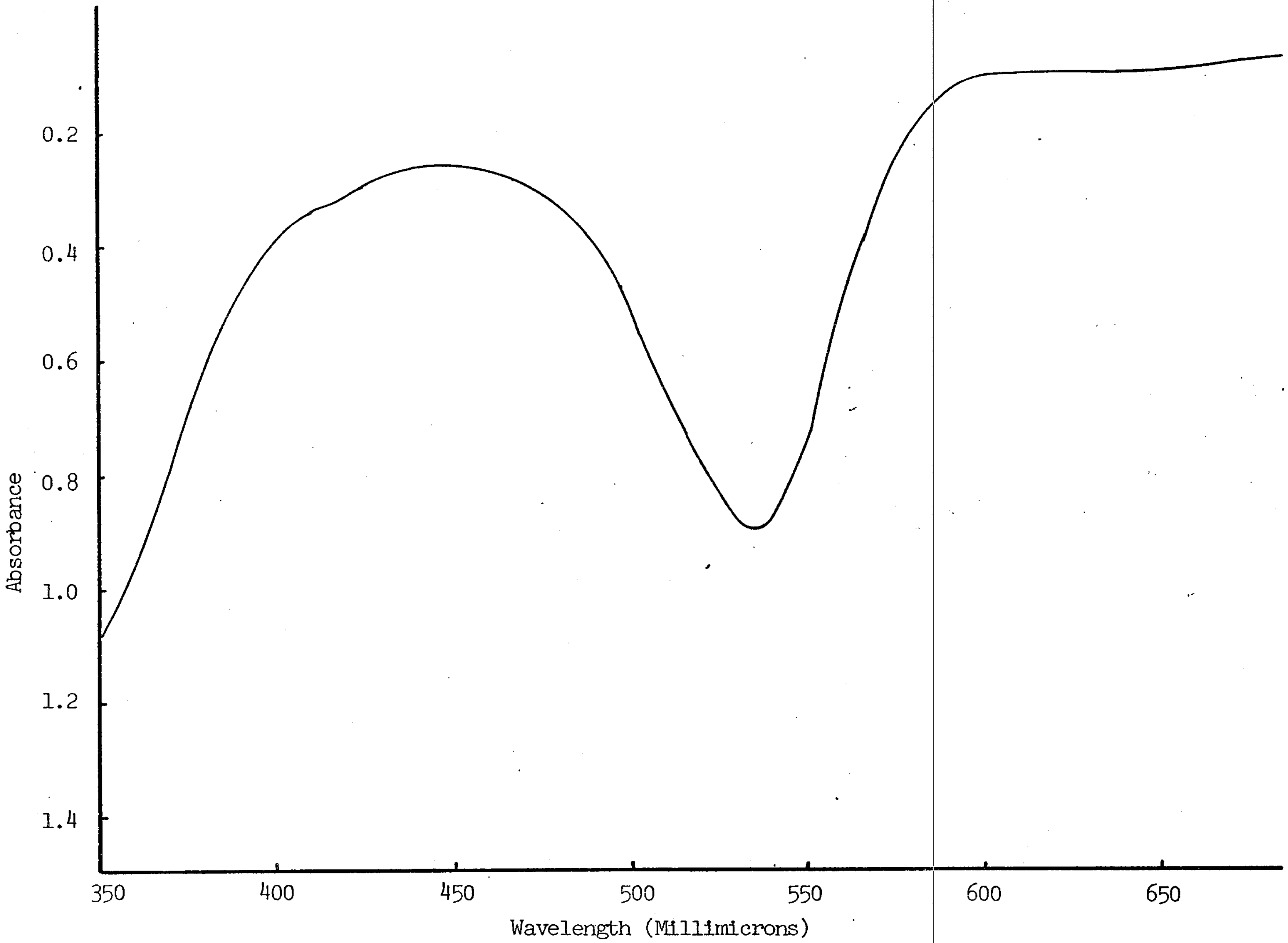


Figure 13: Visible Spectrum of Monochloroorganochromium(III) Ion in 1.0M $HClO_4$.

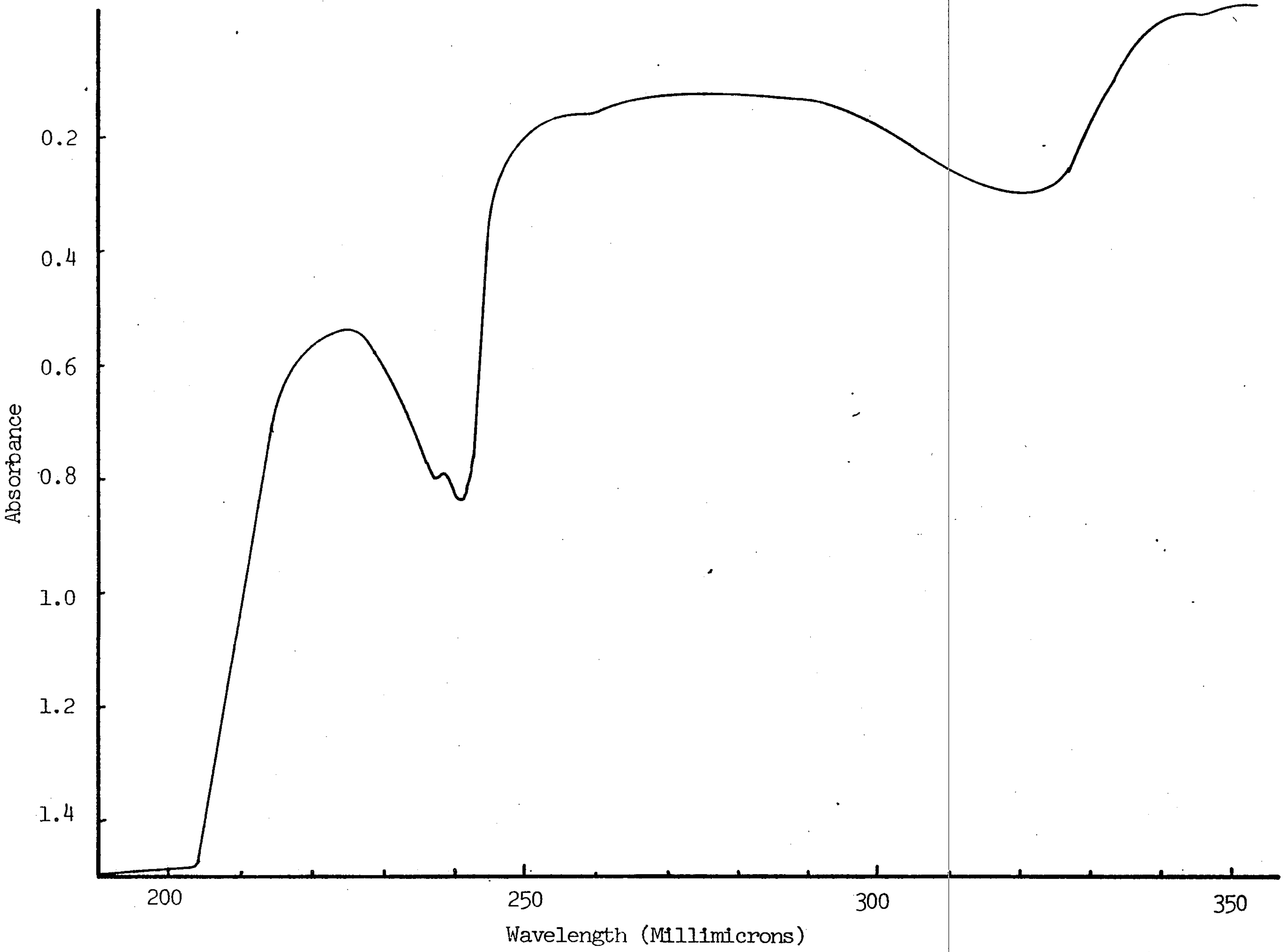


Figure 14: UV Spectrum of Monochloroorganochromium(III) Ion in 1.0M $HClO_4$.

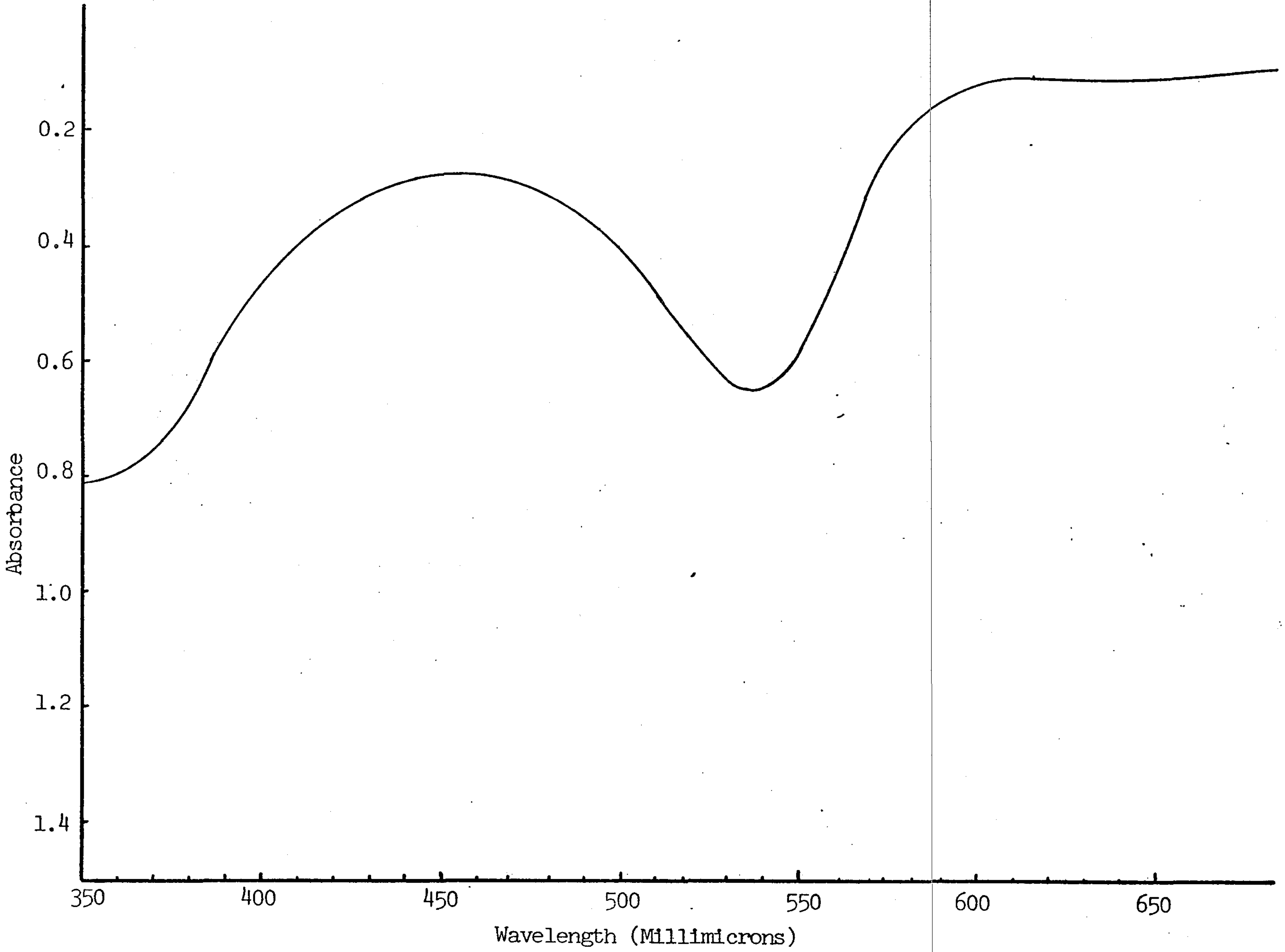


Figure 15: Visible Spectrum of Monobromoorganochromium(III) Ion, in 1.0M $HClO_4$

