

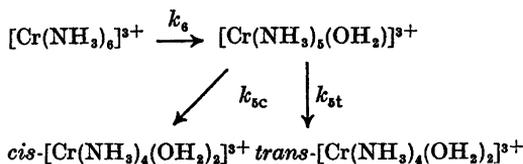
Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. III. The Acid Hydrolysis of Pentaammineaqua- and Hexaamminechromium(III) Ions in Aqueous Perchloric Acid

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The acid hydrolysis of pentaammineaqua- and hexaamminechromium(III) cations has been investigated in 0.5 to 1.0 M perchloric acid at an ionic strength of 1.0, adjusted by the addition of sodium perchlorate, in the temperature range 60–80 °C.

In the possible reaction scheme:



no evidence for the production of the *trans*-tetraamminediaquachromium(III) ion was found. For the well defined kinetic paths rate constants at 70 °C and activation energies were found to be:

$$\begin{array}{l}
 k_{sc}: (47.2 \pm 0.8) \times 10^{-6} \text{ s}^{-1}, 27.1 \pm 0.4 \text{ kcal/mol,} \\
 k_a: (47.5 \pm 1.4) \times 10^{-6} \text{ s}^{-1}, 27.6 \pm 0.8 \text{ kcal/mol,}
 \end{array}$$

whereas for k_{st} an upper limit for the rate constant at 70 °C of $1.0 \times 10^{-6} \text{ s}^{-1}$ (taken as mean value plus twice the standard deviation), was found.

In the acidity range studied no dependence of these rate constants upon the hydrogen ion concentration was found.

It is concluded that the isomerization and ammine hydrolysis reactions of ammineaqua-chromium(III) complexes proceed *via* an intermediate of increased coordination number with an approximate pentagonal bipyramidal structure, and that the two ligands coordinated along the five fold axes in this intermediate play only a secondary role for the kinetics of the reactions.

Similar charges and almost similar sizes should render the isomeric ammineaqua-chromium(III) complexes ideal for the study of stereochemical changes by octahedral substitution reactions, since differences in both the solvation and the ion pair formation of these cations should be small. We have earlier studied the acid hydrolysis of the monoamminepentaqua- and the isomeric diamminetetraqua-,¹ triamminetriaqua-, and tetraamminediaquachromium(III) ions,² and report here the acid hydrolysis of the pentaammineaqua- and the hexaamminechromium(III) ions. The acid hydrolysis and isomerization reactions of all isomers of chromium(III) complexes coordinated with ammonia and water have thus now been investigated.

EXPERIMENTAL

Chemicals. Most chemicals employed have been described earlier.¹ $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_3$ and $[\text{Cr}(\text{NH}_3)_4](\text{NO}_3)_3$ were prepared according to literature methods, and the latter compound transformed into the perchlorate salt by double reprecipitation from water with 70 % perchloric acid.

Preparation of solutions. Solutions of the pentaammineaqua-chromium(III) ion were prepared as follows: pentaammineaqua-chromium(III) nitrate was dissolved in water and adsorbed at the top of a $2 \times 10 \text{ cm}$ Sephadex SE 25C ion exchange column. By use of an ammonium ion-ammonia buffer solution (1.0 M $\text{NH}_4\text{Cl} + 0.1 \text{ M}$ NH_3) pentaamminehydroxochromium(III) was eluted free of other chromium species. After

Table 1. Comparison of spectral characteristics of compounds, prepared and purified as described in the text, with literature values.

