THE KINETICS OF HYDROLYSIS OF TRANS-DIFLUOROTETRAMMINE-CHROMIUM (III) ION IN VARIOUS CONCENTRATED ACID SOLUTIONS

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Abstract

The rate of hydrolysis of trans -$[Cr(NH_3)_4F_2]^+$ was obtained as a function of acid concentration in perchloric, sulfuric and nitric acid at 30°C. The results have been analyzed by the treatment of Bunnett and Olsen. Values of the parameter ∅ in Olsen equation are consistent with the participation of water as a proton-transfer agent in the rate-determining step. The Arrhenius plot for perchloric acid was linear, with an activation energy of 19.8 ± 0.8 KCal K^{-1} $mole^{-1}$.

Introduction

Acid-catalysed reactions occur for the replacement of ligands which are strongly basic or have strong tendency to hydrogen bond, e.g. F^-, NO_2^-, ONO^-, N_3, CN^-, CO_3^{2-} etc., and also for flexible chelate or multidentate ligand complexes e.g. $[Fe(bipy)_2]^{2+}$ (1) $[Ni(en)_3]^{2+}$(2). The acid hydrolysis of trans - $[Cr(AA)_2F_2]^+$ where, AA=en, pn, tn, bipy, phen, have been investigated [3,4]. In all cases, no limiting maximum rate constant was observed.

A similar detailed investigation on the difluorotetrammine chromium (III) complex has not been carried out, although the ionization ratio, I, ($I = [\frac{BH^+}{B}]$ (where $[BH^+]$ and [B] are the concentrations of the protonated and unprotonated complex, respectively,)) of this complex has been measured by spectrophotometric method.

This paper presents a study of acid hydrolysis of difluorotetrammine chromium (III) ion in different concentrated acids.

Keywords: Ethylenediamine (en); Trimethylenediamine (tn); 1,10 - phenanthroline (phen); Propylenediamine (pn), 2,2 - bipyridine (bipy)

Experimental Section

Preparation

Cis and trans-difluorotetrammine chromium (III) iodide

The method of Shaffer [5] was used for the preparation of this salt. In this procedure, difluorotetrapyridine chromium (III) iodide (6g, 0.021mol) was heated overnight in autoclave at 100°C with liquid ammonia (20ml) giving a mixture of cis and trans-diflurotetrammine chromium (III) iodide which was washed with small portions of methanol and extracted on the filter with 20ml of hot 0.1M hydrochloric acid (70°C).

Trans - $[Cr(NH_3)_4F_2]$ I was isolated as the least soluble component of cis-trans iodide as follows:

Trans- difluorotetrammine chromium (III) iodide

A mixture of cis and trans- $[Cr(NH_3)_4F_2]$ I (8.7g, 0.03mol) was dissolved in the least amount of water which had been acidified with a few drops of hydrochloric acid at 70°C, then sodium iodide (2.5g) was added. After cooling, the product was filtered off. This was termed as the "first batch". Yield 5.0g. To the filtrate more sodium iodide (2.5g) was added. On cooling, a second batch which consisted of violet crystals was collected.

The first batches (5g) were taken again and dissolved in the least amount of acidified water with sodium iodide added (1.3g). After cooling, the pure trans - $[Cr(NH_3)_4F_2]$ I was collected. Yield (2.8g). The same procedure was carried out on the second and third batches, until two isomers were isolated. The least soluble isomer was the trans compound. The cis compound was purified by the recrystallization of the "later batches".

Trans-difluorotetrammine chromium (III) perchlorate

Crude trans - $[Cr(NH_3)_4F_2]$ I (5.7g), 0.02mol) was dissolved in water (20 ml) at 60°C and a solution of sodium perchlorate (4.9g, 0.04mol) in water (5 mol) was gradually added. After cooling to room temperature the perchlorate salt was filtered off and washed with cold water. The product was recrystallised from water with a temperature range from 60°C to 0°C. Yield (5.0g).

Anal. Calc. For trans - $[Cr(NH_3)F_2]ClO_4$: Cr, 20.2; N, 21.8; H, 4.6.

Found: Cr, 20.1; N, 21.63; H, 4.73.

Aquotetrammine fluorochromium (III) perchlorate

The complex trans-difluorotetrammine chromium (III) perchlorate (1.0g) was dissolved in perchloric acid (72%, 5mol) and the filtered solution was allowed to stand for 1 hour at room temperature.