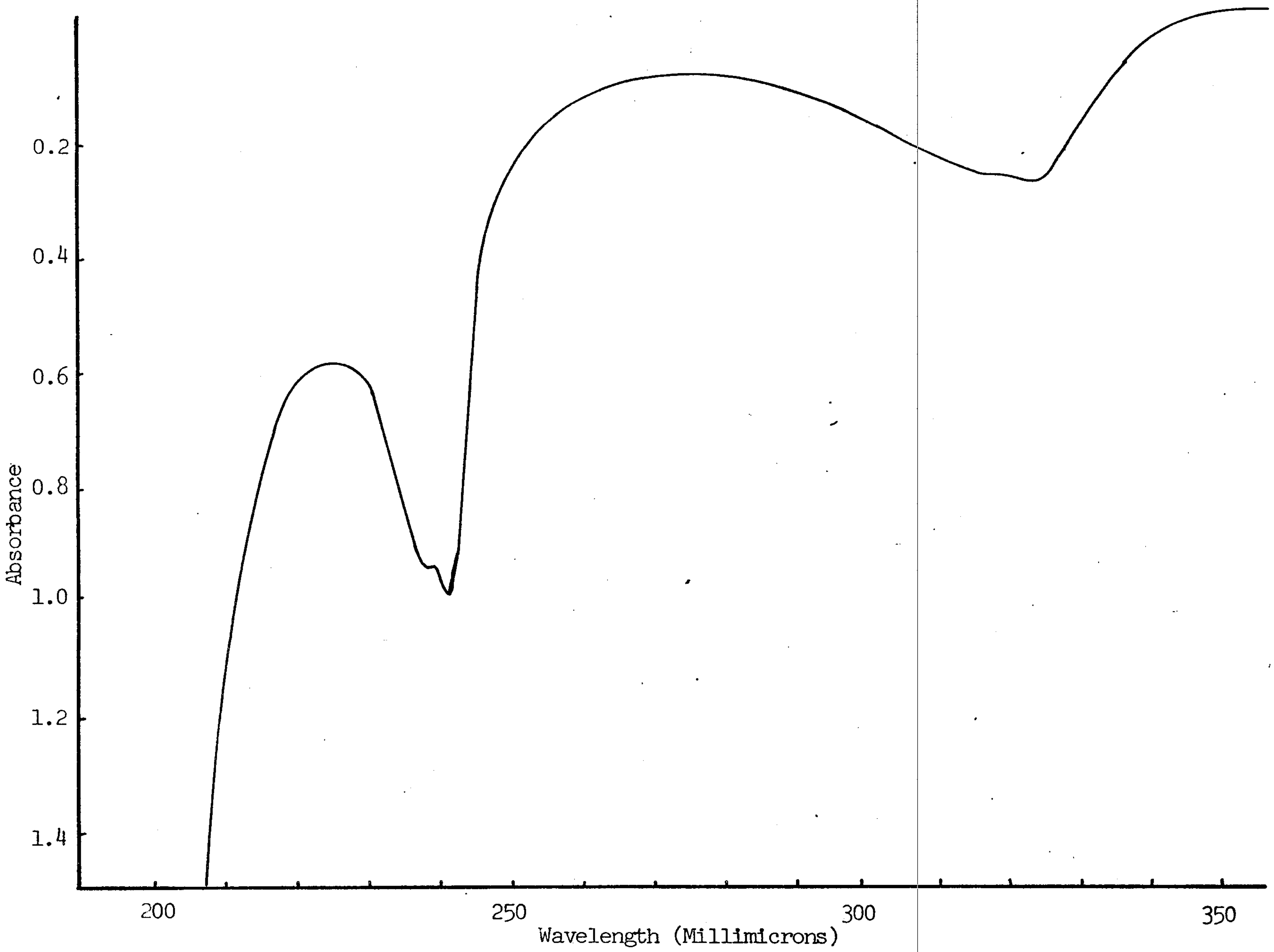


Figure 16: UV Spectrum of Monobromoorganochromium(III) Ion in 1.0M $HClO_4$

TABLE 14

REACTION PRODUCTS OF MONOHALOGENOORGANOCHROMIUM(III) IONS IN THE PRESENCE OF OXYGEN

(a) pentaaquomonochloroorganochromium(III) ion

Moles of Chromium	Moles of carbon dioxide	Moles of Chloride	Cr:C:Cl Ratio
3.80×10^{-4}	3.75×10^{-4}	4.00×10^{-4}	1.00:0.99:1.05
7.50×10^{-5}	7.35×10^{-5}	7.63×10^{-5}	1.00:0.98:1.01
7.21×10^{-4}	7.11×10^{-4}	6.60×10^{-4}	1.00:0.95:0.93
1.30×10^{-4}	1.20×10^{-4}	1.31×10^{-4}	1.00:0.92:1.00

(b) pentaaquomonobromoorganochromium(III) ion

Moles of Chromium	Moles of carbon dioxide	Moles of Bromide	Cr:C:Br Ratio
3.24×10^{-4}	3.12×10^{-4}	3.34×10^{-4}	1.00:0.96:1.03
3.33×10^{-4}	3.30×10^{-4}	3.29×10^{-4}	1.00:0.99:0.98
1.12×10^{-4}	1.10×10^{-4}	1.18×10^{-4}	1.00:0.98:1.05

Products in the absence of oxygen

1. Monochloroorganochromium(III) ions - The aquation products of this ion in the absence of oxygen gave hexaaquochromium(III) ion, chromium(II) (25%), and chloride ion. The organic products were formaldehyde (5%) and carbon monoxide (90-92%). Hexaaquochromium(III) was analyzed as chromate in alkaline solution of hydrogen peroxide. Formaldehyde content was determined from the Beer's law plot for the purple color developed when formaldehyde solution were treated with chromotropic acid and concentrated sulfuric acid as described earlier. Carbon monoxide was determined by converting to carbon dioxide and then absorbing on ascarite. Chloride was determined gravimetrically as silver chloride. Chromium(II) was determined by reacting with Cr(VI) and the unreacted Cr(VI) was obtained spectrometrically at 348 nm. The results are summarized in Table 15.

2. Monobromoorganochromium(III) ion - Hexaaquochromium(III) ion, bromide ion, formaldehyde (6%), formic acid (10%), carbon monoxide (5%), and carbon dioxide (78%) were the products of aquation for this complex. Hexaaquochromium(III), bromide ion, formaldehyde, carbon monoxide, and carbon dioxide were determined in the same manner as in the chlorocomplex. Formic acid was determined spectrophotometrically as formaldehyde after reduction with magnesium turnings and hydrochloric acid. The results are summarized in Table 15b.

Kinetics

Monochloroorganochromium (III) ion.

The kinetics of the aquation of this ion were followed at 350 nm, 406 nm and 536 nm. This was done by measuring the absorbance of the

TABLE 15

AQUATION PRODUCTS OF MONOHALOGENOORGANOCHROMIUM(III) IONS IN NITROGEN ATMOSPHERE

(a) pentaaquomonochloroorganochromium(III) ion

Moles of Chromium(III)	Moles of Chromium(II)	Moles of Chloride	Moles of Carbon Monoxide as Carbon Dioxide	Moles of Formaldehyde
4.07×10^{-5}	1.35×10^{-5}	5.56×10^{-5}	4.88×10^{-5}	2.65×10^{-6}
4.58×10^{-5}	1.54×10^{-5}	5.59×10^{-5}	4.92×10^{-5}	2.55×10^{-6}
4.42×10^{-6}	0.78×10^{-6}	5.25×10^{-6}	4.52×10^{-6}	1.85×10^{-7}

(b) pentaaquomonobromoorganochromium(III) ion

Moles of Chromium	Moles of Bromide	Moles of Formaldehyde	Moles of Formic Acid	Moles of Carbon Dioxide	Moles of Carbon Monoxide
2.24×10^{-6}	2.16×10^{-6}	1.35×10^{-7}	2.32×10^{-7}	1.66×10^{-6}	1.42×10^{-7}
8.15×10^{-7}	8.25×10^{-7}	5.68×10^{-8}	6.52×10^{-8}	6.30×10^{-7}	3.30×10^{-8}
3.33×10^{-6}	3.34×10^{-6}	2.67×10^{-7}	2.85×10^{-7}	2.50×10^{-7}	1.33×10^{-7}

thermostated solutions at different time intervals under nitrogen atmosphere. The data for absorbance vs. time at different temperatures and hydrogen ion concentrations is given in Table 16 to Table 18.

The $\ln(A_t-A_\infty)$ vs. time gave a linear plot up to 60% of the reaction and then started showing curvature becoming faster as the reaction neared completion. The plots were reproducible. A typical plot of $\ln(A_t-A_\infty)$ is given in Figure 17. The initial rate coefficients for the reaction at different temperatures and hydrogen ion concentrations were determined by a computer linear least square analysis for $\ln(A_t-A_\infty)$ vs. time data at the beginning of the reaction. The rate coefficients were found to be independent of hydrogen ion concentration and wavelengths and are summarized in Table 19. The data supported the view that the reaction obeyed a first order rate law during the initial period $\frac{-d[\text{complex}]}{dt} = k[\text{complex}]$ (8)

The rate constants (Table 16) were treated for all temperatures according to the expression $k = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$ and the values for enthalpy and entropy of activation and their standard deviations were obtained by means of a least square analysis of ln k/T vs. 1/T for the temperature range between 25 and 45°C. These values are $\Delta H^{\ddagger} = 19.7 \pm 0.1$ kcal/mole; $\Delta S^{\ddagger} = -27.1 \pm 2.1$ cal/deg-mole.

<u>Monobromoorganochromium(III) ion</u>

The kinetics of monobromoorganochromium(III) ion was followed at 538 nm, 406 nm and 360 nm. The data for the absorbance vs. time at different temperatures and acidities are given in Table 20 - 22.

