

Kinetics of Complex Formation

IV. Rates of Decomposition and Transformation Mechanisms of Chromium(III) Ammines in Aqueous Solution

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The aquation of the hexammine, pentammine and tetrammine chromium(III) ions in acidic as well as in basic solution was studied by chromatographic analysis of the reaction mixtures. Further, the aquation of tetraquodiammine ion was followed by a pH-titration method, and the existence of a relatively stable monammine ion was proved. The monammine which completes the series of chromium(III) amines from hexammine to hexaquo ion was isolated as a cesium alum.

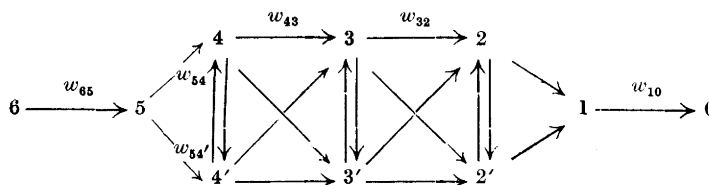
In a previous paper¹ of this series one of the authors has found that the aquation of the hexammine chromium(III) ion in nitric acid solution is independent of the hydrogen ion concentration, and the following expression was found for the pseudo-unimolecular velocity constant (in sec⁻¹)

$$k_{-6} = 10^{12.3} \exp \frac{-26\,000}{RT}.$$

This study has now been extended to the pentammine, tetrammine and diammine chromium complexes both in acidic and alkaline solution (*cf.* Ref.²).

The aquation is most simple in acidic solution because the equilibria between aquo- and hydroxo complexes can be stoichiometrically neglected and are also without importance to the reaction rates which are independent of the hydrogen ion concentration contrary to what is found for most acid complexes, *e.g.* for the aquation of the chloro chromium complexes³. This is in agreement with the fact that the reaction rates, at least for the higher amines, are of the same order of magnitude in a basic solution as in an acidic solution. Hydroxo-pentammine decomposes even more slowly than aquopentammine. It is also an advantage that an acid reaction mixture remains homogeneous and that the formation of polynuclear compounds is suppressed.

The aquation of the luteo ion in acidic solution may then be supposed to consist of 20 consecutive and simultaneous exchanges of ammonia with water and *cis-trans* isomerizations:



The figures give n in $\text{Cr}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}^{+++}$: 2,3,4 stand for the *cis*, and 2',3',4' for the *trans* complexes. w_{65} is the probability per unit time⁴ of the hexammine reacting to form the pentammine. The other w 's are analogously defined.

In basic solution a similar scheme can be established for the hydroxylation of hexammine down to trihydroxotriammine — more or less complicated by the formation of polynuclear compounds (*cf.* Figs. 1 and 2).

The complete solution for every intermediate is rather complex but may be readily calculated by matrix algebra as indicated in the appendix by one of the authors (E.J.).

Such calculations show that the relative amounts, α_j , of reaction product j can be expressed as the following function of t :

$$\alpha_j = \sum_i Q_{ji} \exp(-\lambda_i t)$$

with 10 possible values of λ , which can be identified with the conventional gross velocity constants $k_{-6}, k_{-5}, k_{-4}, k_{-4'}, \dots, k_{-1}$ plus a zero for the components present at equilibria, in this case hexaquo chromium ions only. Q_{ji} is a constant, usually a fraction containing the reaction probabilities, see appendix.

For k_{-6}, k_{-5} and k_{-1} we have the simple expressions:

$$k_{-6} = \frac{-d \ln[\text{Cr}(\text{NH}_3)_6]}{dt} = w_{65}, \quad k_{-5} = w_{54} + w_{54'}, \quad k_{-1} = w_{10},$$

while the other gross constants are complicated functions of the w 's. Of course, k_{-4} and $k_{-4'}$ and similarly $k_{-3}, k_{-3'}$ and $k_{-2}, k_{-2'}$ will only have their intuitive meaning when the *cis-trans* isomerization is very slow compared to the liberation of ammonia. Otherwise it is impossible to attach a definite one of the k 's to a definite one of the tetrammines. Their bearing on the reaction probabilities are such that k_{-4} and $k_{-4'}$ are roots of

$$R^2 - (w_{44'} + w_{43} + w_{43'} + w_{4'4} + w_{4'3} + w_{4'3'}) \cdot R + (w_{44'} + w_{43} + w_{43'}) \cdot (w_{4'4} + w_{4'3} + w_{4'2'}) - w_{44'} \cdot w_{4'4} = 0,$$

and similar expressions exist for $k_{-3}, k_{-3'}$, and $k_{-2}, k_{-2'}$.

The rate experiments were all carried out in darkness at 40°C.

The concentration of the complexes most rich in ammonia in the reaction mixtures were determined by chromatography on alumina as developed by

Bjerrum, Jensen and Woldbye⁵. A separation of some lower amines by chromatographic analysis on alumina was also attempted, but without success due to their low robustness in alkaline solution.