The solution was diluted dropwise with water (2cm^3) and cooled to 0°C in an ice-bath. Violet-red crystals were filtered off, washed with alcohol and diethyl ether and dried.

Anal. Calc. For trans- $[Cr(NH_3)_4(H_2O)F](ClO_4)_2$: Cr, 14.62; N, 15.74; H, 3.93.

Found: Cr, 14.60; N, 15.7; H, 3.91.

Kinetic Measurements

All kinetic measurements were made spectrophotometrically. The reaction solvents were prepared in polythene bottles. A weighed amount of standard stock concentrated acid was placed in the bottle and water was carefully added. When the mixture had cooled, the bottle was reweighed. Thus the percentage by weight of the acid could be calculated and the molarity was deduced with the aid of density tables. The polythene bottle was placed in the thermostat to within 0.1°C of the desired temperature, with exclusion of light to avoid possible photochemical effects. A weighed amount of complex was introduced on a polythene boat, the bottle was again stoppered and the contents shaken rapidly whilst still in the thermostat to ensure that the solution was homogeneous. Aliquot portions (e.g 10 ml) were withdrawn at timed intervals using a polythene pipette. The samples were rapidly cooled by running them into polythene tubes in a cold bath (-30°C). The samples were carefully diluted whilst still in the bath, followed by dilution with water to standard volume (e.g. 25 ml). The optical density at 377 nm was measured using a shimadzu uv-vis spectrophotometer, model 160A using 1 cm silica cell.

Results

The cis-trans isomers of difluorotetrammine chromium (III) iodide differ slightly in colour, with cis arrangement being slightly reddish purple while the trans form is more orange. As would be expected for trans-isomer, solubility differences exist in aqueous solution, with the iodide of the trans complex exhibiting a lower solubility than the corresponding cis material. The visible absorption spectra of the two isomers are shown in Figure (1).

When trans - $[Cr(NH_3)_4F_2]ClO_4$ is dissolved in concentrated aqueous solutions of strong acids e.g. 12 M perchloric acid or 18 M perchloric acid, there is an immediate change in the visible and ultraviolet absorption spectrum.

As shown in Figure 2 this spectral change is reversible

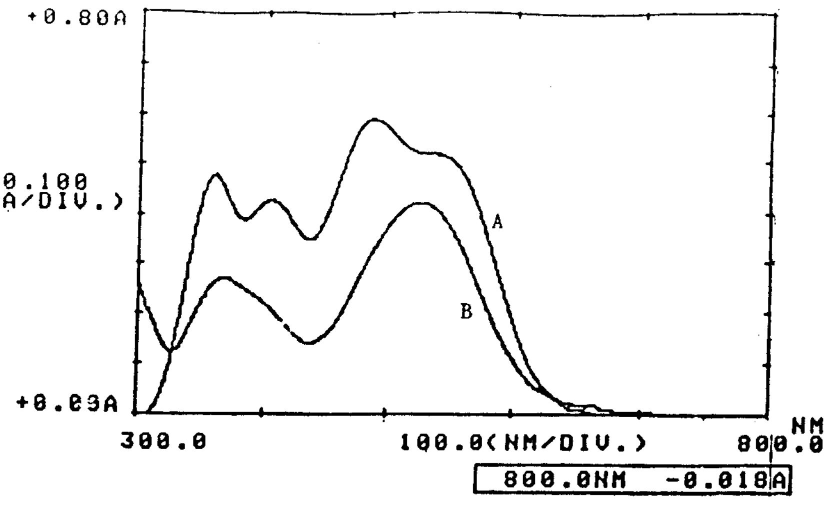

Figure 1. Visible absorption spectra of ...trans - $[Cr(NH_3)_4F_2]^+$ in Water (A), and ... cis -$[Cr(NH3)_4F_2]^+$ in water (B)

if the solution is carefuly diluted. This reversible colour change may be attributed to a reversible protonation of the complex, i,e.

trans-$[Cr(NH_3)_4F_2]^+ + H_3O^+ \rightarrow$ trans$[Cr(NH_3)_4F(HF)]^{2+} + H_2O$

The product of the primary step in the acid hydrolysis of the complex is trans-$[Cr(NH_3)_4F(H_2O)]^{2+}$.