The $\ln(A_t-A_\infty)$ vs. time gave a linear plot initially and then

TABLE 16

ABSORBANCE VS TIME FOR THE AQUATION OF PENTAAQUOMONOCHLORO ORGANOCHROMIUM(III) ION IN ABSENCE OF OXYGEN.

(a) Temperature = 25°C 0.1M $HClO_4$ Cell length = 10 cm.

0.9M $NaClO_4$

Run #1

Time	Absorbance	
(hrs)	(nm) 350	536
00	0.550	0.406
12	0.531	0.398
24	0.512	0.382
36	0.494	0.367
48	0.477	0.355
62	0.467	0.337
72	0.445	0.330
84	0.434	0.321
96	0.402	0.308
108	0.365	0.285
120	0.340	0.253
∞	0.050	0.011

Run #2

Time	Absorbance	
(hrs.)	(nm) 350	536
00	0.362	0.293
12	0.353	0.272
24	0.341	0.253
36	0.328	0.220
48	0.315	0.196
60	0.302	0.162
75	0.288	0.128
88	0.272	0.098
96	0.252	0.076
110	0.205	0.061
∞	0.032	0.010

Table 16 continued.

(b) Temperature = 25°C 1.0M $HClO_4$ Cell length = 10 cm.

Time	Absorbance		
(hrs.)	(nm) 390	406	536
00	0.486	0.387	0.311
2	0.420	0.375	0.287
15	0.418	0.368	0.185
26	0.329	0.366	0.120
39	0.325	0.342	0.058
51	0.284	0.300	0.042
64	0.264	0.277	0.038
76	0.241	0.254	0.034
87	0.225	0.238	0.030
96	0.205	0.216	0.022
108	0.184	0.198	0.015
120	0.168	0.174	0.017
132	0.161	0.167	0.013
156	0.142	0.151	0.011
∞	0.052	0.085	0.006

TABLE 17

ABSORBANCE VS TIME FOR THE AQUATION OF PENTAAQUOMONOCHLORO ORGANOCHROMIUM(III) ION.

(a) Temperature = 35°C   0.1M $HClO_4$ Cell length = 5 cm.
0.9M $NaClO_4$

Time	Absorbance		
(hrs.)	(nm) 350	406	536
00	0.759	0.266	0.596
12	0.654	0.248	0.508
24	0.552	0.230	0.410
39	0.425	0.202	0.304
50	0.290	0.175	0.210
62	0.230	0.169	0.148
73	0.125	0.137	0.070
∞	0.035	0.086	0.050

(b) Temperature = 35°C   0.2M $HClO_4$ Cell length = 2 cm.
0.8M $NaClO_4$

Time	Absorbance	
(hrs.)	(nm) 350	536
00	0.440	0.354
12	0.345	0.275
23	0.300	0.235
35	0.218	0.185
47	0.201	0.149
59	0.114	0.096
71	0.092	0.072
∞	0.031	0.041

Table 17 continued.

(c) Temperature = 35°C $0.4M\ HClO_4$ $0.6M\ NaClO_4$ Cell length = 2 cm.

Time	Absorbance		
(hrs.)	(nm) 350	406	536
00	1.293	0.500	0.988
12	1.126	0.466	0.858
24	0.990	0.434	0.749
36	0.824	0.388	0.631
48	0.717	0.366	0.547
60	0.612	0.342	0.465
71	0.541	0.326	0.396
96	0.336	0.268	0.254
120	0.189	0.234	0.146
∞	0.025	0.125	0.072

(d) Temperature = 35°C $1.0M\ HClO_4$ Cell length = 2 cm.

Run #1

Time	Absorbance		
(hrs.)	(nm) 350	406	536
00	1.235	0.487	0.890
13.25	1.038	0.429	0.752
24	0.925	0.401	0.662
36	0.789	0.365	0.560
48	0.589	0.317	0.404
60	0.502	0.333	0.359
72	0.408	0.267	0.266
84	0.306	0.237	0.189
96	0.244	0.227	0.146
108	0.189	0.213	0.105
∞	0.050	0.107	0.050

Table 17 (d) continued.

Temperature = 35°C 1.0M $HClO_4$ Cell length = 10 cm.

Run #2

Time (hrs)	Absorbance (nm) 380	390	406
00	0.739	0.728	0.633
6	0.632	0.652	0.586
12	0.538	0.577	0.533
18	0.469	0.505	0.504
24	0.417	0.453	0.398
30	0.376	0.412	0.390
36	0.337	0.371	0.352
42	0.314	0.354	0.332
48	0.303	0.337	0.318
54	0.285	0.317	0.299
60	0.279	0.301	0.289
66	0.255	0.281	0.269
72	0.246	0.274	0.264
75	0.246	0.273	0.254
83	0.233	0.259	0.242
95	0.211	0.237	0.227
113	0.198	0.220	0.212
143	0.185	0.204	0.199
∞	0.053	0.083	0.095

TABLE 18

ABSORBANCE VS TIME FOR THE AQUATION OF PENTAAQUOMONOCHLORO ORGANOCHROMIUM(III) ION.

(a) Temperature = 45°C 0.1M $HClO_4$ 0.9M $NaClO_4$ Cell length = 5 cm.

Time	Absorbance		
(hrs.)	(nm) 350	406	536
00	0.935	0.272	0.671
1	0.909	0.266	0.649
5	0.793	0.241	0.552
7	0.752	0.234	0.511
10	0.700	0.219	0.442
12	0.653	0.211	0.401
13	0.631	0.205	0.381
16	0.583	0.198	0.324
24	0.448	0.169	0.185
∞	0.021	0.082	0.005

(b) Temperature = 45°C 1.0M $HClO_4$ Cell length = 5 cm.

Time	Absorbance		
(hrs.)	(nm) 350	406	536
00	0.921	0.266	0.666
1	0.905	0.264	0.645
5	0.785	0.237	0.551
7	0.751	0.230	0.507
10	0.694	0.217	0.437
13	0.628	0.203	0.375
16	0.575	0.191	0.315
25	0.424	0.157	0.173
30	0.341	0.128	0.097
∞	0.005	0.083	0.007

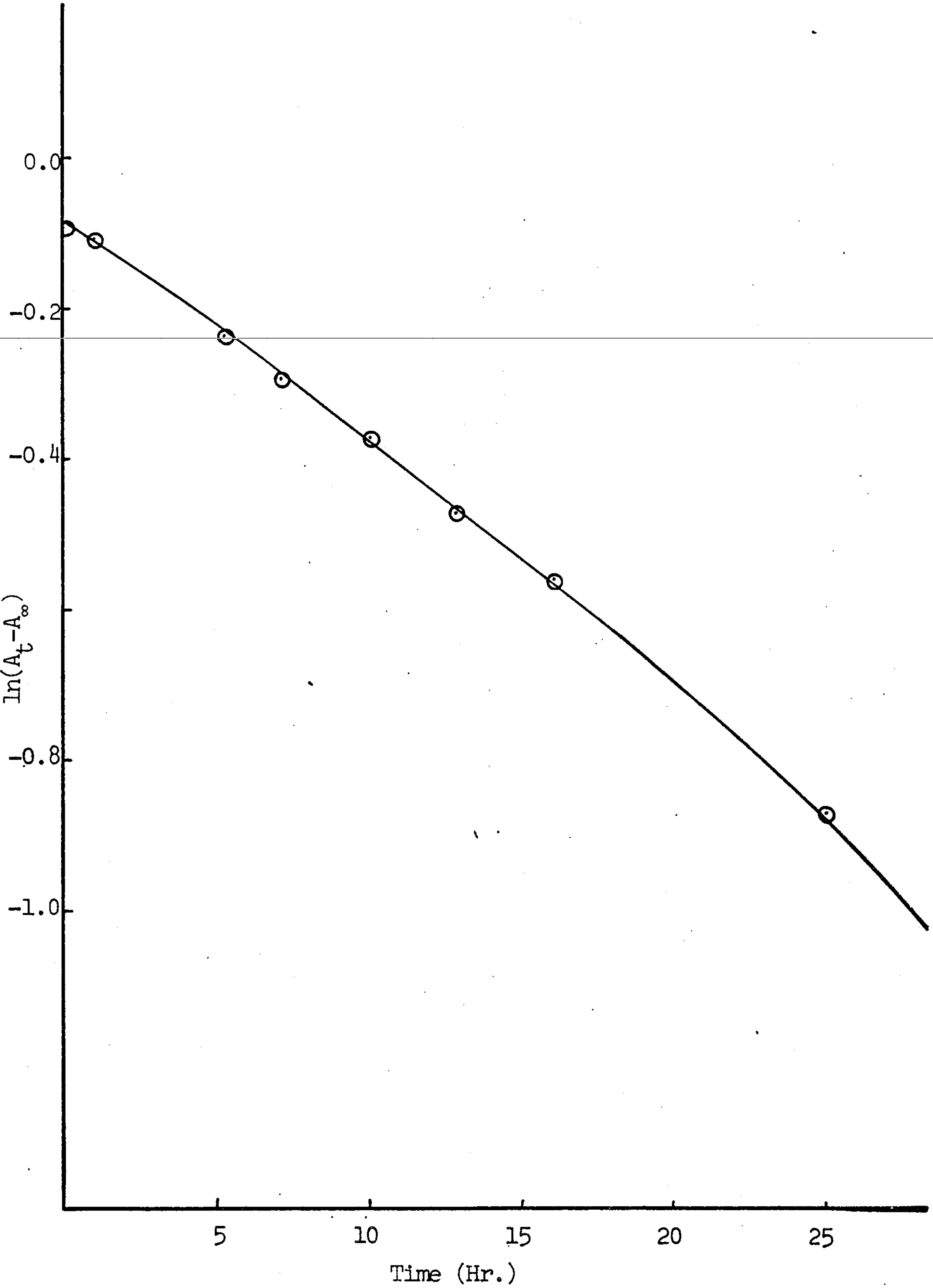


Figure 17: $\ln(A_t-A_\infty)$ vs. Time for the Aquation of Monochloroorganochromium(III) Ion at 45°C and 1.0M $HClO_4$ (λ= 350 nm).

TABLE 19

INITIAL RATE COEFFICIENTS FOR THE AQUATION OF PENTAAQUOMONOCHLOROORGANOCHROMIUM(III) AS FUNCTION OF TEMPERATURE AND HYDROGEN ION CONCENTRATION.[a]

$$\frac{-d[\text{complex}]}{dt} = k[\text{complex}]$$

Hydrogen ion Concentration $\underline{M}$	$k \times 10^{6}$ sec		
	25°C	35°C	45°C
0.1	0.95 ± 0.10	3.95 ± 0.35	11.50 ± 0.20
0.2		3.82 ± 0.40	
0.4		4.00 ± 0.05	
1.0	0.90 ± 0.10	3.90 ± 0.10	11.75 ± 0.15

[a] I = 1.0 ($HClO_4$, Na ClO_4)

TABLE 20

ABSORBANCE VS TIME FOR THE AQUATION OF PENTAAQUOMONOBROMO ORGANOCHROMIUM(III) ION

(a) Temperature = 25°C $0.1M\ HClO_4$ $0.9M\ NaClO_4$ Cell length = 5 cm.