A representative selection of experiments in nitric acid solution ($c_{\text{HNO}_3} + c_{\text{KNO}_3} = 0.4 \text{ M}$) is given in Tables 1–4, and similarly in alkaline solution ($c_{\text{NaOH}} + c_{\text{KNO}_3} = 0.4 \text{ M}$) in Tables 5–7.

When the ammine complexes split off ammonia, an equivalent amount of acid is neutralized, and in a number of experiments also the amount of free acid has been determined in order to calculate the average number of ammonia bound per chromium atom in the reaction products. It was done by a pH titration and the equivalence point was estimated from the appearance of the titration curve. This procedure was used in the experiments with hexammine, pentammine and tetrammine chromium(III) salts. Some more accurate titrations of this kind were carried out in order to follow the aqation of the tetraquodiammine chromium(III) ion since in this case we were unable to analyze the mixture of amines by chromatography. Most of these results are given in Table 8.

EXPERIMENTAL

Preparation of salts. The complex salts used were the following: $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$. Anal. Calc.: Cr 15.29; NH_3 30.02. Found: Cr 15.23; NH_3 29.76. $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{NO}_3)_3$. Anal. Calc.: Cr 15.24. Found: Cr 15.16.

trans(?)- $[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{OH})_2]\text{Cl}_2\cdot\text{H}_2\text{O}$ Anal. Calc.: Cr 24.81; NH_3 16.25; OH 16.23; Cl 16.91. Found: Cr 24.69; NH_3 16.30; OH 16.22; Cl 17.15.

cis- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]\text{SO}_4$ and *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]\text{S}_2\text{O}_6$.

With minor modifications the complex salts were prepared according to methods described in the literature. The *cis*-hydroxoquatetrammine chromium(III) sulphate was kindly supplied by C. E. Schäffer, who also suggested making the dichlorodiaquodiammine chromium(III) chloride which was used in preparing the dihydroxiaquodiammine chloride by oxidizing the Reinecke salt with hydrogen peroxide: The hydrogen peroxide (30 %) was added dropwise to the solid Reinecke salt moistened with concentrated hydrochloric acid. The vigorous reaction was slowed down by cooling in ice. The dark red solution was frequently decanted off and the joined fractions were saturated with hydrogen chloride in the cold. The solution was placed at room temperature till the next day. The precipitate formed was used for the next preparation after a single reprecipitation with hydrochloric acid.

Reinecke salt has been shown to be the *trans*-diammine compound⁶, and we have assumed that the tetraquodiammine ion also has *trans*-configuration.

Chromatography. 2–5 ml were brought to the approximate composition of the eluting liquid by adding the necessary electrolytes⁵. The dimension of the column was usually $11 \times 200 \text{ mm}$. For the separation of hexammine and pentammine solutions were used of the following composition: 0.1 M KOH, 0.2 M KCl, 0.8 M $(\text{C}_2\text{H}_5)_4\text{NBr}$ followed by 0.1 M KOH, 1.0 M KCl. Pentammine passes first. Hexammine is recovered practically quantitatively by addition of the latter solution. A shorter column was used for the separation of pentammine and tetrammine. Pentammine is displaced quickly with a solution of the composition 1.0 M NH_3 , 0.1 M NH_4Cl , 1.0 M NaNO_3 with a loss of about 10 %, after which the tetrammine is displaced with 0.1 M NaOH, 1.0 M LiCl. Separation of tetrammine from the lower amines was performed with solutions of the composition 0.1 M NaOH, 1.0 M NaNO_3 , giving a loss of approximately 30 % due to the relatively low robustness of the tetrammine. The lower amines were completely decomposed by this treatment.

The concentration in the eluate was in a few cases determined from the optical density, but in the majority of cases the acidified solutions were boiled until there was complete transformation to hexaquo ions. The chromium(III) ions were oxidized by

persulphate, using silver ions as catalyst. The chromate formed was then titrated with ferrous ions⁷.

pH-titrations. A pH Meter 22 (Radiometer) was used. In order to increase its sensibility in the more accurate titrations (Table 8) it was supplied with an external meter covering the pH range 6–8. Between the calomel electrode and the input was inserted a pH-standard (PHN 2a, Radiometer). It was then possible to change the input voltage in jumps which correspond to one half unit in pH.

The procedure for the experiments given in Table 8 was the following: A sample of 10 ml of the reaction mixture was taken out and cooled. The extinction at 570, 540, 520, 480 and 385 m μ was measured in a Beckman DU spectrophotometer. Then it was transferred into the titration vessel together with 15 ml 0.5 M NaNO₃, and the titration curve was determined at ca. 20°C. with 0.5018 M NaOH as titrant.