Replacement of the second fluoro-group appears to be very slow. The corresponding aquofluoro-complex may be isolated in good yield in a very pure state.

First-order rate constants were obtained as a function of acid concentration in perchloric, sulfuric and nitric acids at 30°C. The data are listed in Table 1.

Bunnett and Oslen described the acid catalysed reactions by the equation;

$$\text{Log}_{10}K_1 + H_0 = \varnothing\,(H_0 + \log_{10}C_{H^+}) + D \qquad (1)$$

Where K_1 is the first-order rate constant at a given acid concentration, H_0 is the Hammett acidity function of that concentration. The parameter $\varnothing$ is the slope, D is the intercept of the plot of the left side of equation. 1 vs. the right side.

Figure 3 shows a graph of the data according to equation. 1 and the values of $\varnothing$ for acids are presented in Table II. Note that in three acids $\varnothing$ varies from 0.85 to 0.95 in all cases. These values are consistent with the participation of water as a proton-transfer agent in the rate-determining step.

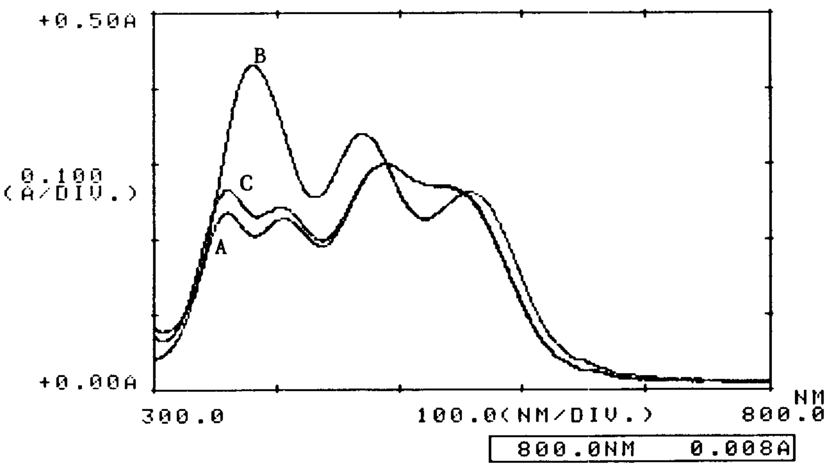

Figure 2. Effect of acid and dilution on the visible and ultraviolet absorption spectra of trans $[Cr(NH_3)_4F_2]ClO_4$

A: trans-$[Cr(NH_3)_4F_2]ClO_4$ in water

B: trans-$[Cr(NH_3)_4F_2]ClO_4$ in $HClO_4$ (12.OM)

C: as B, but diluted after 10 sec.

* **Table 1.** Pseudo-first-order rate constants for hydrolysis of trans-difluorotetrammine chromium (III) in different acids at 30°C

$[HClO_4]$ M	$10^4K/s^{-1}$	$[H_2SO_4]$ M	$10^4K/s^{-1}$	$[HNO_3]$ M	$10^4K/s^{-1}$
2.00	0.71± 0.03	2.04	0.47± 0.06	2.01	1.07± 0.1
3.97	0.88± 0.09	4.17	1.17± 0.2	4.05	1.48± 0.1
4.91	2.35± 0.1	6.33	2.14± 0.2	5.07	1.61± 0.2
6.01	3.87± 0.1	7.43	2.68± 0.6	6.07	2.56± 0.2
6.96	5.29± 0.6	8.51	3.07± 0.4	7.10	2.83± 0.3
8.03	7.60 ± 0.5	9.60	3.53± 0.5	8.10	3.59± 0.5
9.3	8.96± 0.7	10.71	6.34± 0.6	9.08	4.20± 0.5
10.13	12.29± 0.7	11.75	9.71± 0.7	10.06	5.80± 0.6
11.23	19.28± 0.7	12.25	13.48± 0.7		
		12.89	15.16± 0.7		

*The values quoted are the mean and range of at least three determinations.