Complex ion	Medium	λ_1 max (nm)	ϵ_1 max l/(mol cm)	λ_2 max (nm)	ϵ_2 max l/(mol cm)	ϵ_1 max/ ϵ_2 max	Ref.
[Cr(NH ₃) ₆] ³⁺	0.1 M HCl	465	39.7	351	32.9	1.21	^a
	0.1 M HNO ₃	465	39	345	35	1.1	5 ^b
	0.05 M HClO ₄	466	40.7	354	33.7	1.20	8
	0.05 M HClO ₄	463	41	355	35	1.2	7 ^b
[Cr(NH ₃) ₅ (OH ₂)] ³⁺	0.5 M HClO ₄ + 0.5 M NaClO ₄	480	35.1	359	30.3	1.16	^a
	0.1 M HClO ₄	475	34	360	29	1.2	5 ^b
	0.05 M HClO ₄	484	35	360	29	1.2	7,8
	0.1 M HClO ₄	480	35	360	28.5	1.2	6 ^b

^a This work. ^b Estimated from the graph in this reference.

acidification of the pentaamminehydroxochromium(III) eluate a solution of the pure pentaammineaquachromium(III) ion in perchloric acid was obtained as described previously.¹ Solutions of the hexaamminechromium(III) ion in perchloric acid were obtained by directly dissolving the perchlorate salt in perchloric acid. The limited solubility of hexaamminechromium(III) perchlorate at room temperature in a 1 M perchlorate medium prevented the preparation of solutions with greater chromium(III) concentrations than approximately 10⁻⁴ M. Spectral characteristics of the hexaamminechromium(III) perchlorate salt dissolved in 0.1 M hydrochloric acid, and of the pentaammineaquachromium(III) solution prepared by the above method are given in Table 1 and Fig. 1.

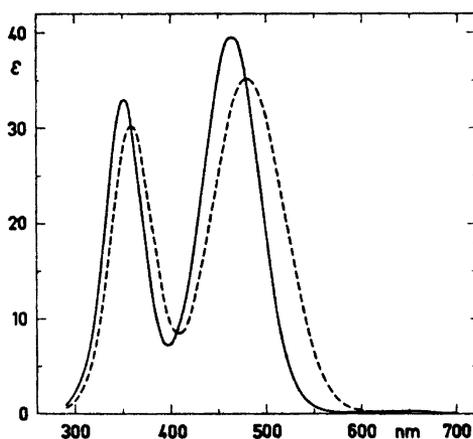


Fig. 1. Visible absorption spectra of compounds prepared and purified as described in the text. - - -, [Cr(NH₃)₅(OH₂)]³⁺; —, [Cr(NH₃)₆]³⁺. No hydrogen ion dependence of these spectra was observed in the acidity range 0.5 to 1.0 in 1 M (Na⁺ + H⁺)ClO₄ solution.

Kinetic measurements and the *Methods of analysis* and *calculation* were essentially those described previously.^{1,2}

RESULTS AND DISCUSSION

Contrary to the kinetic behaviour in acid solution of the previously studied ammineaquachromium(III) complexes, that of the pentaamminequa- and hexaamminechromium(III) ions is fairly uncomplicated. From the hexaamminechromium(III) ion only the pentaammineaquachromium(III) ion can be formed, and from this latter ion only *cis*- and *trans*-tetra-

Table 2. Initial composition of reaction kinetic experiments started with hexaammine- and pentaammineaquachromium(III) ions.

Exp. No.	[Cr(III)] (mmol/l)	[H ⁺] (mol/l)	Temp. (°C)	Max. react. time (h)
[Cr(NH ₃) ₅ (OH ₂)] ³⁺				
1 ^a	2.163 ± 0.005	1.0	60.18	143
2 ^a	2.170 ± 0.006	1.0	69.70	143
3	2.975 ± 0.011	1.0	80.15	24
[Cr(NH ₃) ₆] ³⁺				
4 ^a	0.1051 ± 0.0006	1.0	60.00	30
5	0.0238 ± 0.0004	1.0	70.00	6
6 ^a	0.1057 ± 0.0009	1.0	70.55	6
7	0.1008 ± 0.0004	1.0	80.25	3
8	0.1018 ± 0.0006	0.5	80.04	5

^a These four solutions were pairwise prepared from the same stock solutions.

