Acta Chemica Scandinavica A 28 (1974) 23—28

Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. II. The Acid Hydrolysis of Facial and of Meridional Triamminetriaquachromium(III) and of *cis*- and of *trans*-Tetraamminediaquachromium(III) Ions in Aqueous Perchloric Acid

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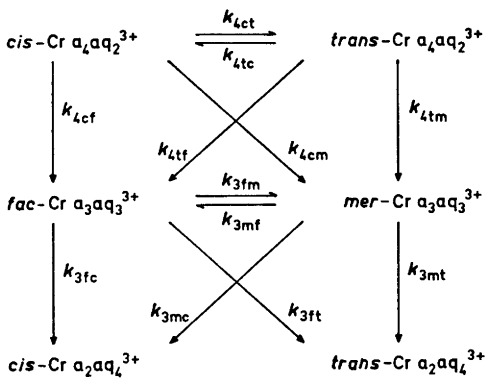
The acid hydrolysis of facial and of meridional triamminetriaquachromium(III) and of *cis*- and of *trans*-tetraamminediaquachromium(III) cations has been investigated in 0.5 to 1.0 M perchloric acid at an ionic strength of 1.0, adjusted by the addition of sodium perchlorate, in the temperature range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

In the reaction scheme (a = ammonia, aq = = water):



most reaction pathways were found to be kinetically significant. Rate constants at 70°C and activation energies were found to be:

k_{3mf}: $(1.1 \pm 0.4) \times 10^{-6}$ sec^{-1}, 26 ± 9 kcal/mol, and k_{4tc}: $(4.2 \pm 0.8) \times 10^{-6}$ sec^{-1}, 26 ± 5 kcal/mol for the well defined isomerization reactions and k_{3fc}: $(7.6 \pm 0.3) \times 10^{-6}$ sec^{-1}, 27.6 ± 0.9 kcal/mol, k_{3mc}: $(23.5 \pm 0.5) \times 10^{-6}$ sec^{-1}, 26.1 ± 0.5 kcal/mol, k_{4cf}: $(25.3 \pm 1.0) \times 10^{-6}$ sec^{-1}, 24.5 ± 0.9 kcal/mol, k_{4cm}: $(3.7 \pm 0.9) \times 10^{-6}$ sec^{-1}, 24 ± 4 kcal/mol, and k_{4tm}: $(44.2 \pm 1.0) \times 10^{-6}$ sec^{-1}, 26.4 ± 0.6 kcal/mol.

for the well defined hydrolysis reactions.

The remaining paths were not kinetically well defined, but upper limits for the rate constants at 70°C (taken as the mean value plus twice the standard deviation) were found to be: k_{3ft}: 0.5×10^{-6} sec^{-1}, k_{3fm}: 0.8×10^{-6} sec^{-1}, k_{3mt}: 1.5×10^{-6} sec^{-1}, k_{4ct}: 1.6×10^{-6} sec^{-1} and k_{4tf}: 3×10^{-6} sec^{-1}.

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

As part of a continued research on the acid hydrolysis of chromium(III) ammine complexes, of which results for the monoammine-pentaaqua- and the isomeric diamminetetra-aquachromium(III) ions have been given earlier,[1] we here present data for the reactions of the isomeric triamminetriaqua- and the isomeric tetraamminediaquachromium(III) complexes.

In spite of numerous investigations of halide hydrolysis in both *cis*- and *trans*-tetraamminedi-halogenido- and aquahalogenidochromium(III) systems, no quantitative investigations of the further reactions of the *cis*- and *trans*-tetra-amminediaquachromium(III) ions produced by these reactions seem to have been carried out. Qualitative observations indicate the non-significance of chromium nitrogen bond breaking in the time necessary for the study of

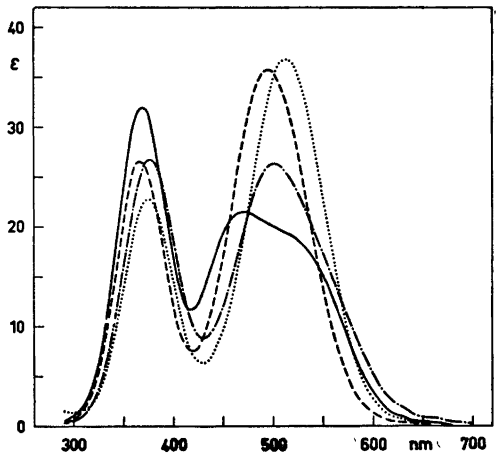


Fig. 1. Visible absorption spectra of ammineaquachromium(III) complexes prepared and purified as described in the text.
···, facial $[Cr(NH_3)_3(OH_2)_3]^{3+}$; – . – , meridional $[Cr(NH_3)_3(OH_2)_3]^{3+}$; – – – , *cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ and ———, *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$.
No hydrogen ion dependence of these spectra was observed in the acidity range 0.5 to 1.0 in 1 M $(Na^+ + H^+)ClO_4$ solution.