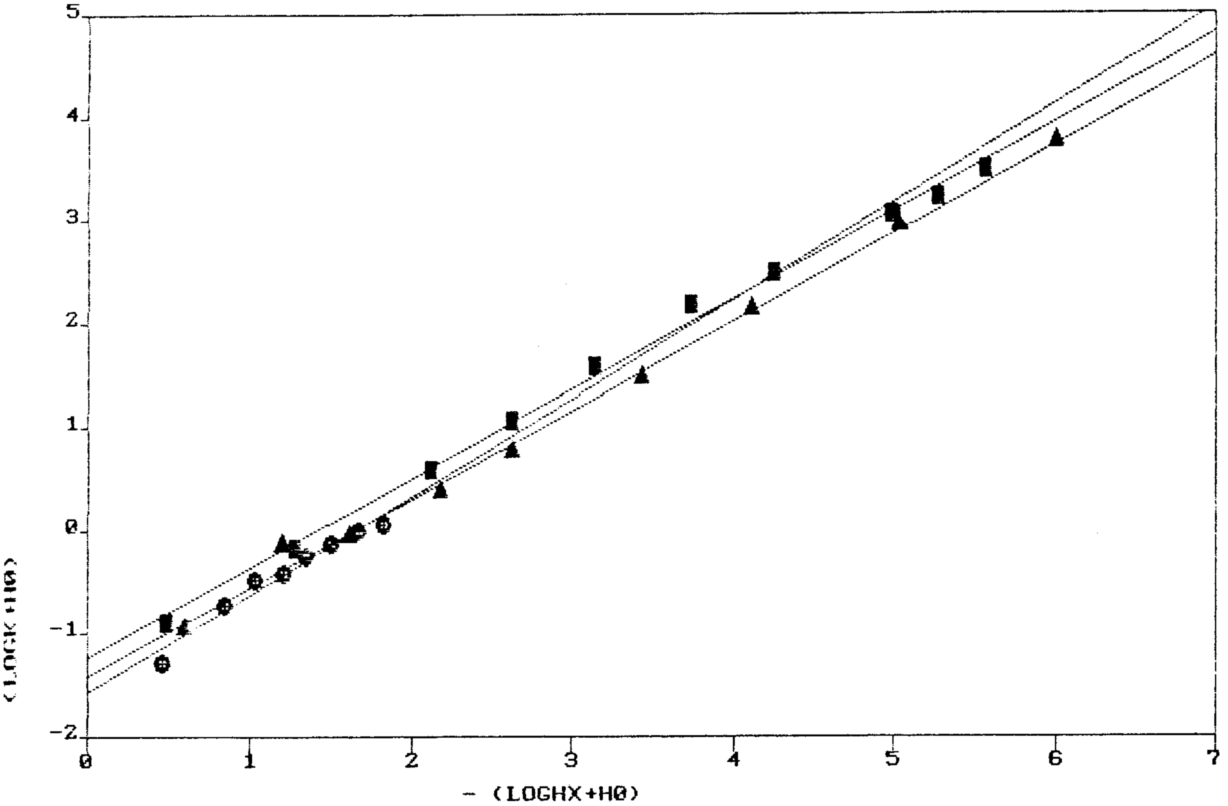

Figure 3. Plots of Log $K_{obs} + H_0$ vs Log(acid) H_0 for trans-$[Cr(NH_3)_4F_2]^+$ ion in acid solutions at 30.0°C. ▲, $HClO_4$; ■, H_2SO_4; ●, HNO_3

THE REGRESSION POLYNOMIAL OF LINE 1-
(-1.412E + 00) + (8.561E - 01)*x
THE VARIANCE - 9.356E - 03

THE REGRESSION POLYNOMIAL OF LINE 2-
(-1.226E + 00) + (8.633E - 01) *x
THE VARIANCE - 6.237E - 03

THE REGRESSION POLYNOMIAL OF LINE 3-
(-1. 575E + 00) + (9.506E - 01) *x
THE VARIANCE - 5.914E - 03

Table II. Values of ∅ for hydrolysis of trans - $[Cr(NH_3)_4F_2]^+$ in three acids at 30°C

Acid	$Conce_{(M)}$ range	∅
Perchloric	2- - - -11.23	0.85
Sulfuric	2- - -12.89	0.86
Nitric	2- - 10.06	0.95

Activation energy data for hydrolysis of trans - $[Cr(NH_3)_4F_2]^+$ in perchloric acid

Table III. Variation of K_{obs} with temperature for hydrolysis of trans -$[Cr(NH_3)_4F_2]^+$ in 5.0 M perchloric acid

Temp	$10^5 K sec^{-1}$
283.2	1.25 ± 0.13
293.2	5.75 ± 0.4
308.2	23.49 ± 0.73

The first-order rate constant was determined as a function of temperature in 5.0 M perchloric acid. These data are listed in Table III and the Arrhenius plot is shown in Figure 4.