Run #1

Time (hrs.)	Absorbance (nm) 360	406	538
00	0.835	0.499	0.584
24	0.782	0.465	0.542
87	0.524	0.315	0.379
111	0.454	0.278	0.326
143	0.364	0.233	0.269
182	0.282	0.198	0.210
210	0.204	0.168	0.149
238.5	0.175	0.154	0.128
∞	0.036	0.077	0.055

Temperature = 25°C $0.1M\ HClO_4$ $0.9M\ NaClO_4$ Cell length = 2 cc.

Run #2

Time (hrs.)	Absorbance (nm) 360	406	538
00	1.283	0.612	1.032
24	1.234	0.575	1.009
48	1.134	0.526	0.934
72	1.094	0.485	0.872
96	0.918	0.427	0.763
120	0.801	0.388	0.657
∞	0.040	0.087	0.052

Table 20 continued.

(b) Temperature = 25°C 1.0M $HClO_4$ Cell length = 2 cm.

Time	Absorbance		
(hrs.)	(nm) 360	406	538
00	1.768	0.767	1.484
24	1.694	0.732	1.419
36	1.637	0.715	1.373
48	1.537	0.669	1.300
72	1.430	0.631	1.219
96	1.327	0.601	1.175
114	1.152	0.510	0.994
∞	0.043	0.109	0.068

(c) Temperature = 29°C 1.0M $HClO_4$ Cell length = 5 cm.

Time	Absorbance		
(hrs.)	(nm) 360	406	538
00	2.092	1.182	1.484
24	1.826	1.030	1.323
48	1.561	0.894	1.140
111	0.921	0.601	0.660
124	0.699	0.505	0.487
156	0.423	0.391	0.268
197	0.175	0.284	0.079
224	0.144	0.254	0.072
∞	0.028	0.125	0.062

TABLE 21

ABSORBANCE VS TIME FOR THE AQUATION OF PENTAAQUOMONOBROMO ORGANOCHROMIUM(III) ION

(a) Temperature = 35°C $0.1M\ HClO_4$ $0.9M\ NaClO_4$ Cell length = 2 cm

Time (hrs.)	Absorbance (nm) 360	406	538
00	0.557	0.260	0.449
12	0.500	0.238	0.407
24	0.437	0.205	0.365
36	0.393	0.190	0.332
48	0.297	0.160	0.248
63	0.204	0.134	0.168
74	0.129	0.113	0.098
∞	0.031	0.048	0.030

(b) Temperature 35°C $0.2M\ HClO_4$ $0.8M\ NaClO_4$ Cell length = 2 cm.

Time (hrs.)	Absorbance (nm) 360	406	538
00	1.326	0.575	1.165
12	1.194	0.515	1.059
23	1.092	0.497	0.962
35	0.992	0.480	0.853
47	0.968	0.455	0.790
59	0.890	0.419	0.710
71	0.844	0.401	0.653
94	0.732	0.362	0.480
118	0.596	0.325	0.320
142	0.492	0.300	0.299
∞	0.040	0.123	0.040

Table 21 continued.

(c) Temperature = 35°C $\quad$ 0.4M $HClO_4$

0.6M $NaClO_4$ $\quad$ Cell length = 2 cm.

Time	Absorbance		
(hrs.)	(nm) 360	406	538
00	0.984	0.432	0.842
12	0.892	0.391	0.771
24	0.820	0.356	0.702
35	0.750	0.320	0.653
59	0.619	0.273	0.548
83	0.516	0.247	0.454
∞	0.033	0.072	0.032

(d) Temperature = 35°C $\quad$ 1.0M $HClO_4$ $\quad$ Cell length = 2 cm.

Run #1

Time	Absorbance		
(hrs.)	(nm)	406	538
00	1.107	0.480	0.928
12	0.940	0.389	0.802
24	0.852	0.369	0.729
36	0.751	0.336	0.632
48	0.667	0.306	0.563
60	0.578	0.277	0.482
72	0.492	0.254	0.408
84	0.419	0.233	0.337
96	0.338	0.215	0.263
108	0.262	0.196	0.196
120	0.195	0.178	0.136
132	0.144	0.162	0.084
∞	0.052	0.089	0.060

Table 21 (d) continued.

Temperature = 35°C 1.0M $HClO_4$ Cell length = 2 cm.

Run #2

Time	Absorbance		
(hrs.)	(nm) 360	406	538
00	0.616		0.491
14.6	0.498		0.407
26.9	0.448		0.372
49	0.350		0.304
75.4	0.251		0.220
123	0.139		0.120
∞	0.021		0.030

TABLE 22

ABSORBANCE VS TIME FOR THE AQUATION OF PENTAAQUOMONOBROMO ORGANOCHROMIUM(III) ION

(a) Temperature = 45°C $0.1M\ HClO_4$
$0.9M\ NaClO_4$ Cell length = 2 cm.

Time	Absorbance		
(hrs)	(nm) 360	406	538
00	0.971	0.315	0.824
2	0.910	0.295	0.729
5	0.821	0.273	0.575
7	0.772	0.252	0.485
9	0.721	0.231	0.392
12	0.653	0.202	0.265
14	0.553	0.162	0.187
∞	0.070	0.101	0.035

(b) Temperature = 45°C $1.0M\ HClO_4$ Cell length = 2 cm.

Time	Absorbance		
(hrs.)	(nm) 360	406	538
00	1.287	0.485	1.124
3	1.183	0.454	1.011
5	1.112	0.433	0.947
7	1.045	0.418	0.885
10	0.948	0.393	0.786
13	0.839	0.358	0.683
16	0.731	0.324	0.581
19	0.442	0.261	0.294
24	0.264	0.209	0.132
∞	0.078	0.110	0.050

showed curvature becoming larger as the reaction approached completion (Figure 18). The plots were reproducible. The curvature was more pronounced when the initial concentration of the complex ion was larger. Monobromoorganochromium(III) ion showed a much greater curvature in the $\ln(A_t - A_\infty)$ vs. time plots than the monochloroorganochromium(III) ion.

The initial rate coefficients for the reaction at different temperatures and hydrogen ion concentrations were obtained in the same manner as in chloro-complex, and were found to be independent of hydrogen ion concentration and wavelengths and are given in Table 23.

The data supports the view that the reaction obeyed a psuedo-first order rate law during the initial period as in the case of monochloroorganochromium(III) ion.

Enthalpy and entropy of activation was calculated as described in the preceeding section. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are given below:

$\Delta H^\ddagger = 17.7 \pm 0.5$ kcal/mole

$\Delta S^\ddagger = -25.2 \pm 1.5$ cal-deg^{-1}mole^{-1}

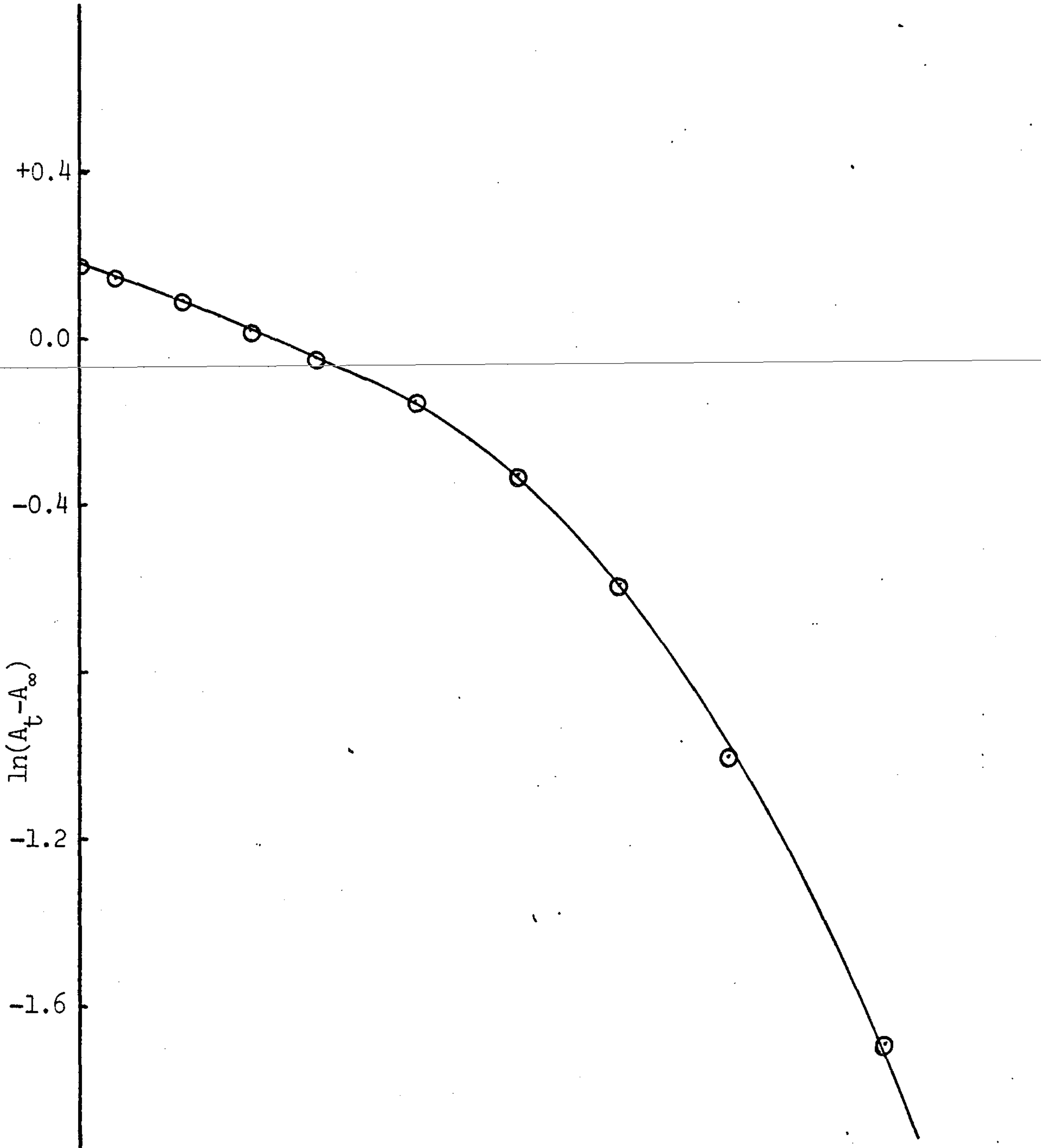


Figure 18: $\ln(A_t-A_\infty)$ vs. Time for the Aquation of Monobromoorganochromium(III) Ion at 45°C and 1.0M $HClO_4$ (λ= 360 nm).