The equivalence point is not a sharp point of inflection, and the various complexes have different values for the first acid dissociation exponent, pK_{a1}. It was, therefore, necessary to determine both equivalence point and a mean value of pK_{a1} for every titration. The interdependence of these quantities is, under the conditions of the experiments in Table 8 (0.473 mmole chromium complex contained in 25 ml liquid), expressed by

$$\text{pH}_{\text{utr}} = 0.5 \left\{ \text{p}K_{a1} - \log \left(\frac{10^{-\text{pH}_0 + 1.372}}{x(25 + x)} - 10^{-\text{pH}_{\text{utr}}} \right) \right\}$$

where

x : ml 0.5018 M NaOH used until the equivalence point

pH_{utr}: pH at the equivalence point

pH₀: pH of the initial solution before the titration

pK_{a1}: calculated from the data when the first aquo group in the complex is 50 % neutralized.

The true values for x , pH_{utr} and pK_{a1} are then found by iteration.

Table 1. 0.0478 M Cr(NH₃)₆⁺⁺⁺ in 0.4 M HNO₃ at 40°C.

Time (hours)	Hexammine		found	Aquo-pentammine		NH ₃ /Cr in products
	found	$k_{-6} : 0.0051$		$k_{-6} : 0.0051$	$k_{-6} : 0.085$	
0	—	0.0478	—	—	—	—
5	0.0468	466	0.0008	0.0009	2.9	2.9
18	420	437	17	21	2.2	2.2
50	364	370	19	23	1.7	1.7
74	313	328	21	21	1.6	1.6
122	234	257	10	16	1.2	1.2
167	199	204	10	13	0.9	0.9
218	152	157	7	10	0.7	0.7
289	108	109	—	7	0.5	0.5
384	66	67	—	4	0.3	0.3
501	32	37	—	2	—	—
670	19	16	—	1	—	—

Table 2. 0.0569 M Cr(NH₃)₅(H₂O)⁺⁺⁺ in 0.4 M HNO₃ at 40°C.

Hours	found	$k_{-5} : 0.085$	NH ₃ /Cr in products	
			found	
0	0.0538	0.0569	—	—
1	504	522	3.0	3.0
2	475	480	2.6	2.6
3	431	441	2.8	2.8
5	355	372	2.6	2.6
8	280	288	2.7	2.7
25	58	68	2.2	2.2

Table 3. 0.0597 M $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{+++}$ in 0.2 M HNO_3 , 0.2 M KNO_3 at 40°C.

Hours	Aquo-pentammine		Diaquotetrammine		
	found	$k_{-5} : 0.088$	found	$k_{-4} : 0.10$	$k_{-4}' : 1.0$
0	0.0521	0.0597	—	—	—
0.5	520	570	0.0028	0.0026	0.0020
1	486	546	26	49	32
2	473	500	21	88	41
3.5	386	438	36	132	41
5	333	385	41	163	37
7	302	322	35	189	31

Table 4. *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ in 0.4 M HNO_3 at 40°C.

Hours	found	$k_{-4} : 0.10$	
0	0.0187	0.0211	
4	132	141	
9.5	72	82	

Hours	found	$k_{-4} : 0.12$	NH_3/Cr in products
0	0.0220	0.0323	—
2	181	254	2.6
5	134	177	2.6
10	70	97	2.5
20	20	29	2.4

Table 5. 0.0534 M $\text{Cr}(\text{NH}_3)_6^{+++}$ in 0.1 M NaOH , 0.3 M KNO_3 at 40°C.

Hours	Hexammine		Hydroxopentammine	
	found	$k_{-5} : 0.0100$	found	$k_{-5} : 0.0100$ $k_{-5} : 0.035$
1	0.0505	0.0529	0.0010	0.0006
3	484	518	19	17
6	457	503	36	31
24	400	420	54	82
35	345	376	65	98
46	322	337	76	103
55	298	308	72	103
75	228	252	63	95
101	188	194	51	80

Table 6. 0.0530 M $\text{Cr}(\text{NH}_3)_5\text{OH}^{+++}$ in 0.1 M NaOH 0.3 M KNO_3 at 40°C.

Hours	found	$k_{-5} : 0.035$
0.0	0.0485	0.0530
0.5	442	521
1.0	437	512
2.0	420	494
3.0	405	477
4.0	388	461
8.0	320	401
12.0	304	348
19.8	227	265
28.5	176	196
36.0	134	150

Table 7. 0.0309 M *cis*-Cr(NH₃)₁(OH)₂⁺ in 0.1 M NaOH, 0.3 M KNO₃ at 40°C.

Hours	found	$k_{-4} : 3$
0.0	0.0165	0.0309
0.1	132	239
0.2	76	177
0.3	50	131
0.4	48	97

Table 8. 0.0473 M Cr(NH₃)₂(H₂O)₄⁺⁺⁺ in 0.2046 M HNO₃, 0.2 M KNO₃ at 40°C.
a. pH-titration data, and measured molar extinction coefficients.