Discussion

Bunnett and Olsen proposed that acid catalysed ractions could be described by the equation:

$$\mathrm{Log}\,K_{obs} + H_0 = \varnothing\,(H_0 + \mathrm{Log} H_3O) + \mathrm{Log}_{10}\left(\frac{K_I}{K_{SH^+}}\right) \text{ where}$$

K_{obs} is the first order rate constant, H_0 is the value of the Hammett acidity function for that concentration, and ∅ is the slope of plots of $\mathrm{Log}K_{obs} + H_0$ vs $\mathrm{Log}H_3O^+ + H_0$.

Bunnett *et al.* [6] examined the validity of this equation for many organic reactions and suggested that plots $\log(K_{obs} + H_0)$ against $H_0 + \mathrm{Log}H_3O^+$ are linear and the ∅ parameter could be used as a criterion for reaction mechanism.

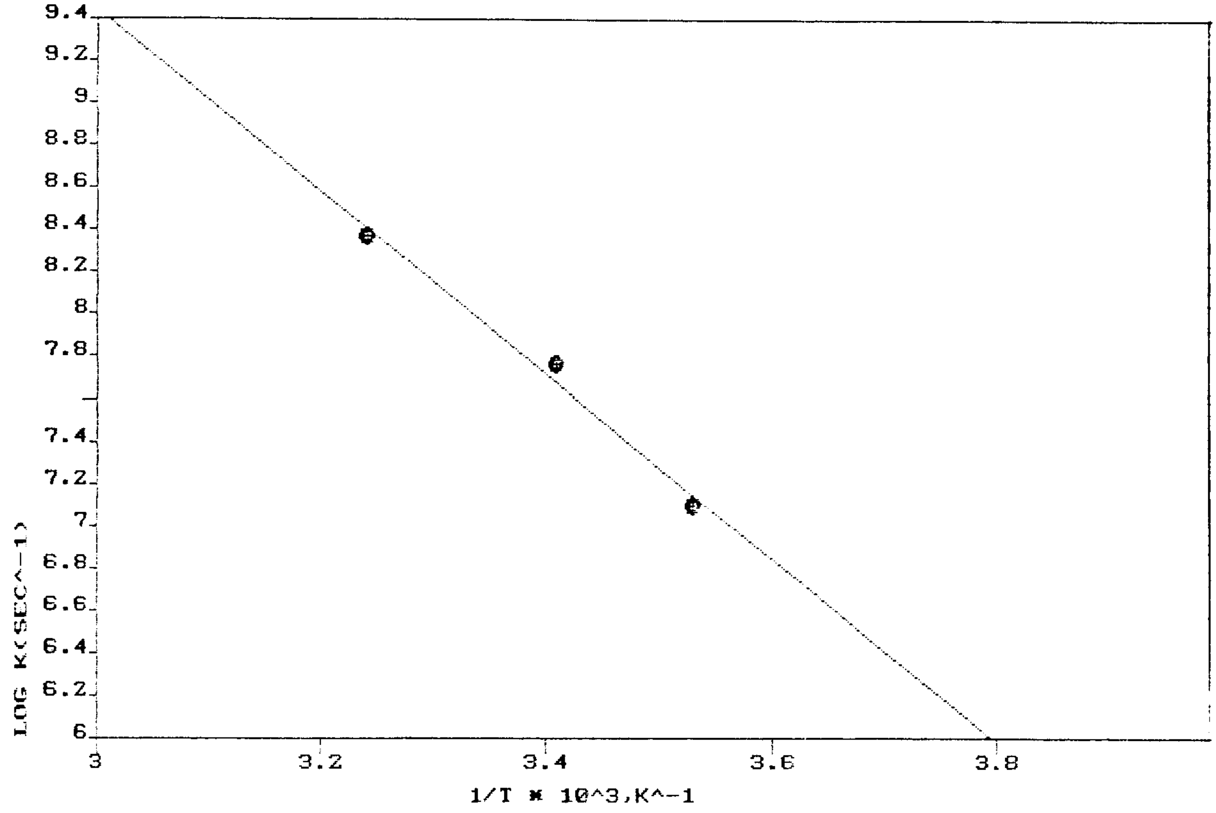

Figure 4. Arrhenius plot for the hydrolysis of trans-$[Cr(NH_3)_4F_2]^+$ in perchloric acid_From the Arrhenius plot, activation energy of 19.8±0.8 KCal for 5.0M acid is obtained.