TABLE 23

INITIAL RATE COEFFICIENTS FOR THE AQUATION OF PENTAAQUOMONOBROMOORGANOCHROMIUM(III) AS FUNCTION OF TEMPERATURE AND HYDROGEN ION CONCENTRATION.

$$\frac{-d[\text{complex}]}{dt} = k[\text{complex}]$$

Hydrogen ion Concentration	$k \times 10^6$ sec		
	25°C	35°C	45°C
0.1	8.20 ± 0.15	3.4 ± 0.25	10.8 ± 0.20
0.2		3.35 ± 0.20	
0.4		3.15 ± 0.20	
1.0	8.10 ± 0.15	3.2 ± 0.10	10.50 ± 0.10

DISCUSSION

A. Pentaaquotrifluoromethylchromium(III) ion.

Pentaaquotrifluoromethylchromium ion was formed by the reduction of trifluoromethyl iodide with chromous perchlorate. The mechanism of this reduction ocrresponds to that suggested for other organic halides (7,8,21,22) i.e. the abstraction of an iodide atom to give an organic radical, $\cdot CF_3$, which is captured by another chromous ion.

$$ICF_3 + Cr^{2+} \longrightarrow CrI^{2+} + \cdot CF_3 \qquad (9)$$

$$\cdot CF_3 + Cr^{2+} \longrightarrow CrCF_3^{2+} \qquad (10)$$

Chromous ion reacts rapidly with pentaaquodiiodomethylchromium(III) (23) at 25°C to give pentaaquomonoiodomethylchromium(III) ion but reacts very slowly with $(H_2O)_5CrCF_3^{2+}$ ion without forming difluoro-, or monofluoromethylchromium(III) species. This is probably due to the differences in C-F and C-I bond strengths.

The aquation of the ion $CrCF_3^{2+}$ was followed at different temperatures and hydrogen ion concentrations. The plots of $\ln(A_t - A_\infty)$ vs. time showed that the reaction obeyed a pseudo-first order rate law initially, but curvature appeared after some time as the reaction rate increased. More curvature appeared in less time in lower hydrogen ion concentration (Figure 19). The initial aquation products for $CrCF_3^{2+}$ ion, in acidic aqueous media and under nitrogen atmosphere were hexaaquochromium(III), carbon monoxide, F^- or HF but no CrF^{2+}. Therefore, the following reaction can be written for the initial aquation of $CrCF_3^{2+}$ ion: $(H_2O)_5CrCF_3^{2+} + 2H_2O + H^+ \longrightarrow Cr(OH_2)_6^{3+} + CO + 3HF$ (11)

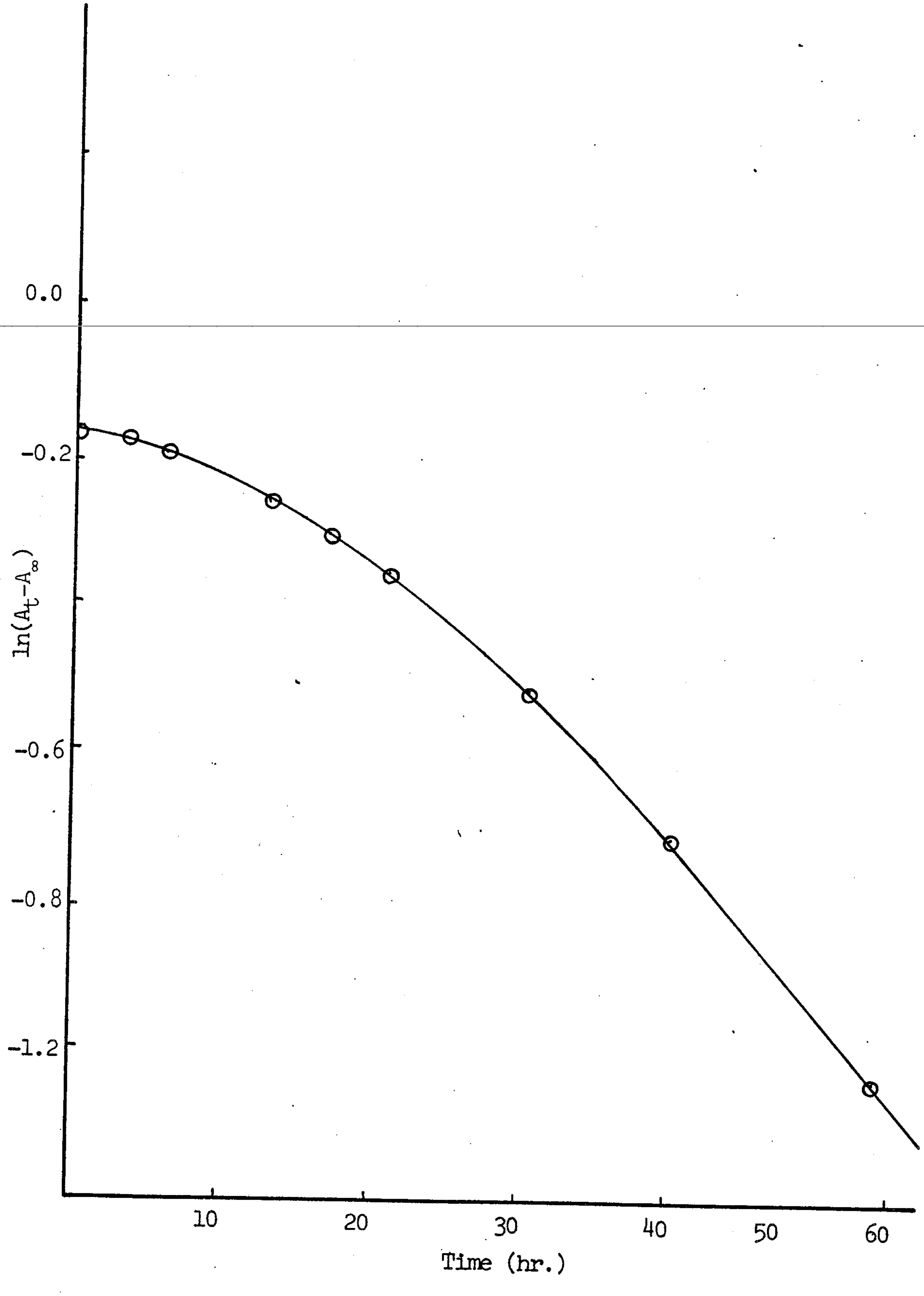


Figure 19-a: $\ln(A_t-A_\infty)$ for the Aquation of $CrCF_3^{2+}$ at 55.2°C and 0.1M $HClO_4$ (λ , 500 nm)

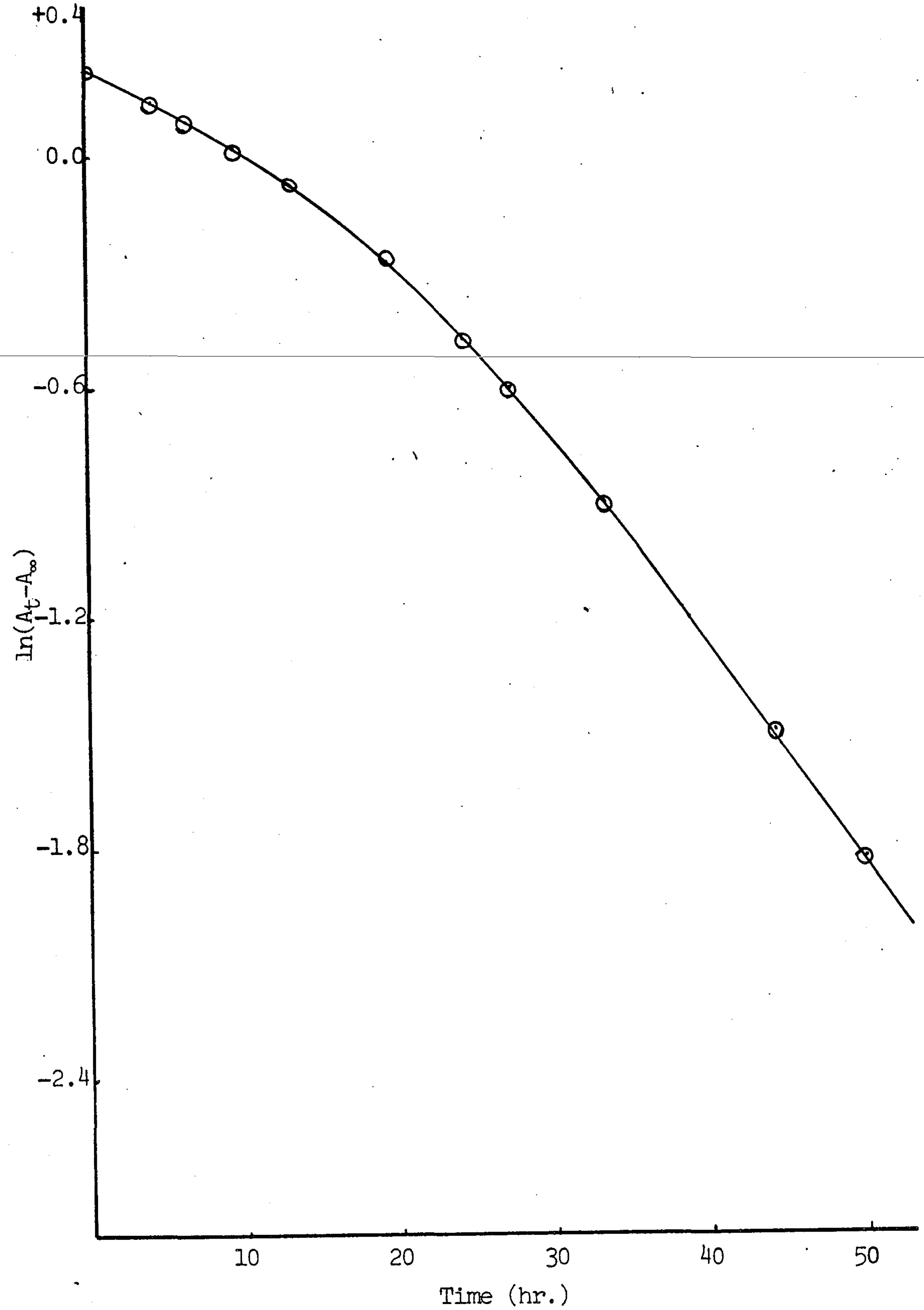


Figure 19-b: $\ln(A_t-A_\infty)$ vs. Time for Aquation of $CrCF_3^{2+}$ at 55.2°C and 1.0M $HClO_4$ (λ, 486 nm).