Hours	x ml NaOH 0.5018 M	$-\Delta[\text{H}^+]$	ϵ_{570}	ϵ_{540}	ϵ_{520}	ϵ_{480}	ϵ_{385}
0.35	4.058	0.0005	12.2	19.5	21.2	12.2	24.4
0.60	4.044	0.0012	12.4	19.8	21.4	12.4	24.7
2	4.020	0.0024	12.7	19.5	20.9	11.9	24.1
4	3.954	0.0057	13.2	19.7	20.9	11.8	24.1
8	3.844	0.0112	13.5	19.4	20.0	10.8	22.7
12	3.745	0.0161	13.9	19.5	19.5	10.4	22.2
22	3.542	0.0263	14.7	19.2	18.6	9.43	20.7
34	3.336	0.0366	15.1	18.6	17.1	8.12	18.7
52	3.123	0.0472	15.9	18.2	15.9	7.15	17.5
76	2.974	0.0546	15.8	16.9	14.3	6.16	16.2
142	2.686	0.0690	15.2	14.7	11.4	4.67	14.4
225	2.477	0.0794	14.3	12.5	9.23	3.87	12.9
338	2.355	0.0855	14.2	11.4	8.08	3.81	12.7
506	2.281	0.0892	13.6	10.4	7.11	3.45	12.0
646	2.246	0.0910	13.4	10.2	6.95	3.33	11.8
∞	2.173	0.0946	13.6	10.1	6.90	3.44	11.9

b. pK_{a1} and calculated distribution of chromium on the various complexes.
 $n = 2$, $pK_{a1} = 4.11$, $pK_{a2} = 6.59$, $pK_{a3} = 9.17$.

Hours	pK_{a1}	\bar{n}_{exp}	$\alpha_2 + \alpha_1'$	α_1	α_0	\bar{n}_{calc}	α_2
0.35	4.11	1.989	0.988	0.012	0.000	1.988	0.002
0.6	4.11	1.975	0.979	0.021	0.000	1.978	0.003
2	4.12	1.949	0.932	0.068	0.000	1.932	0.011
4	4.15	1.880	0.870	0.128	0.002	1.867	0.021
8	4.19	1.764	0.759	0.232	0.009	1.750	0.038
12	4.22	1.659	0.666	0.315	0.019	1.646	0.052
22	4.23	1.445	0.487	0.458	0.055	1.431	0.079
34	4.28	1.227	0.349	0.540	0.111	1.238	0.098
52	4.30	1.003	0.233	0.563	0.204	1.028	0.110
76	4.36	0.845	0.162	0.514	0.324	0.838	0.114
142	4.33	0.541	0.108	0.316	0.576	0.532	0.102
225	4.26	0.321	0.086	0.162	0.752	0.333	0.083
338	4.24	0.192	0.064	0.071	0.865	0.200	0.062
506	4.22	0.114	0.042	0.026	0.932	0.111	0.041
646	4.26	0.077	0.030	0.015	0.955	0.075	0.029
∞	4.26	0	0	0	1	0	0

RESULTS AND DISCUSSION

The rate constants which head the third column of Tables 1—7 are evaluated graphically from the slope of the straight line obtained by plotting the logarithm of the experimental complex concentrations (given in the second column) against the time measured in hours. The concentrations in the third column are calculated from the rate constant and the initial complex concentration. When the figures of these two columns are compared, it is easily seen that the agreement is satisfactory only when due regard is paid to the loss of chromium on the column during the chromatographic analysis. This is certainly the case with the tetrammine chromium ions and particularly with the figures of Table 7. The value of k_{-4} is in this case given only as a size of order guess. As a whole, however, the numerical values of the rate constants are considered reliable. The value of k_{-6} given in the previous publication¹ from an altogether different way of analysis is $1.34 \times 10^{-6} \text{ sec}^{-1} = 0.0048 \text{ h}^{-1}$.

In Tables 1 and 5 are also given the concentrations of aquopentammine and hydroxopentammine found during the aquation and hydroxylation, respectively, of the hexammine, and they are seen to agree with the concentrations which can be calculated from the expression for the intermediate in two consecutive unimolecular reactions, see for example the second example in the appendix. Similarly, in Table 3 the concentration of tetrammine accumulated during the aquation of pentammine is given but does not at all correspond to the rate constant found for *cis*-diaquotetrammine (Table 4). It must then be concluded that the aquopentammine aquates mainly through the *trans*-diaquotetrammine. A column in Table 3 shows the concentrations of tetrammine to be expected if the pentammine was aquated through the *trans*-diaquotetrammine exclusively and if this complex disappeared at a rate ten times faster. It will be seen that this assumption gives a rather good agreement. It should be mentioned that *cis-trans* isomerization has been completely neglected.

The last column in Tables 1, 2 and 4 indicates the average number of ammonia per chromium atom in the aquated reaction products exclusive of the initial complex. The figures give immediately the impression that di- and monammine are just as robust as hexammine and that triammine roughly is as robust as pentammine.