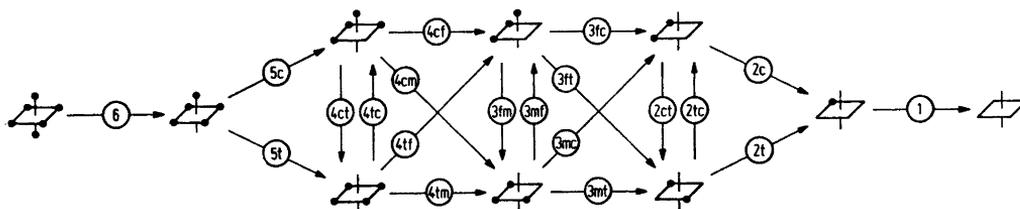


Fig. 2. Isomerization and hydrolysis reactions of ammineaquachromium(III) complexes. Filled circles depict coordinated ammonia, whereas the coordinated water is shown only by the absence of such circles. Reaction pathways are indicated by the subindices of the symbols used for the reaction rate constants.

Table 3. Rate constants at 60, 70, and 80 °C and activation energies for the hydrolysis reactions of the hexaammine- and the pentaammineaquachromium(III) ions calculated from all kinetic experiments and all kinetic experiments in 1 M acid, respectively.

($\times 10^6$)	All experiments			E_A (kcal/mol)	Experiments in 1 M acid	
	60 °C (s ⁻¹)	70 °C (s ⁻¹)	80 °C (s ⁻¹)		80 °C (s ⁻¹)	E_A (kcal/mol)
k_6	14.2 ± 0.8	47.5 ± 1.4	149 ± 3	27.6 ± 0.8	154 ± 3	28.0 ± 0.9
k_{5c}	14.3 ± 0.4	47.2 ± 0.8	145 ± 3	27.1 ± 0.4	145 ± 3	27.1 ± 0.4
k_{5t}	0.00 ± 0.14	0.0 ± 0.5	0.0 ± 1.4	—	0.3 ± 1.4	—

amminediaquachromium(III) ions are possible reaction products. Rate constants and activation energies from the kinetic experiments of Table 2, and those of our earlier publications in this series of papers,^{1,2} interpreted within the reaction scheme of Fig. 2 are shown in Table 3. In agreement with what was found for the complexes with a smaller number of coordinated ammonia molecules, no dependence of the acidity at hydrogen ion concentrations between 0.5 and 1.0 M, upon the rate constants for the hydrolysis of the hexaammine- and the pentaammineaquachromium(III) ions was observed.

In Table 4 kinetic parameters for the total experimental material are exhibited, and the corresponding correlation coefficients are shown in Table 5. From this latter table it is seen that correlation terms are particularly important among rate constants and activation energies that describe different reaction pathways from the same reactant species. These correlation coefficients are collected in blocks along the diagonal in the matrix of Table 5. Outside these blocks correlation is almost non-existent except in very few instances. That correlation terms among the rate constants and the activation

Table 4. Reaction rate constants at 70 °C and activation energies calculated from all ammine-aquachromium(III) hydrolysis experiments within the reaction scheme of Fig. 2 in a 1 M perchlorate medium.

Reaction	10 ⁶ × Rate constant (s ⁻¹)	Activation energy (kcal/mol)
6	47.5 ± 1.4	27.6 ± 0.8
5c	47.2 ± 0.8	27.1 ± 0.4
5t	0.0 ± 0.5	—
4cf	24.2 ± 0.6	25.7 ± 0.5
4cm	3.3 ± 0.6	26 ± 2
4ct	0.0 ± 0.6	—
4tm	44.4 ± 0.8	26.3 ± 0.5
4tf	0.8 ± 0.6	—
4tc	4.2 ± 0.6	26 ± 4
3fc	7.6 ± 0.3	27.6 ± 0.6
3ft	0.03 ± 0.19	—
3fm	0.3 ± 0.3	—
3mc	23.5 ± 0.4	26.0 ± 0.5
3mt	0.5 ± 0.4	—
3mf	1.1 ± 0.3	26 ± 7
2c	3.39 ± 0.08	27.0 ± 0.4
2ct	0.00 ± 0.14	—
2t	17.5 ± 0.3	26.3 ± 0.4
2tc	5.25 ± 0.19	27.6 ± 1.0
1	1.108 ± 0.011	28.6 ± 0.2