Table 8, contains a summary of the observed initial rate coefficients, k_{obs}, for the aquation of $CrCF_3^{2+}$ ion. The plot of k_{obs} vs. H^+ ion concentration shows an increase in observed rate coefficients with increase in hydrogen ion concentration. This dependence of observed rate coefficients on hydrogen ion concentration is consistent with two terms in the expression $k_{obs} = k_o + k_1(H^+)$ and two parallel, independent pathways (Figure 20).

The rate coefficients for the aquation of dichloromethylchromium(III) and monochlorochromium(III) species at 45°C are 60 and 20 times greater than the values for $CrCF_3^{2+}$ ion (24). This is evidence that the chromium-carbon bond is much stronger in trifluoromethylchromium(III) ion than in other halomethylchromium(III) species. The rate coefficients for the acid hydrolysis of pentaaquochromium(III) complexes with inorganic ligands (25) at 25°C, are 20-200 fold greater than the extrapolated rate coefficient of $CrCF_3^{2+}$ at 25°C, $6.5 \times 10^{-8} sec^{-1}$. Only fluoropentaaquochromium(III) ion has a lower value for its rate coefficient for aquation. Thus the Cr-C bond in $CrCF_3^{2+}$ is more substitution inert than most bonds between chromium and inorganic ligands.

The aquation products for $CrCF_3^{2+}$ at the beginning of the reaction consisted of hexaaquochromium(III), carbon monoxide and HF but no fluoropentaaquochromium(III); but fluorochromium(III) and difluorochromium(III) along with hexaaquochromium(III), carbon monoxide and HF were present at the completion of the aquation reaction.

The presence of carbon monoxide in the aquation products is strong evidence for the formation of a difluorocarbene in the dissociation

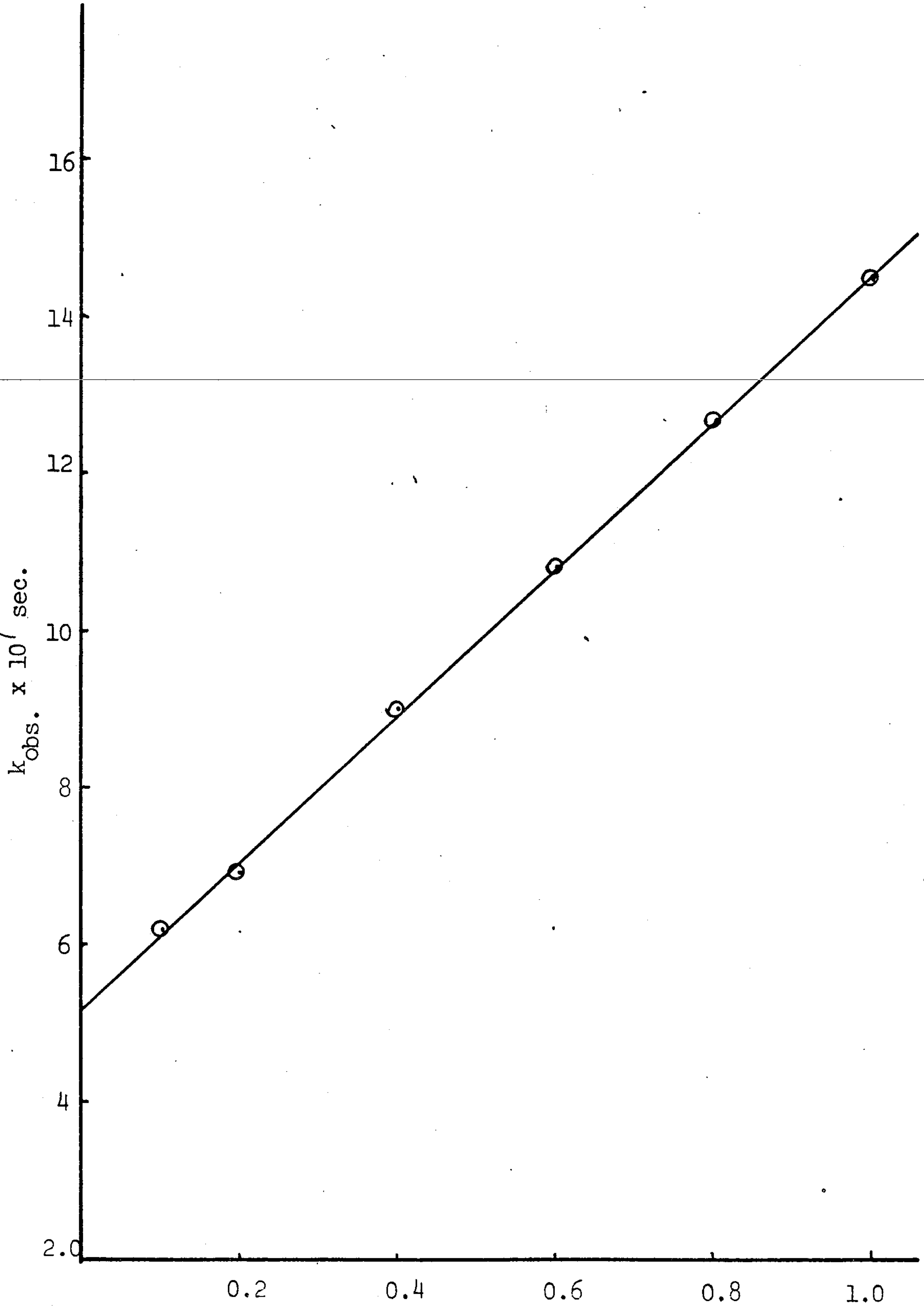
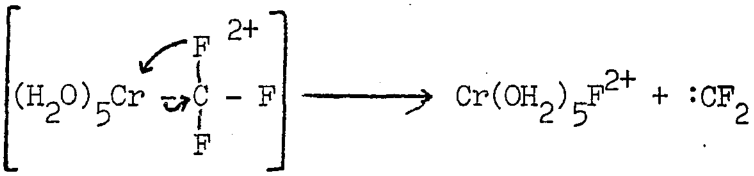


Figure 20: $k_{obs.}$ vs. $[H^+]$ at 45.0°C for $CrCF_3^{2+}$ Ion.

of $CrCF_3^{2+}$ ion. It has been reported (21,26) that dihalocarbenes are readily hydrolyzed by water to give carbon monoxide

$$:CX_2 + H_2O \longrightarrow CO + 2HX \qquad (X = F, Cl, Br, I) \qquad (12)$$

One plausible mechanism for the dissociation of $CrCF_3^{2+}$ which could give difluorocarbene involves the transfer of fluoride ion from carbon to the adjacent chromium, producing fluorochromium(III) ion and a difluorocarbene intermediate which would rapidly react with water to give carbon monoxide (27). This can be shown as

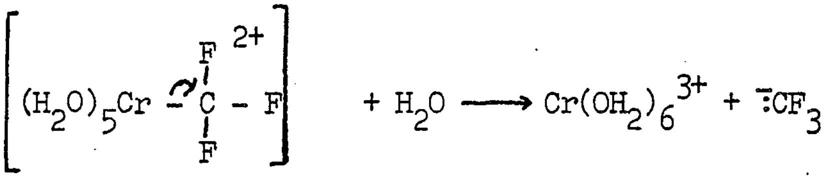


$$\left[(H_2O)_5Cr \rightarrow \overset{F}{\underset{F}{C}} - F\right]^{2+} \longrightarrow Cr(OH_2)_5F^{2+} + :CF_2 \qquad (13)$$

$$:CF_2 + H_2O \longrightarrow CO + 2HF \qquad (14)$$

This mechanism is unlikely due to the fact that it produces fluoropentaaquochromium(III) ion which was not present in the initial products of aquation. Moreover, due to the fact that fluorine can form strong H - bonds with water and hydronium ions, the transfer of fluoride ion might be difficult.

A second possible mechanism which could operate in the aquation reaction is the dissociation of $CrCF_3^{2+}$ to give hexaaquochromium(III) and trifluorocarbanion which could hydrolyze to give carbon monoxide. This could be represented as

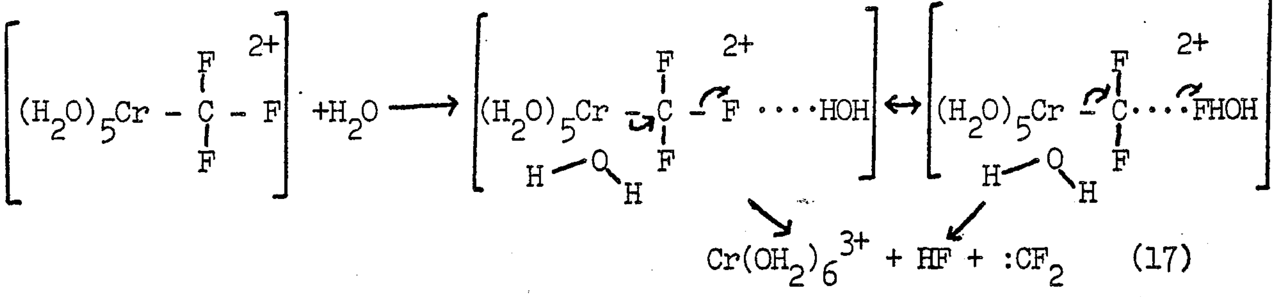


$$\left[(H_2O)_5Cr - \overset{F}{\underset{F}{C}} - F\right]^{2+} + H_2O \longrightarrow Cr(OH_2)_6^{3+} + \bar{:}CF_3 \qquad (15)$$

$$\bar{:}CF_3 + H_2O + H^+ \longrightarrow CO + 3HF \qquad (16)$$

The decomposition of CF_3^- to F^- and $:CF_2$ must be considered since fluorine is the poorest of all the halogens at stabilizing trihalomethyl anions and the best at stabilizing dihalomethylenes (28). These two factors work together to increase the probability that a trifluoromethyl anion, once formed, will decompose to difluoromethylene rather than protonate to produce fluoroform. But if this is true in the present case, it contradicts the findings of Verhoek and coworkers (29). They reported that the decomposition of sodium trifluoroacetate in ethylene glycol and boric acid gives fluoroform in a quantitative yield showing that the trifluoromethyl anion formed initially in their reaction is protonated to give fluoroform. If trifluoromethyl anion is formed as suggested in the above mechanism in the dissociation of $CrCF_3^{2+}$ ion; in acidic solution its most likely fate would be to give fluoroform. The absence of fluoroform in the initial aquation products indicates that this mechanism is not very likely to be operating in the aquation reaction of $CrCF_3^{2+}$ ion.