The interpretation of the experimental results concerning the aquation of tetraquodiammine given in Table 8 requires a somewhat different practice. Already a look at the experimental values of pK_{a1} in Table 8b shows qualitatively that there must exist an intermediate of comparatively high stability with a higher value of pK_{a1} than that of the diammine and hexaquo ion. To the quantitative treatment we have the following relationships: The decrease in the hydrogen ion concentration $- \Delta[\text{H}^+]$ according to the appendix can be described by

$$\frac{- \Delta[\text{H}^+]}{C_{\text{Cr}}} = 2 - a_1 \exp(-k_{-2}t) - a_2 \exp(-k_{-2}t) - a_3 \exp(-k_{-1}t)$$

or

$$\bar{n} = a_1 \exp(-k_{-2}t) + a_2 \exp(-k_{-2}t) + a_3 \exp(-k_{-1}t)$$

where C_{Cr} is the total chromium concentration, and \bar{n} is the average number of ammonia molecules bound per chromium atom in the reaction mixture.

The experimental values for \bar{n} which are given in the third column of Table 8b are now fitted to these expressions by trial and error. A particularly systematic "least square method" has not been used because of the overwhelming number of numerical calculations necessary. Due regard is paid to the fact that the 6 parameters are not independent. From the appendix it will be seen that a_1, a_2, a_3 can be expressed by 4 independent parameters: $k_{-1}, k_{-2}, k_{-2'}$ and $w_{2'1}$. In addition there are 3 different possibilities for choosing k_{-1} , but for the remaining two the indices are exchangeable. For the eighteen experimental results, most of them given in Table 8, the following parameters were chosen:

$$\begin{array}{lll} a_1: 0.60 & a_2: 0.36 & a_3: 1.04 \\ k_{-2'}: 0.041 & k_{-2}: 0.0025 & k_{-1}: 0.0093 \end{array}$$

The seventh column contains \bar{n} calculated from these parameters.

w_{10} is identical with $k_{-1} = 0.0093$ and $w_{2'1}$ can be directly calculated as the sum $a_1 k_{-2'} + a_2 k_{-2} + a_3 k_{-1} = 0.035$.

It is now possible to calculate the relative amounts of *cis* and *trans* diammine ($\alpha_2 + \alpha_2'$), monammine α_1 and hexaquo chromium ion α_0 as a function of time, since the previously mentioned Q_{ij} 's contain $k_{-2'}$, k_{-2} , k_{-1} and $w_{2'1}$ only. They are listed in Table 8b and show quantitatively that the monammine is the predominant complex for the period of 30–80 h after the start of the reaction.

If we denote the measured properties of the reacting solution (pK_{a1} and the molar extinction coefficients at various wavelenths) by U , the corresponding property of the monammine is obtained as the slope of the straight line in a plot of $\frac{U - \alpha_0 u_0}{\alpha_2' + \alpha_2}$ versus $\frac{\alpha_1}{\alpha_2' + \alpha_2}$. This relationship should only be a straight line when the properties of *cis* and *trans* diammine are only slightly different, and this seems to be the case with a possible exception for ϵ_{480} , in which case the plot indicates a higher extinction for the *cis* than for the *trans* isomer.

The estimated properties for the monammine are given in Table 9 compared with the corresponding properties for the diammine and the hexaquo chromium ion. The molar extinctions of the monammine are also represented as crosses in Fig. 3.

Table 9. Estimated properties for the pentaquomonammine chromium(III) ion at $\sim 20^\circ\text{C}$.

	pK_{a1}	ϵ_{570}	ϵ_{540}	ϵ_{520}	ϵ_{480}	ϵ_{385}
$\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{+++}$	4.11	12.1	19.2	21.0	12.1	24.2
$\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_5^{+++}$	4.4	18	20	17	5.5	16
$\text{Cr}(\text{H}_2\text{O})_6^{+++}$	4.26	13.6	10.1	6.9	3.44	11.9

The remaining reaction probabilities are related by

$$\begin{aligned} k_{-2}k_{-2'} &= w_{2'2}w_{21} + w_{22'}w_{2'1} + w_{2'1}w_{21} \\ k_{-2} + k_{-2'} &= w_{2'2} + w_{2'1} + w_{22'} + w_{21} \end{aligned}$$

giving

$$w_{2'2} \cong 0.0056 \quad w_{21} + w_{22'} \cong 0.0027$$

The distribution of the diammine chromium ion between the *cis* and *trans* isomer throughout the reaction can also be approximated, and it is seen from the last column of Table 8b that the maximum amount of the *cis* isomer is more than 11 %. However, it is necessary to make serious reservations regarding this figure as well as regarding the estimates of $w_{2'2}$ and $w_{21} + w_{22'}$, because the rate equation is not critically influenced by these quantities.