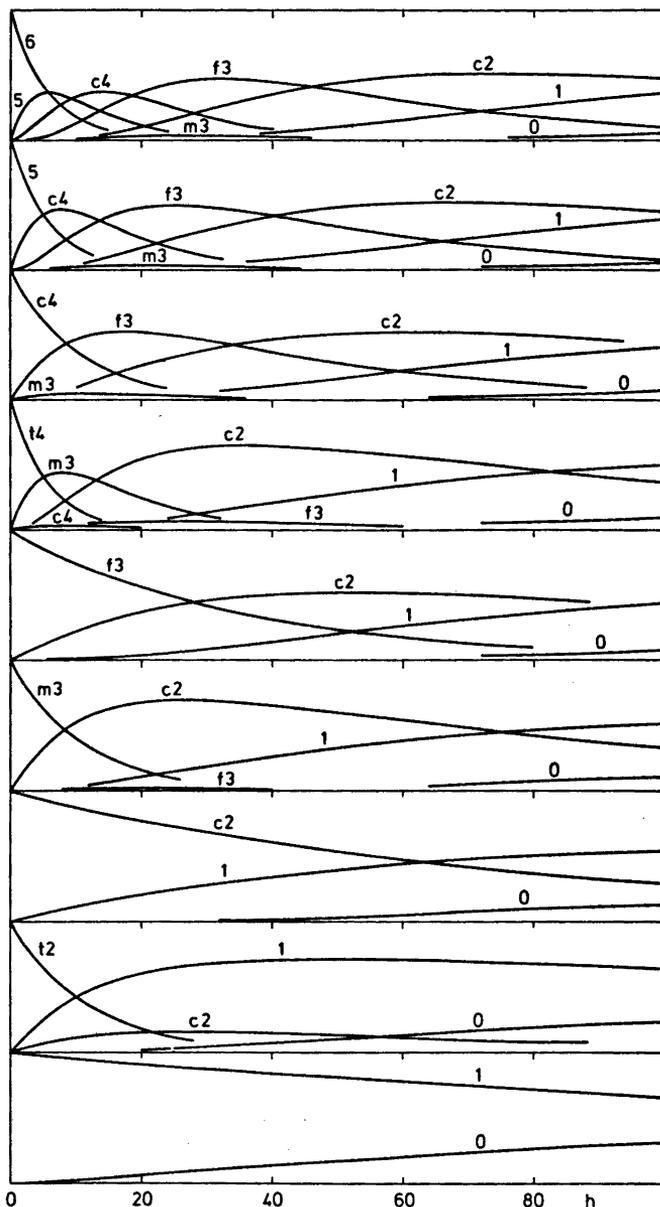


Fig. 3. Calculated time evolution of complex concentrations in 1 M perchloric acid solution at 70 °C started from pure ammineaquachromium(III) isomers. Isomer names are based upon the number of coordinated ammonia molecules, extended where necessary with prepositioned letters to indicate, c, *cis*; t, *trans*; f, *fac*; or m, *mer* isomers.

energies are also on the average of practically no importance, is of course due to the fact that the rate constants are evaluated at a temperature not very far from the average temperature of all the experimental data.

In Fig. 3 the time evolution, of hydrolysis experiments started with the pure ammineaquachromium(III) isomers, is calculated from the reaction rate constants of Table 4. This figure illustrates the complicated nature of the mix-

tures that are produced even after very short reaction times, and also the absence of both the *trans*-tetraamminediaqua- and the *trans*-diamminetetraaquachromium(III) ions as reaction products.

Reactions of some chromium(III) ammine complexes have earlier been studied in media containing nitrate ions.^{5,6} In Table 6 these data are compared with those of the present work in a 1 M perchlorate ion medium. The absence of any simple correlation between the reactivity parameters in the two media, and also in most cases the magnitude of the differences in the reaction rate constants, cannot reasonably be attributed only to unspecific medium effects.