the chromium halogen bond breaking. The hydrolysis of the *cis*-tetraamminediaquachromium(III) ion has been investigated by Jørgensen and Bjerrum.[2] Since their study, however, was made in a medium containing nitrate ions and in some cases sulphate or dithionate ions also, and since all these ions are now known to excert specific influence upon the hydrolysis of chromium(III) ammine complexes, a reinvestigation of the reactions of this cation in perchloric acid solution was undertaken together with the investigation of the reactions of the *trans*-tetraamminediaquachromium(III) ion and the isomeric triamminetriaquachromium(III) ions. For these latter ions no quantitative data seem to have been produced previously.

EXPERIMENTAL

Preparation of solutions. The *cis*-tetraamminediaquachromium(III) ion and the isomeric triamminetriaquachromium(III) ions were purified by the ion exchange method described in detail in Ref. 1, after being formed in solution as described below. By this method chromium complexes with different numbers of coordinated ammonia molecules were easily separated. The greater the number of coordinated water molecules the easier the elution from the resin column with 2 M sulphuric acid took place. Contrary to what was observed for the isomeric diammines, both the isomeric triammines and tetraammines were rather easily separated from each other. The meridional triamminetriaquachromium(III) ion was eluted before the corresponding facial isomer and the *trans*-tetraamminediaquachromium(III) ion was

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.
facial							
$[Cr(NH_3)_3(OH_2)_3]^{3+}$	0.5 M $HClO_4$ + 0.5 M $NaClO_4$	513	36.6	374	22.6	1.62	[a]
	2 M $HClO_4$	513[b]	34.5	374	22.2	1.55	8
meridional							
$[Cr(NH_3)_3(OH_2)_3]^{3+}$	0.5 M $HClO_4$ + 0.5 M $NaClO_4$	502	26.3	376	26.8	0.98	[a]
	3 M $HClO_4$	503	25.6	373	25.6	1.00	9
	0.6–2 M $HClO_4$	504	26.3	376	26.0	1.01	6
cis-							
$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.5 M $HClO_4$ + 0.5 M $NaClO_4$	495	35.8	366	26.8	1.34	[a]
	1 M $HClO_4$	495	36.1	366	26.6	1.36	10
	0.5 M HNO_3	495	36	365	26.5	1.36	2[c]
trans-							
$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.5 M $HClO_4$ + 0.5 M $NaClO_4$	470	21.5	369	32.1	0.67	[a]
	1 M $HClO_4$	476	20.6	368	29.7	0.69	10

[a] This work. [b] Frequently misquoted as 518 in the literature. [c] Estimated from the graph is this reference.

eluted before the corresponding *cis*-isomer. Both these observations are in agreement with numerous observations in other closely related systems, in which such behaviour has been rationalized qualitatively in terms of the dipole moments of the ions in question. In connection with this purification technique the exclusion of light is especially important, except for the *cis*-tetraamminediaquachromium(III) ions, as light greatly accelerated the isomerization reactions, and to a lesser extent also the hydrolysis reactions.

trans-*Tetraamminediaquachromium(III)*. Since the decomposition of this ion was greatly accelerated not only by Dowex 50 W resins as noted earlier [3] but also by the Sephadex resin employed, solutions of the *trans*-tetraamminediaquachromium(III) ion were prepared by dissolving *trans*-tetraammineaquahydroxochromium(III) perchlorate [4] directly in perchloric acid.

cis-*Tetraamminediaquachromium(III)*. A stock solution of this ion in perchloric acid was prepared as follows: 5 g of *cis*-tetraammineaquachloridochromium(III) chloride [5] was treated with 10 ml of 2 M sodium hydroxide solution at room temperature for about 2 min. *cis*-Tetraamminediaquachromium(III) perchlorate was precipitated from this solution, cooled to 0°C, by the dropwise addition of 150 ml of 70 % perchloric acid. The perchlorate thus prepared was filtered off, washed with a little ice cold 70 % perchloric acid, dissolved in about 100 ml of water, and reprecipitated with 100 ml 70 % perchloric acid as described above. Finally the precipitate was dissolved in 50 ml 1 M perchloric acid. This solution could be kept almost unchanged in the dark at 0°C for several months. The small amounts of triamminetriaquachromium(III) complexes initially present and formed during the storage were readily removed in the final steps of the purification procedure.