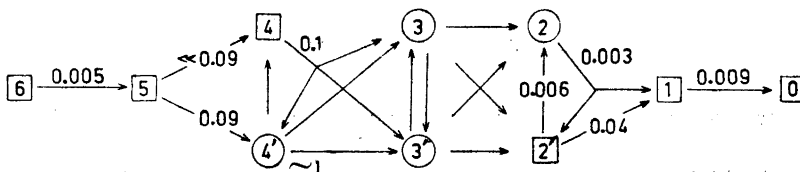


Fig. 1. Velocity constants (hour⁻¹) in > 0.1 M HNO₃ at 40°C.

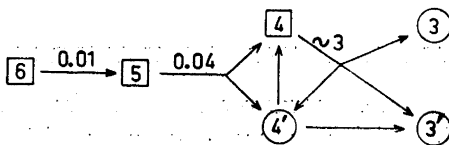


Fig. 2. Velocity constants (hour⁻¹) in ~ 0.1 M NaOH at 40°C.

The reaction probabilities found in acidic and basic solution are summarized in Figs. 1 and 2. As a whole, the hydroxo-ammine complexes are less robust than the corresponding aquo complexes. It is therefore remarkable that hydroxopentammine is seen to decompose more slowly than the aquopentammine chromium ion. Triaquotriammine chromium(III) salts have been prepared by Werner⁸ but have not been utilized in this study. The squares in Figs. 1 and 2 indicate the components which have been used in our experiments. The spectra of these complexes in acidic solution are recorded in Fig. 3, which also gives the spectrum of the monammine. This compound was obtained in crystalline form in a preliminary attempt to prepare it from the reaction mixture. The data which were calculated from the mixed spectra are seen to be represented by the curve fairly well.

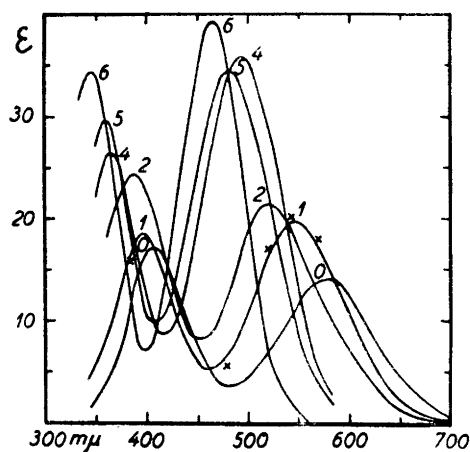


Fig. 3. Some absorption spectra of aquoammine chromium(III) ions in 0.5 M nitric acid at room temperature.

Curve 6: hexamine, 5: aquo-pentammine, 4: *cis*-diaquo-tetrammine, 2: *trans*(?) tetra-aquodiammine, 1: penta-aquomonammine (0.1 M HNO₃) and 0: hexaquo ions (1 M HNO₃). ×-points for the monammine are calculated from the data given for the mixed spectra in the reaction mixtures of Table 8.

PREPARATION OF THE MONAMMINE AS CONSTITUENT OF A CESIUM ALUM

The monammine, which completes, apart from isomers, the series $\text{Cr}(\text{NH}_3)_6^{+++} \dots \text{Cr}(\text{H}_2\text{O})_6^{+++}$, was prepared in the following way. 0.440 g $[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{OH})_2]\text{Cl}$ was dissolved in 40 ml 0.55 M HNO₃ and placed at 40°C for 48 h. After this time the reaction mixture contained the maximum amount of monammine, *cf.* Table 8. It was now intended to precipitate the hexaquo ions as the cesium alum, which according to N. Bjerrum and Faurholt⁹ is shown to be a very complete precipitation under the following conditions: To the cold solution 1 ml 2 M H₂SO₄ and 2 g cesium sulphate were added, followed by 20 ml 96 % alcohol after 1 h. It was remarkable that the precipitate did not have the greyish violet colour of the hexaquo ion but had a distinct purple colour probably due to the presence of monammine. The supernatant was placed for some hours at 0°C and a slight precipitate was formed which consisted of cyclamen coloured octaeters. An examination under the polarization microscope showed them to be isotropic. The crystals were not isolated but dissolved in 4–5 ml 0.1 M HNO₃ after rinsing with alcohol. After the spectrum had been taken, the concentrations of chromium and ammonia were found to be 0.0252 M and 0.0259 M, respectively. It is thus shown to be a monammine, and the octaeterform of the crystals suggests it to be an alum, $\text{CsCr}(\text{SO}_4)_2 \cdot \text{NH}_3 \cdot 11 \text{H}_2\text{O}$.

In order to confirm the presence of monammine in the main precipitate it was dissolved in 40 ml of water and 1/4 ml H₂SO₄, and 2 g cesium sulphate

was added. The precipitate was still somewhat more reddish than the hexaquo chromium ion. The concentrations of chromium and ammonia in the supernatant were 0.00815 M and 0.00842 M, respectively.