Nitrate ions are seen significantly to accelerate the reactions of those chromium(III) ammine complexes that contain coordinated water, while the effect of nitrate ions in the case of the hydrolysis reaction of the hexaamminechromium(III) ion is negligible. This would be expected if inner sphere nitrate complexes are formed from the aqua complexes. Such complexes are probably formed so rapidly compared to the other reactions in the system, that the kinetic pattern of the slower reactions is not seen to be effected. Such fast complex formation between aqua ions and oxyanions has been demonstrated⁹ in a number of cases, where the aniono complexes are probably formed without chromium(III) oxygen bond breaking. It is interesting to note that nitrate ions have no similar great effect upon the halide ion hydrolysis reactions of aquahalogenidochromium(III) complexes. This suggests that an intramolecular interaction between coordinated ammonia and coordinated nitrate ions may play an important role for the ammine-aquachromium(III) hydrolysis reactions.

Table 6. Comparison between chromium(III) ammine hydrolysis and isomerization rate constants at 40 °C in 0.4 M nitrate⁵ and 1 M perchlorate media.

Reaction	$k(\text{ClO}_4^-)/k(\text{NO}_3^-)$
6	0.73
5c + 5t	0.04
4cf + 4cm + 4ct	0.03
2c + 2ct	0.09
2t	0.04
2tc	0.07
1	0.008

In the literature data on some chromium(III) polyamine hydrolysis reactions has appeared.¹⁰⁻¹⁴ The ammonia displacement reactions investigated by us are found invariably to be slower than the reactions involving the other amines, if chromium(III) complexes equivalently coordinated with amine nitrogen atoms and water are compared.* Except for the hydrolysis of the *mer*-amminetriaqua(1,2-ethanediamine)chromium(III) ion,¹¹ the rate differences, between complexes with the same configuration of nitrogen and oxygen donor atoms around the chromium center, seem mainly to be associated with differences in the activation energies of the processes. Published data on amine chromium(III) reactions are, however, still rather sparse.

Qualitative intercomparison of the data for the reactions of the chromium(III) complexes, differently coordinated with ammonia and water, suggests that when these reactions take place, major stereochemical ligand movements involve only four coplanar ligands, whereas the two ligands above and below this plane are not intimately involved in the reactions.

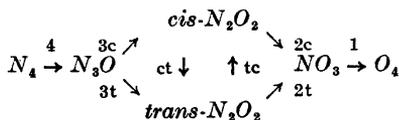
A quantitative description in these terms may be obtained, if the octahedron is regarded as composed of three square planes, each of which contains four half ligands and one third of the central atom. If the reaction rate constants for each of these substructural units of the octahedron is assumed to follow an Arrhenius type equation:

$$k = Z \exp(-E/RT)$$

the experimentally observed rate constants may be expressed as:

$$k_{\text{obs}} = \sum Z_{ij} \exp(-E_{ij}/RT)$$

The index *i* is a description of the reaction of the square planar ligand arrangements labelled according to the ligand atom reaction



* Investigations on other amine chromium(III) hydrolysis reactions have shown that this behaviour is not generally adopted by chromium(III) complexes, as, e.g., tetraaqua(1,3-propanediamine)chromium(III) aquates considerably slower at 80 °C than does *cis*-diamminetetraaquachromium(III).

Table 7. Analytical expressions and calculated rate constants at 70 °C for the reaction scheme of Fig. 2, within the model presented in the text.