Facial triamminetriaquachromium(III). 10 ml of the stock solution of the *cis*-tetraamminediaquachromium(III) ion was diluted five times with 1 M perchloric acid, and the resulting solution was aged in the dark at 50°C for 75 h. The triammines were separated as described above from the complex mixture of chromium(III) ammine complexes thus formed. This mixture of triammines, with the facial isomer as main constituent, was used directly for the kinetic experiments. A solution of the pure facial triamminetriaquachromium(III) ion, needed in order to obtain the visible absorption spectrum of this ion, which was necessary for the chosen calculation procedure, was prepared in the following way: The mixture of triammines was rechromatographed at 0°C on a 2 × 25 cm column packed with Dowex 50W X8 200/400 mesh resin; 2 M sulphuric acid was employed as the eluent. Spectrophotometric control of the effluent showed that small amounts of the meridional isomer was eluted first mixed with the facial isomer. After the first few fractions the chromium species in the eluent had a constant absorption spectrum, judged both by the ratio of the absorbance of the first spin allowed band to the absorbance of the second spin allowed band, and by the constant position of these two bands. The indistinguishable fractions were assumed to contain the pure facial triamminetriaquachromium(III) ion.

Meridional triamminetriaquachromium(III). This ion was generated in solution by mercury(II) accelerated hydrolysis of the chloride ligands in the meridional triammineaquadichloridochromium(III) ion dissolved as the chloride [6,7] in dilute perchloric acid. No facial triamminetriaquachromium(III) ions could be detected in solutions thus prepared. For some kinetic experiments the triammine mixture, with the meridional triamminetriaquachromium(III) ion as main constituent, from solutions of the *trans*-tetraamminediaquachromium(III) ion aged in 1 M perchloric acid at 50°C for 75 h was employed.

Chemicals, kinetic measurements and the *method of analysis* were essentially as described earlier,[1] and for the *method of calculation* the discussion given for the hydrolysis of the isomeric diamminetetraaqua- and the monoamminepentaaquachromium(III) ions applies also to the present work. In connection with the calculation procedure it should also be mentioned that experiments with a mixture of complex ions as initial reactants, as was always the case in experiments with predominantly the facial triamminetriaquachromium(III) ion, gave reaction rate constants of comparable accuracy to those experiments where only one complex ion was initially present. This was investigated by comparing the experiments started with the pure meridional triamminetriaquachromium(III) ion with those started with the mixture of the isomeric triammines obtained by the hydrolysis of the *trans*-tetraamminediaquachromium(III) ion. For this reason no great effort was made to further purify the solutions of the facial triamminetriaquachromium(III) ion used for kinetic runs.

RESULTS AND DISCUSSION

When an acid solution of the *trans*-tetraamminediaquachromium(III) ion is left to hydrolyse small amounts of the facial triamminetriaquachromium(III) ion appear. If the uptake of ammonia by the chromium(III) complexes is not taken into consideration, then the formation of this cation may occur in the following four different ways (see Fig. 2):

(i) Directly by hydrolysis of the *trans*-tetraamminediaquachromium(III) ion (4tf-path).

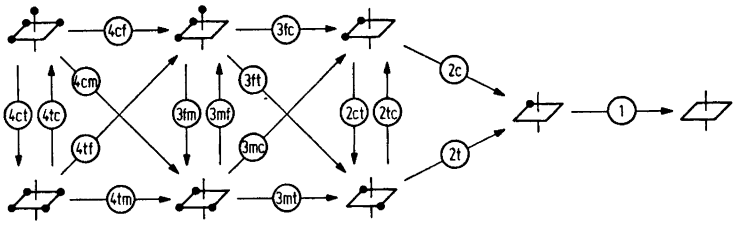


Fig. 2. Isomerization and hydrolysis reactions of $[Cr(NH_3)_n(OH_2)_{6-n}]^{3+}$ ions ($n = 4, 3, 2, 1$). Filled circles depict coordinated ammonia whereas the coordinated water is shown only by the absence of such circles. Reaction pathways are indicated by the subindices of the symbols used for the reaction rate constants.