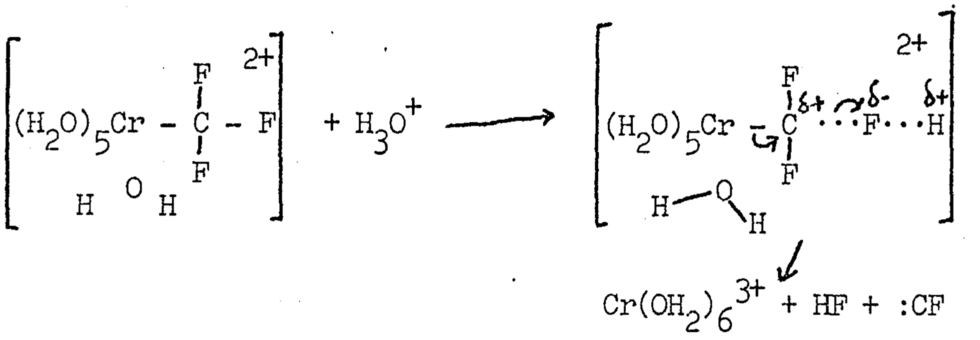
Another mechanism for the dissociation which could operate in the case of $CrCF_3^{2+}$ ion involves the formation of an activated complex in which the dissociation to the products is solvent assisted (11,30). This solvent assisted dissociation of the activated complex takes place in a concerted manner to give hexaaquochromium(III) and difluorocarbene without a trifluorocarbanion intermediate as shown



(17)

$$:CF_2 + H_2O \longrightarrow CO + 2HF \qquad (18)$$

a similar mechanism for the acid dependent pathway could be represented as



$$\left[(H_2O)_5Cr-CF_3 \cdot H_2O\right]^{2+} + H_3O^+ \longrightarrow \left[(H_2O)_5Cr-CF_2\cdots F\cdots H \cdot H_2O\right]^{2+} \longrightarrow Cr(OH_2)_6^{3+} + HF + :CF \qquad (19)$$

$$:CF_2 + H_2O \longrightarrow CO + 2HF \qquad (20)$$

These last mechanisms seem to best fit the initial products and the rate law for the aquation of $CrCF_3^{2+}$ ion. The formation of difluoromethylene is represented as taking place via a concerted mechanism as shown above. This formation of difluoromethylene via a concerted manner has been noticed in the decomposition of chlorodifluoroacetic acid (27).

Further, the enthalpy of activation (19.1 kcal/mole) found for the acid-independent path is 5-10 kcal lower than the enthalpies for the acid hydrolysis of most pentaaquochromium(III) complexes with inorganic ligands (25). This suggests the formation of an activated complex in which dissociation to the products is 'solvent assisted' (11,30). If the solvent does enter the activated complex it would most likely be in a position so as to take advantage of well-known hydrogen bonding of water with fluorine. The entropy for the acid-independent aquation of $CrCF_3^{2+}$ (-27.4 cal/deg-mole) is somewhat more negative than that found for many pentaaquochromium(III) complexes (-5 e.u.) with inorganic ligands (25). This may be due to loss of freedom of movement of a solvent water in the activated complex due to hydrogen bonding of the water with fluorine. The activation parameters for the aquation of $CrCF_3^{2+}$ ion are close to that found by Kochi ($\Delta H^{\ddagger}$ = 16.2 kcal/mole, $\Delta S^{\ddagger}$ = -13.9 e.u.) for the aquation of benzylchromium ion to toluene (9). However, under his conditions the anionic buffer is involved in the reaction mechanism. The enthalpy of activation for the hydrogen-ion-dependent path for $CrCF_3^{2+}$ ion (23.4 kcal/mole) is very close to that of the hydrogen-ion-independent path. The slightly lower entropy (-12.7 cal/deg-mole) for this path could be due to release of H_2O as solvated protons form H-bonds with $CrCF_3^{2+}$.

The aquation products at the completion of the reaction were found to contain large amounts of fluorochromium(III) and difluorochromium(III) ions; whereas these were not formed at initial stages of the reaction (prior to the appearance of curvature). One possible way to account for the formation of CrF^{2+} was that the fluoride ion produced in the initial reaction was replacing a water molecule in hexaaquochromium(III) ion. $Cr(OH_2)_6^{3+} + F^- \longrightarrow Cr(OH_2)_5F^{2+} + H_2O$ (21)

But the larger amounts of CrF^{2+} formed with time at 55.2°C (Table 4a) in the aquation reaction of $CrCF_3^{2+}$ compared to the reaction of $Cr(OH_2)_6^{3+}$ and F^- ions show that CrF^{2+} cannot be the result of the anation reaction (Table 4b).

Addition of fluoride ion to $CrCF_3^{2+}$ solution increased the rate of reaction (Table 10). The aquation products contained large amounts of CrF^{2+} and CrF_2^{1+} when additional fluoride was added. Chloride ion, also, accelerated the reaction slightly. Upon addition of fluoride ion, the orange color of $CrCF_3^{2+}$ solution turned pink immediately in

0.01M perchloric acid. The pink solution was found to contain $FCrCF_3^{1+}$ ion and also some other pink chromium species of zero charge. It was observed that fluoro-substituted trifluoromethylchromium(III) complexes aquate very rapidly. The acid hydrolysis products of $FCrCF_3^{1+}$ are mainly fluorochromium(III) and difluorochromium(III) species.

It was observed that $FCrCF_3^{1+}$ establishes a rapid equilibrium with $CrCF_3^{2+}$ ion in acid solutions. The equilibrium constant for the equilibrium $CrCF_3^{2+} + HF \rightleftharpoons FCrCF_3^{1+} + H^+$ at 25°C was found to be 0.75.

The formation of $FCrCF_3^{1+}$ ion could be explained due to the fact that trifluoromethyl ligand might be exerting a strong labilizing effect on coordinate water molecules cis or trans to it, which then undergoes an exchange with fluoride ion present in solution. The fact that the addition of excess of fluoride ion to $CrCF_3^{2+}$ ion gives immediately a 1+ charge complex and also a zero charge chromium(III) species support this labilizing effect of trifluoromethyl ligand. The rate of exchange of water in $Cr(OH_2)_6^{3+}$ at 25°C is $3.3 \times 10^{-6} sec^{-1}$ (25) which is very slow when compared to the rapid formation of 1+ charge chromium(III) species. Like fluoride ion, azide and thiocyanate ions showed similar effects. This kind of labilizind effect for some ligands in octahedral complexes of chromium(III) and rhodium(III) is very common (31,32). This has been postulated for pentaaquochromium(III) complexes having inorganic ligands such as iodide (31). The exchange of water molecules with fluoride ion is represented by the reactions:

$$(H_2O)_5CrCF_3^{2+} + HF \longrightarrow (H_2O)_4FCrCF_3^{1+} + H^+ + H_2O \qquad (22)$$

$$(H_2O)_4FCrCF_3^{1+} + HF \longrightarrow (H_2O)_3F_2CrCF_3^{0} + H^+ + H_2O \qquad (23)$$

and is supported by the separation of $FCrCF_3^{1+}$ and $FCrCF_3^{o}$ ions from the reaction mixture of $CrCF_3^{2+}$ with added fluoride ions. Another important observation was that $FCrCF_3^{1+}$ was separated from the aquation reaction of $CrCF_3^{2+}$ in 0.1M and 0.05M perchloric acid solutions at 25°, 45° and 55°C.

The fact that the curvature in the plots of $\ln(A_t-A_\infty)$ vs. time for the aquation of $CrCF_3^{2+}$ ion, does not appear immediately suggests that the fluoride ion is first produced in the aquation reaction and then combines with $CrCF_3^{2+}$ ion to give $FCrCF_3^{1+}$ ion. Therefore, the incorporation of fluoride ion into the substantial fraction of the reaction products, as CrF^{2+} and CrF_2^{1+}, might be explained as resulting from the prior formation of some $(H_2O)_4FCrCF_3^{1+}$ ion which then aquates rapidly to give CrF^{2+} and CrF_2^{1+} species. This sequence of the reactions in the aquation of $CrCF_3^{2+}$ ion is represented below

$$(H_2O)_5CrCF_3^{2+} + 2H_2O \xrightarrow{k_o} Cr(OH_2)_6^{3+} + CO + 2HF + F^- \qquad (24)$$

$$(H_2O)_5CrCF_3^{2+} + 2H_2O + H^+ \xrightarrow{k_1} Cr(OH_2)_6^{3+} + CO + 3HF \qquad (25)$$

$$(H_2O)_5CrCF_3^{2+} + HF \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (H_2O)_4FCrCF_3^{1+} + H^+ + H_2O \qquad (26)$$

$$3(H_2O)_4FCrCF_3^{1+} + 6H_2O + 6H^+ \longrightarrow Cr(OH_2)_6^{3+} + (H_2O)_5CrF^{2+} + (H_2O)_4CrF_2^{1+} + 3CO + 12HF \qquad (27)$$

This mechanism best fits the rate law, reaction products, kinetic data, activation parameters and a strong labilizing effect of trifluoromethyl ligand.

This strong labilizing effect has been observed in the organic ligands derived from other organic halides like haloforms and dihalo methanes in the present work. Further work is strongly suggested to investigate fully this labilizing effect of a Cr–C sigma bond.

B. Pentaaquomonohalogenoorganochromium(III) ions

The monohalogenoorganochromium(III) species were formed by the reduction of carbon tetrachloride and carbon tetrabromide with chromium(II) perchlorate. When solutions of chromium(II) were added to carbon tetrahalide, a deep red color developed immediately which was probably due to $CrCX_3^{2+}$. The mechanism for this reduction of carbon tetrahalides probably corresponds to that suggested for many reactive halides (7,8,21,22) i.e. the abstraction of a halogen atom by chromous ion to give an organic radical which is captured by another chromous ion.

$$CX_4 + Cr^{2+} \longrightarrow CrX^{2+} + \cdot CX_3 \qquad (28)$$

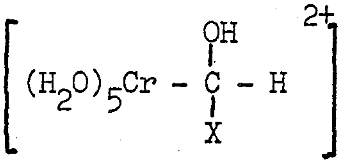
$$\cdot CX_3 + Cr^{2+} \longrightarrow \underset{\text{(deep red)}}{CrCX_3^{2+}} \qquad (X = Cr,\ Br) \qquad (29)$$

This deep red color then faded in a matter of minutes to bluish-gray color. This bluish-gray solution, when passed through an ion-exchange column, DOWEX 50W-X8, 100-200 mesh in hydrogen form, under nitrogen atmosphere gave a pink organochromium(III) species of 2+ charge.

This pink species has a chromium:carbon:halide ratio of 1:1:1 but is definitely not monohalomethylchromium(III) which has been synthesized by an independent procedure. The uv-visible spectra of these organochromium(III) species show unusually high values for molar absorbancy indices (chloro-complex E_{536}, $154M^{-1}cm^{-1}$; bromo-complex E_{538}, $128M^{-1}cm^{-1}$) in the 500 nm region. The molar absorbancy indices for other known compounds having a chromium-carbon bond in the 515 nm - 540 nm range vary between $20M^{-1}cm^{-1}$ and $45M^{-1}cm^{-1}$ (8,11), whereas these values for chromium(III) complexes having an inorganic ligand range from 7 - $14M^{-1}cm^{-1}$ (15).