Reaction	Analytical expression	$10^6 \times k_{\text{calc}}$ (s ⁻¹)	$10^6 \times k_{\text{obs}}$ (Table 4) (s ⁻¹)
6	$3Z_4$ } $\times \exp(-E_6/RT)$	48.3	47.5
5c	$(2Z_{3c} + Z_4)$ } $\times \exp(-E_5/RT)$	48.5	47.2
5t	$2Z_{3t}$ } $\times \exp(-E_5/RT)$	0.0	0.0
4cf	$2Z_{3c}$ } $\times \exp(-E_{4c}/RT)$	22.7	24.2
4cm	$(Z_{3c} + 2Z_{3t})$ } $\times \exp(-E_{4c}/RT)$	3.6	3.3
4ct	Z_{ct} } $\times \exp(-E_{4c}/RT)$	0.0	0.0
4tm	$(2Z_{3t} + Z_4)$ } $\times \exp(-E_{4t}/RT)$	45.2	44.4
4tf	0 } $\times \exp(-E_{4t}/RT)$	0.0	0.8
4tc	$2Z_{tc}$ } $\times \exp(-E_{4t}/RT)$	4.8	4.2
3fc	$3Z_{3c}$ } $\times \exp(-E_{3f}/RT)$	7.9	7.6
3ft	0 } $\times \exp(-E_{3f}/RT)$	0.00	0.03
3fm	$3Z_{ct}$ } $\times \exp(-E_{3f}/RT)$	0.0	0.3
3mc	$(Z_{3t} + Z_{3c})$ } $\times \exp(-E_{3m}/RT)$	22.3	23.5
3mt	$(Z_1 + Z_{3t})$ } $\times \exp(-E_{3m}/RT)$	1.7	0.5
3mf	Z_{tc} } $\times \exp(-E_{3m}/RT)$	1.9	1.1
2c	$(2Z_1 + Z_{2c})$ } $\times \exp(-E_{2c}/RT)$	3.34	3.39
2ct	Z_{ct} } $\times \exp(-E_{2c}/RT)$	0.00	0.00
2t	$2Z_{2t}$ } $\times \exp(-E_{2t}/RT)$	17.6	17.5
2tc	$2Z_{tc}$ } $\times \exp(-E_{2t}/RT)$	5.28	5.25
1	$2Z_1$ } $\times \exp(-E_1/RT)$	1.125	1.108

The *j*-index similarly describes the whole complex ion that reacts, named by an integer that reflects the number of nitrogen donor atoms, extended where necessary with a postpositioned letter to indicate *cis*, *trans*, *mer*, or *fac* isomers, respectively.

Initial calculations within this model with the additional empirical requirements:

$$Z_{ij} = Z_{ik} (= Z_i)$$

and

$$E_{ij} = E_{kj} (= E_j)$$

showed that although no well defined values of $\ln Z_{3t}^*$ and $\ln Z_{ct}^*$ could be obtained all the kinetic experiments, previously described with the parameters of Table 4, were equally well described within this simpler model.** Exclusion of Z_{3t} and Z_{ct} from the calculations caused no change in the overall agreement between model and data. In Table 7 analytical expressions for

* Since the calculations were performed in a linearized model $\ln Z$'s were used as parameters rather than the Z 's themselves.

the rate constants of Fig. 2 are tabulated together with a comparison between the rate constants of Table 4 and those calculated in this restricted model from the estimated parameters of Table 8. The linear correlation between the $\ln Z$ values in this table for the ammine hydrolysis reactions and the natural logarithm of the number of coordinated nitrogen atoms in the reacting plane, n , with a slope about 2.0 should be noted, as should also the minor difference between $\ln Z_{2t}$ and $\ln Z_{2c}$. The

** This statement may be tested rigorously by a variance ratio test. Let x be an n dimensional experiment vector. X the corresponding $n \times n$ experiment variance matrix, and Q a matrix with columns q_i that diagonalizes X . The rank of X , r ($r \leq n$), may then be taken as the number of non negative expressions of the type ($\omega \geq 0$):

$$|q_i^T x| - \omega(q_i^T X q_i)^{1/2} \quad (i = 1, 2, \dots, n)$$

For the present data and $\omega = 0, 2$, or 3, ranks of the experiment variance matrix, in the last reduction of the data, of 422, 283, or 256 are calculated. Consequently $P\{\nu^2(f_1, f_2) > s_1^2/s_2^2\}$ ¹⁵ is found to be about 1 %, 5 %, and 10 %, respectively, in these three cases.