THE ACID-BASE CONSTANTS OF THE TETRAQUODIAMMINE
CHROMIUM(III) ION

From the data for the titration of the tetraquodiammine solution the second and third dissociation exponents, pK_{a2} and pK_{a3} , were estimated in addition to pK_{a1} . The following values (also mentioned in Table 8b) were determined in ~ 0.5 M nitrate solution at $\sim 20^\circ\text{C}$:

$$pK_{a1} = 4.11, \quad pK_{a2} = 6.59, \quad pK_{a3} = 9.17.$$

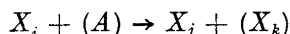
A slow drift towards larger values of pH took place when more than 2 mole NaOH per chromium atom was added, showing that $[\text{Cr}(\text{NH}_3)_2(\text{OH})_3\text{H}_2\text{O}]$ splits off its ammonia rather quickly at room temperature. This drift was accounted for by the estimate of pK_{a3} . A drift in the opposite direction was observed in the 22 hours' reaction mixture after an addition of 1.33 base equivalents, and after the lapse of a longer time even after addition of little more than one base equivalent per chromium atom due to the formation of polynuclears from the increasing amount of $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2^+$.

Our thanks are due to Mr. C. E. Schäffer for valuable help in the preparing of salts.

APPENDIX

(by Erik Jørgensen)

The reactions dealt with in this paper belong to a rather common class. The partial reactions can be expressed by



X_i is the i 'th of the time dependent components and A is a component in great excess (or a component the concentration of which for some other reason can be kept constant during the reaction), it may be the solvent molecules. A and X_k are bracketed as they need not necessarily enter the scheme.

The calculations necessary to obtain the integrated rate expression can be systematized and simplified by introducing matrix methods. In the following it will be aimed at bringing this class of reactions within the framework of matrix algebra as, for example, it is formulated by Margenau and Murphy¹⁰ whose widespread book is referred to concerning definitions and symbolism.

Let the initial component be X_1 and the reaction products $X_2, X_3, X_4, \dots, X_n$ in a convenient numerical order, X_n being one of the components present at equilibrium.

Setting c_{X_i} equal to x_i , we will define the *concentration vector* x as the column vector $\{x_1, x_2, x_3, \dots, x_n\}$. The mass action law determines a matrix A which transfers x to $-dx/dt$.

$$-dx/dt = Ax \quad (1)$$

A contains only constants at the conditions given. These constants are the "microscopic velocity constants" in question, which we according to Christiansen⁴ may call "reaction probabilities per unit time" and represent by $w_{i,j(k)}$ for the above-mentioned partial reaction.

The characteristic matrix of A is $K = (\lambda E - A)$. The eigenvalues will be called λ_i — one of them, let it be λ_n , always being zero. If all the eigenvalues are different, which is practically no qualification, A can be reduced to true diagonal form.

Two orthogonal matrices, P and Q , may be constructed for this purpose in the following way:

$$P_{ij} = \frac{K^{jn}(\lambda_i)}{K^{1n}(\lambda_i)} \quad Q_{ij} = \frac{P^{ji}}{|P|} \quad (2)$$

$$\text{Now} \quad PAQ = \{\lambda_i \delta_{ij}\} \quad (3)$$

Forming another concentration vector

$$y = Px \quad (4)$$

i.e. $x = Qy$, we get from (1)

$$-Qdy/dt = AQy$$

which multiplied by P gives

$$dy/dt = -\{\lambda_i \delta_{ij}\}y$$

with the solution

$$y = \{c_1 \cdot \exp(-\lambda_1 \cdot t), c_2 \cdot \exp(-\lambda_2 \cdot t), \dots, c_n \cdot \exp(-\lambda_n \cdot t)\}$$

Setting the initial concentration of x_1 equal to x_1^0 , we have at $t = 0$ from (4)

$$y = x_1^0 \{P_{11}, P_{21}, P_{31}, \dots, P_{n1}\}$$

From (2) it is seen that $P_{11} = 1$, meaning that the c 's are all equal to x_1^0 . Then the complete solution including the boundary condition is

$$y = x_1^0 \{\exp(-\lambda_1 \cdot t), \exp(-\lambda_2 \cdot t), \dots, \exp(-\lambda_n \cdot t)\}$$

or

$$x = x_1^0 Q \{\exp(-\lambda_1 \cdot t), \exp(-\lambda_2 \cdot t), \dots, \exp(-\lambda_n \cdot t)\} \quad (5)$$

P and Q may also be valuable tools for additive molar properties of the n components — conductivity, optical density, etc. If $u = \{u_1, u_2, \dots, u_n\}$ is the vector containing these properties, the total property, $U = \tilde{u}x$, can be described as a function of time by $\tilde{u}_\lambda \{\exp(-\lambda_1 \cdot t), \exp(-\lambda_2 \cdot t), \dots, \exp(-\lambda_n \cdot t)\}$.

Now the following relations hold between the property vector u and the coefficient vector u_λ :

$$u_\lambda = x_1^0 \tilde{Q}u \quad (6)$$

$$u = (x_1^0)^{-1} \tilde{P}u_\lambda \quad (7)$$

Differentiation of U with respect to t and setting t equal to zero leads to another useful formula:

$$\tilde{u} \{A_{11}, A_{21}, \dots, A_{n1}\} x_1^0 = \tilde{u}_\lambda \{\lambda_1, \lambda_2, \dots, \lambda_n\} \quad (8)$$

How the matrix algebra is to be applied should be evident from the following rather simple examples.