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THE REGRESSION POLYNOMIAL OF LINE 1-
(2.244E + 01) + (-4.330E +00) *x
THE VARIANCE - 3.941E - 03
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The mechanistic interpretation of $\varnothing$ values is summarised below for substrates protonated on oxygen and nitrogen.

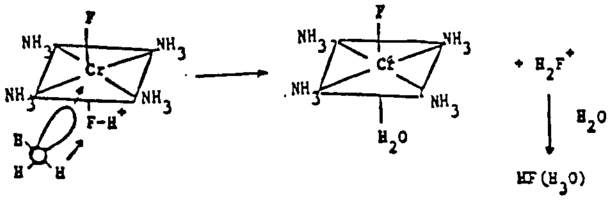
$0.34<\varnothing<0$ Water is not involved

$0.18<\varnothing<0.47$ Water acting as nucleophile

$\varnothing>0.47$ Water acting as a proton transfer agent

The $(\log K_{obs}+H_0)$ against $(H_0+\log H_3O^+)$ for trans - $[Cr(NH_3)_4F_2]^+$ is linear over a wide range of acidic solutions and value of $\varnothing$ is varied between 0.82-0.95 for different acids, Table II. The observed $\varnothing$ values are consistent with water acting as a proton - transfer agent, in the rate determining step.

Therefore, the mechanism of the acid catalysed hydrolysis of the complex may be as follows:



$$[F(NH_3)_4Cr\text{-}F] + H_3O^+ ====== [F(NH_3)_4Cr\text{-}FH]^{2+} + H_2O$$

This would also explain the observations made by previous workers [7,8] that the acid catalysed equations all proceed with retention of configuration.

Furthermore, De Jovin *et al.* [3] suggested such retention of configuration in the acid - hydrolysis of trans - $[Cren_2F_2]^+$in a fairly concentrated acidic solution (H^+ 4.0 M).

The H_3O^+ ion would have to approach the complex ion adjacent to the leaving fluoro-group. This would allow the proton to bond with the HF-ligand and also ensure retention of geometric configuration.

Considering the pre-equilibrium protonation of the fluoro complex and because of the great protonating effect of $HClO_4$, it is reasonable to expect that the rate of reactions in perchloric acid should be greater than in the other two acids.

Activation energies plus rate constants provide more reliable information about a reaction than rate alone, since a compound with a higher activation energy than another will accelerate its rate more with increasing temperature. In fact it may react more slowly than other compounds at low temperatures and more rapidly at high temperatures. This is only possible, however, if the frequency factor A, in the expression $K= A\exp = \frac{-E}{RT}$ is greater for the first compound, Thus, the Arrhenius parameter was evaluated for trans - $[Cr(NH_3)_4F_2]^+$ ion at 5.OM $HClO_4$ at three different temperatures, and collected in Table IV with Arrhenius parameters for some other compounds.

Table IV. Arrhenius parameters for acid catalysed hydrolysis of some transition metal complexes

Complex	Acid	$(\mathrm{Kcal}^{E}\mathrm{mol}^{-1})$	LogA	Ref
$[Rh(NH_3)_5N_3]^{2+}$	$HClO_4$	24.6	9.6	(9)
$[Cr(NH_3)_5N_3]^{2+}$	H_2SO_4	19.7	12.6	(10)
trans-$[Coen_2(No_2)_2]^+$	$HClO_4$	24.9	13.7	(11)
trans-$[Coen_2F_2]^+$	HNO_3	29.0	—	(8)
trans-$[Cr(NH_3)_4F_2]^+$	$HClO_4$	19.8	16.4	

A comparison of activation energies (in KCal. mol^{-1}) for trans - $[Cr(NH_3)_4F_2]^+$ with Co (III) Rh (III) complexes shows that chromium (III) complexes have lower activation energy than cobalt (III). This is easily understandable, since the reaction being bimolecular (SN_2CA), the replaced group is -FH instead of -F. The Cr-F bond is expected to be more weakened than Co-F as a result of hydrogen-bonding to form Cr-FH, Cr (III) is a softer acid than Co (III), thus explaining the relatively high rate and lower activation energy.

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