Table 8. Estimated reaction parameters and correlation coefficients for reactions of the square planar octahedral substructural units presented in the text.

Parameter name	Parameter value	Correlation coefficients						
Z_4	exp (28.26 ± 0.18) s ⁻¹							
Z_{sc}	exp (28.02 ± 0.13) s ⁻¹	-.09						
Z_{sc}	exp (26.88 ± 0.13) s ⁻¹	-.11	.92					
Z_{st}	exp (27.07 ± 0.14) s ⁻¹	.83	-.03	-.05				
Z_1	exp (25.79 ± 0.17) s ⁻¹	.56	-.19	-.21	.73			
Z_{tc}	exp (25.86 ± 0.14) s ⁻¹	.88	-.02	-.04	.97	.73		
E_4	26.87 ± 0.13 kcal/mol	.99	-.09	-.10	.83	.56	.87	
E_5	26.72 ± 0.07 kcal/mol	.67	.67	.59	.28	.63	.67	
E_{sc}	26.87 ± 0.09 kcal/mol	-.10	.99	.94	-.03	-.19	-.03	.66
E_{st}	26.46 ± 0.11 kcal/mol	.98	-.08	-.09	.92	.64	.94	.67
E_{st}	27.09 ± 0.09 kcal/mol	-.11	.90	.99	-.05	-.21	-.04	-.08
E_{st}	26.63 ± 0.07 kcal/mol	.31	.87	.78	.44	.23	.44	.58
E_{sc}	27.28 ± 0.06 kcal/mol	.34	.61	.65	.51	.60	.53	.87
E_{st}	26.40 ± 0.10 kcal/mol	.83	-.03	-.05	.99	.73	.97	.62
E_{tc}	27.40 ± 0.12 kcal/mol	.56	-.19	-.21	.74	.99	.75	.82
								.56
								.28
								.66
								.97
								.67
								.92
								.58
								.10
								.87
								.36
								.40
								.62
								.87
								.77
								.82
								.65
								.44
								.51
								.91
								.03
								.64
								.21
								.60
								.73

regularity of the calculated activation energies should also be noted, and although the differences are yet unexplained attempts will be made to rationalize these data.

From these calculations we concluded that the two ligands perpendicular to the reacting plane play only a secondary role in the formation of the transition state by these reactions. In view of the very similar reactivity parameters for the different hydrolysis and isomerization reactions for the individual complexes, it is not unreasonable to assume a common intermediate for these different types of reactions. If this is accepted we must conclude that ammonia is not lost in the activated complex. Consequently the reactions of the complexes proceed by an associative mechanism *via* an intermediate of increased coordination number. The most plausible geometry of this intermediate is that of five of the ligands situated in a plane, that also contains the chromium atom, and those remaining two ligands of minor importance for the reaction coordinated above and below this plane, *i.e.* a distorted pentagonal bipyramid. Preferential attack of solvent water, hydrogen bonded to a coordinated water molecule, may rationalize the absence of Z_{st} and Z_{ct} terms, as such attack will not separate neighbouring coordinated ammonia molecules when the reactive intermediate is formed.

From the limited amount of data on water exchange reactions in chromium(III) complexes^{16,17} it seems that such reactions proceed so much faster, particularly in the pentaammineaquachromium(III) ion, than both the isomerization and the ammine hydrolysis reactions, that it does seem plausible that the water exchange reactions proceeds *via* a somewhat different intermediate than the other reactions discussed. This is also in favour of an associative mechanism for the hydrolysis and isomerization reactions, as water exchange and isomerization should be expected to parallel each other if a dissociative mechanism is assumed. Probably, however, the transition state in all the types of reactions just discussed contains additional water, in which case the intermediate in the water exchange reactions can be a first and less intimate stage in the just hypothesized attack by the water of the first solvent shell of the complex ion.

It is obvious that a more concise mechanistic

picture of the reactions discussed must await further information, especially about water exchange, in a more generous number of chromium(III) aqua complexes.

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