Table 2. Initial composition of reaction kinetic experiments in 1.0 M perchlorate medium, started with triamminetriaquachromium(III) ions.

Exp. No.	Chromium concentration		Hydrogen ion concentration[a] (mol/l)	Temp. (°C)	Max. reaction time (h.)
	facial (mmol/l)	meridional (mmol/l)			
1	0.723 ± 0.006	0.169 ± 0.007	1.0	60.18	410
2	0.150 ± 0.006	0.932 ± 0.007	1.0	60.18	96
3	1.207 ± 0.010	0.252 ± 0.012	1.0	69.70	263
4	0.042 ± 0.008	0.924 ± 0.009	1.0	69.70	48
5	–	1.102 ± 0.003	1.0	80.15	24
6	–	1.060 ± 0.005	1.0	80.02	12
7	1.513 ± 0.010	0.232 ± 0.012	1.0	80.15	72

[a] The hydrogen ion concentration was only varied in experiments started with the tetraamminediaquachromium(III) ions (Table 3). This was done since tetraamminediaquachromium(III) solutions were easier to prepare than triamminetriaquachromium(III) solutions. As the *trans*-tetraamminediaquachromium(III) ion reacts to give mainly the meridional triamminetriaquachromium(III) ion and the *cis*-tetraamminediaquachromium(III) ion gives mainly the facial triamminetriaquachromium(III) ion no effects from this restriction should be observed.

(ii) By hydrolysis of the *cis*-tetraamminediaquachromium(III) ion formed by isomerization of the *trans*-isomer (4tc + 4cf paths).

(iii) By isomerization of the meridional triamminetriaquachromium(III) ion formed by hydrolysis of the initial *trans*-compound (4tm + 3mf paths), or

(iv) by a combination of the two above isomerization reactions with the hydrolysis reaction of the *cis*-tetraamminediaquachromium(III) ion to yield the meridional triamminetriaquachromium(III) ion (4tc + 4cm + + 3mf paths).

Similar uncertainties exist for the origin of most other reaction products. Therefore, in order to deal with this ambiguity of the origin of the reaction products in a rigorous fashion, the reaction scheme of Fig. 2 in which all isomerization- and hydrolysis reactions are included was employed for the interpretation of the kinetic data. No experimental evidence for the uptake of ammonia by the ammineaquachromium(III) complexes investigated, in solutions as acid as those employed in this research ($[H^+] \geq 0.5$ mol/l), have been found. These reactions have consequently not been included in the reaction scheme used to explain the kinetic data.

Tables 2 and 3 show the reaction kinetic experiments with triamminetriaqua- and tetraamminediaquachromium(III) ions as reactants, respectively. In Table 4, rate constants at 60, 70, and 80°C and activation energies calculated from those experiments and those of Ref. 1 are tabulated. As seen from this table there are no significant differences between the rate con-

Table 3. Initial composition of reaction kinetic experiments in 1.0 M perchlorate medium, started with tetraamminediaquachromium(III) ions.

Exp. No.	Chromium concentration *cis* (mmol/l)	Chromium concentration *trans* (mmol/l)	Hydrogen ion concentration (mol/l)	Temp. (°C)	Max. reaction time (h.)
8[a]	2.044±0.014	–	1.0	60.18	264
9[a,b]	0.137±0.010	2.120±0.013	1.0	60.18	216
10[a]	2.052±0.014	–	1.0	69.70	144
11[a,b]	0.119±0.009	2.138±0.011	1.0	69.70	216
12	2.633±0.004	–	1.0	80.15	24
13	1.197±0.006	–	0.5	80.02	24
14	–	1.969±0.006	1.0	80.15	12
15	–	1.468±0.005	0.5	80.02	12

[a] These four solutions were pairwise prepared from the same stock solutions. [b] Unfortunately the stock solution used for these experiments was exposed to light for some time. This accounts for the *cis*-isomer present. Since the rate constants, however, were almost as equally well defined in these experiments as in those started with the pure isomer the experiments were not repeated.

Table 4. Rate constants at 60, 70, and 80°C and activation energies [a]calculated from the experiments of tables 2 and 3 and Ref. 1.