The products of aquation are carbon monoxide, formaldehyde, formic acid, hexaaquochromium(III) ion and halide ion. Chromium(II) was observed in the aquation products of monochloroorganochromium(III) ion whereas carbon dioxide was found in monobromoorganochromium(III) aquation products. It was observed that the aquation reaction obeys a first order rate law for 50-60% of the reaction and then the rate is accelerated as the reaction proceeds (Figures 21 and 22). The acceleration in the aquation rate with time for monochloroorganochromium(III) complex could be caused by chromium(II) which might be formed by the initial homolytic cleavage of the chromium-carbon bond. Chromium(II) is known to very rapidly reduce monoiodomethylchromium(III) ions (23). However, large negative values of $\Delta S^{\ddagger}$ (-27.1 cal/deg-mole) found in the present work do not agree with the large positive values of $\Delta S^{\ddagger}$ (+37 cal/deg-mole) reported for a homolytic cleavage of benzilbentaaquochromium(III) ion (33).

The identification of the pink organochromium(III) species could not be achieved but there are several possibilities which fit the observed chromium:carbon:halide ratio. These are

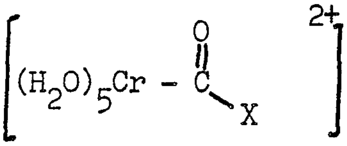


$$\left[(H_2O)_5Cr - \overset{OH}{\underset{X}{C}} - H\right]^{2+}$$

1

α-haloalcohol

as ligand



$$\left[(H_2O)_5Cr - \overset{O}{\overset{\|}{C}} - X\right]^{2+}$$

2

acyl halide

as ligand

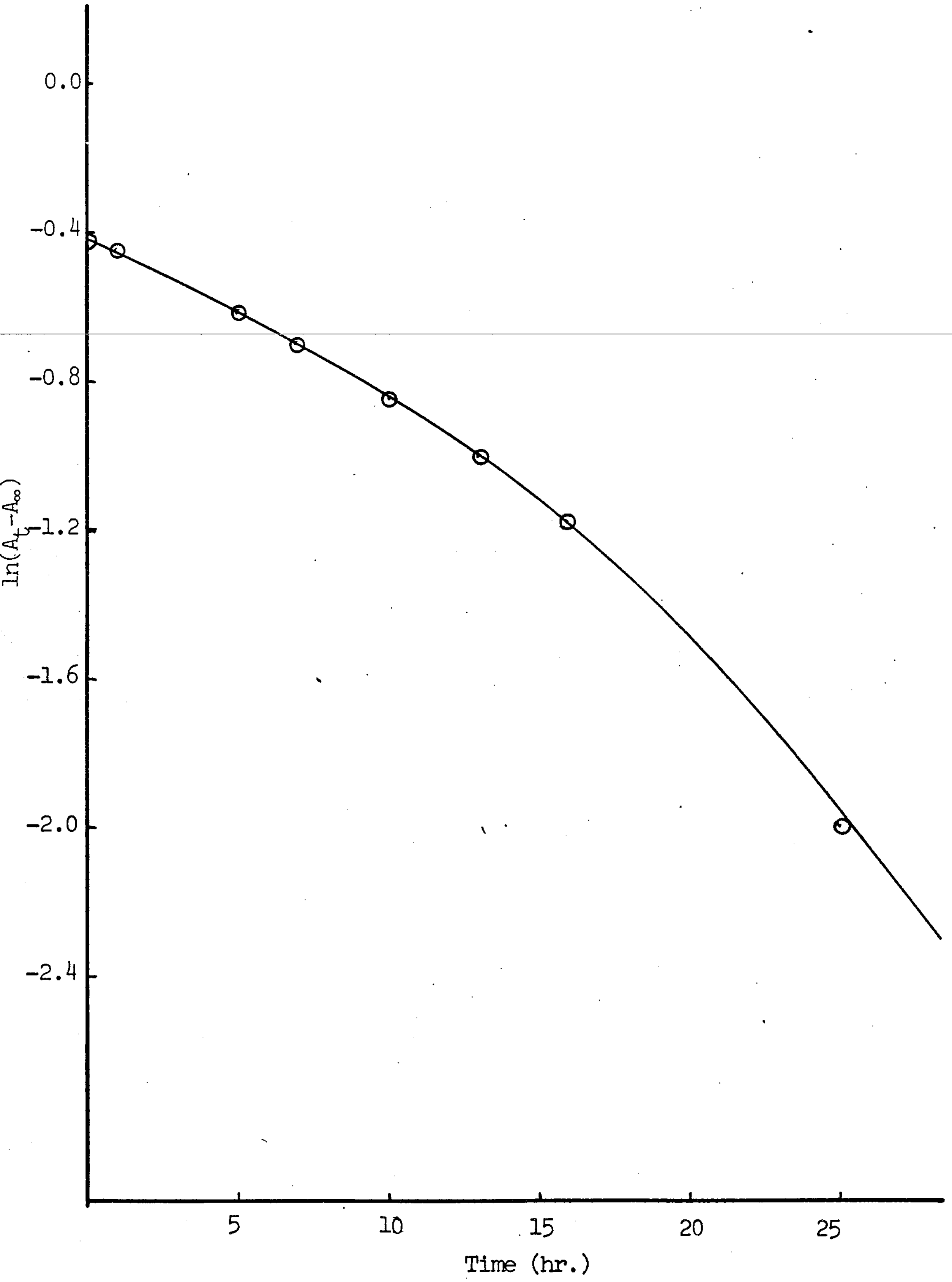


Figure 21: $\ln(A_t - A_\infty)$ for Aquation of Monochloroorganochromium(III) at 45°C and 1.0M $HClO_4$ (λ , 536 nm).

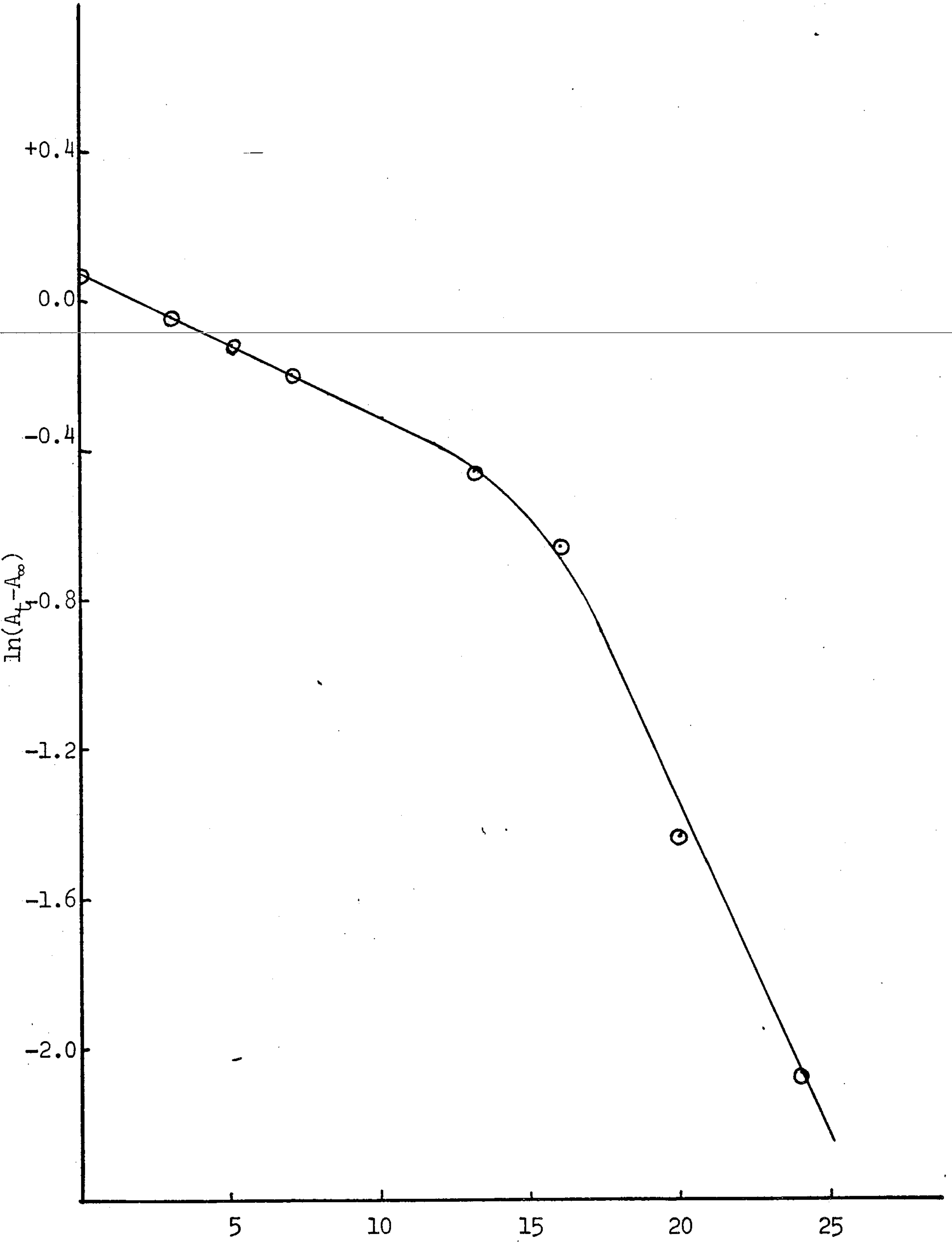


Figure 22: $\ln(A_t - A_\infty)$ vs. Time for Aquation of Monobromoörganochromium(III) Ion at 45°C and 1.0M $HClO_4$ (λ = 538 nm).

The pink organochromium species show unusually high absorbancies in the 500 nm region as compared to the other chromium-carbon complexes. Structure 1 contains a Cr-C sigma bond and should give a spectrum similar to other pentaaquochromium(III) complexes with organic ligands. The unusual spectra of these species suggests that structure 1 is not a very good choice for these species. Structure 2 best accounts for the unusual spectra of these species, since carbon has different hybridized orbitals than in any known pentaaquoorganochromium(III) complex.

Another evidence for structure 2 is that the $CrCX_3^{2+}$ ion formed in the initial stage of the reduction of carbon tetrahalides with Cr(II) may be hydrolyzed to give complex (structure 2) in a similar way as the acid hydrolysis of 1,1,1-trihalides, RCX_3 (X = Cl, Br, I), gives $R - \overset{O}{\overset{\|}{C}} - X$. Generally, the acyl halides are not stable compounds in aqueous acidic solutions. But in certain cases, these do form stable compounds when they are shielded with a charge as in this case. Therefore, structure 2, for the pink organochromium species is possible.

Further study is suggested in order to establish the identity of these haloorganochromium(III) species.

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