($\times 10^6$)	All experiments 60°C (sec^{-1})	70°C (sec^{-1})	80°C (sec^{-1})	E_A (kcal/mol)	Experiments in 1 M acid. 80°C (sec^{-1})	E_A (kcal/mol)
k_1	0.314±0.006	1.109±0.012	3.64±0.05	28.6±0.3	3.56±0.07	28.3±0.3
k_{2c}	1.03±0.04	3.38±0.12	10.4±0.4	27.0±0.4	10.5±0.4	27.2±0.5
k_{2ct}	0.00±0.06	0.00±0.18	0.0±0.6	–	0.0±0.6	–
k_{2t}	5.50±0.17	17.5±0.3	52.4±1.1	26.3±0.5	53.6±1.3	26.7±0.5
k_{2tc}	1.56±0.13	5.3±0.2	16.5±0.9	27.6±1.2	17.0±1.1	28.0±1.3
k_{3fc}	2.25±0.15	7.6±0.3	23.8±1.2	27.6±0.9	23.7±1.2	27.4±0.9
k_{3ft}	0.03±0.11	0.1±0.2	0.3±0.8	–	0.2±0.9	–
k_{3fm}	0.06±0.15	0.2±0.3	0.6±1.1	–	0.6±1.1	–
k_{3mc}	7.5±0.3	23.5±0.5	69±2	26.1±0.5	69±2	26.0±0.6
k_{3mt}	0.1±0.2	0.5±0.5	1.3±1.9	–	1±2	–
k_{3mf}	0.3±0.2	1.1±0.4	3.2±1.4	26±9	2.9±1.5	26±10
k_{4cf}	8.6±0.6	25.3±1.0	69.9±1.6	24.5±0.9	70.4±1.7	24.5±0.9
k_{4cm}	1.3±0.4	3.7±0.9	10±2	24±4	10±2	24±4
k_{4ct}	0.0±0.3	0.0±0.8	0±2	–	0±2	–
k_{4tf}	0.2±0.4	0.6±0.8	2±3	–	1±3	–
k_{4tm}	13.8±0.6	44.2±1.0	132±4	26.4±0.6	137±4	26.7±0.6
k_{4tc}	1.3±0.5	4.2±0.8	13±2	26±5	14±3	27±4

[a] It should be noted that the standard deviations upon the tabulated parameters are correlated, that is, the quoted standard deviations cannot be used as realistic error estimates independently of each other. The full table of correlation coefficients will be given later in connection with additional data for the reactions of the hexaammine- and the pentaammineaquachromium(III) ions.

stants and activation energies calculated from all the experiments and those calculated from the experiments in 1 M acid only. This means that the reactions of deprotonated ammineaquachromium(III) complexes plays no important role at hydrogen ion concentrations greater than 0.5 mol/l.

It is noteworthy that the standard deviations associated with the parameters k_{2c} and k_{2ct} are somewhat smaller than the values reported in Ref. 1. This is due to the fact that many of the experiments of Tables 2 and 3 have been followed for such an extended period of time as to contain an appreciable amount of information about the reactions of the *cis*-diamminetetraaquachromium(III) ion. Both the isomeric triammines form this ion almost exclusively by their hydrolysis reactions. The results obtained for the standard deviations of the parameters k_{2t} and k_{2tc}, which are seen to be almost unchanged from those of the earlier research, also illustrate this fact. That the standard deviation upon the parameter k_1 is also unchanged simply reflects that only few of the additional experiments have been followed for so long a time as to produce significant amounts of the hexaaquachromium(III) ion.

The inclusion of the data from Ref. 1 in the calculation of the parameters of Table 4 should also be noted. These data are needed in order to have information about the reactions of the *trans*-diamminetetraaquachromium(III) ion, as this ion, as already mentioned, is not formed in significant quantities by the hydrolysis reactions of the isomeric triamminetriaquachromium(III) ions. Consequently, problems analogous to those discussed at length in Ref. 1, in connection with those kinetic experiments started with the pure *cis*-diamminetetraaquachromium(III) ion, where also no *trans*-diamminetetraaquachromium(III) ions are formed, would have been encountered, had these data not been used.

A further discussion of the results given here will be presented in connection with data for the acid hydrolysis of the hexaammine- and the pentaammineaquachromium(III) ions, when the investigations into the reactions of these ions have been concluded.

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Received August 28, 1973.