The first example is that of isomerism between 2 components. In this case

$$X_1 \rightleftharpoons X_2$$

$$A = \begin{bmatrix} w_{12} & -w_{21} \\ -w_{12} & w_{21} \end{bmatrix} \quad K = \begin{bmatrix} \lambda - w_{12} & w_{21} \\ w_{12} & \lambda - w_{21} \end{bmatrix}$$

$$\lambda_1 = w_{12} + w_{21} \quad \lambda_2 = 0$$

$$K^{12} = -w_{12} \quad K^{22} = \lambda - w_{12}$$

$$P = \begin{bmatrix} 1 & -\frac{w_{21}}{w_{12}} \\ 1 & 1 \end{bmatrix} \quad Q = \begin{bmatrix} \frac{w_{12}}{w_{12} + w_{21}} & \frac{w_{21}}{w_{12} + w_{21}} \\ -\frac{w_{12}}{w_{12} + w_{21}} & \frac{w_{12}}{w_{12} + w_{21}} \end{bmatrix}$$

The second example is the wellknown one of two consecutive reactions:

$$X_1 \rightarrow X_2$$

$$X_2 \rightarrow X_3$$

$$A = \begin{bmatrix} w_{12} & 0 & 0 \\ -w_{12} & w_{23} & 0 \\ 0 & -w_{23} & 0 \end{bmatrix} \quad K = \begin{bmatrix} \lambda - w_{12} & 0 & 0 \\ w_{12} & \lambda - w_{23} & 0 \\ 0 & w_{23} & \lambda \end{bmatrix}$$

$$\lambda_1 = w_{12} \quad \lambda_2 = w_{23} \quad \lambda_3 = 0$$

$$K^{13} = w_{12}w_{23} \quad K^{23} = -w_{23}(\lambda - w_{12}) \quad K^{33} = (\lambda - w_{12})(\lambda - w_{23})$$

$$P = \begin{bmatrix} 1 & 0 & 0 \\ 1 & \frac{w_{12} - w_{23}}{w_{12}} & 0 \\ 1 & 1 & 1 \end{bmatrix} \quad Q = \begin{bmatrix} 1 & 0 & 0 \\ -\frac{w_{12}}{w_{12} - w_{23}} & \frac{w_{12}}{w_{12} - w_{23}} & 0 \\ \frac{w_{23}}{w_{12} - w_{23}} & \frac{-w_{12}}{w_{12} - w_{23}} & 1 \end{bmatrix}$$

The third example is the reaction scheme which has been necessary to describe the aquation of the *trans*-tetraquodiammine chromium(III) ion in the present paper. Therefore, the indices have been changed to conform with those of the main text (2'~1, 2~2, 1~3, 0~4).

$$\begin{aligned} X_{2'} &\rightleftharpoons X_2 \\ X_{2'} &\rightarrow X_1 \\ X_2 &\rightarrow X_1 \\ X_1 &\rightarrow X_0 \end{aligned}$$

$$A = \begin{bmatrix} w_{2'2} + w_{2'1} & -w_{2'2} & 0 & 0 \\ -w_{2'2} & w_{22'} + w_{21} & 0 & 0 \\ -w_{2'1} & -w_{21} & w_{10} & 0 \\ 0 & 0 & -w_{10} & 0 \end{bmatrix}$$

$$\lambda_1 \cdot \lambda_2 = k_{-2'} \cdot k_{-2} = w_{2'2}w_{21} + w_{22'}w_{2'1} + w_{2'1}w_{21}$$

$$\lambda_1 + \lambda_2 = k_{-2'} + k_{-2} = w_{2'2} + w_{2'1} + w_{22'} + w_{21}$$

$$\lambda_3 = k_{-1} = w_{10} \quad \lambda_4 = 0$$

$$K^{14} = -k_{-1}(k_{-2'}k_{-2} - w_{2'1}\lambda) \quad K^{24} = -k_{-1}(k_{-2'}k_{-2} - w_{21}\lambda)$$

$$K^{34} = -k_{-1}(\lambda - k_{-2})(\lambda - k_{-2'}) \quad K^{44} = (\lambda - k_{-1})(\lambda - k_{-2})(\lambda - k_{-2'})$$

$$P = \begin{bmatrix} 1 & \frac{k_{-2} - w_{21}}{k_{-2} - w_{2'1}} & 0 & 0 \\ 1 & \frac{k_{-2'} - w_{21}}{k_{-2'} - w_{2'1}} & 0 & 0 \\ 1 & \frac{k_{-2'}k_{-2} - w_{21}k_{-1}}{k_{-2'}k_{-2} - w_{2'1}k_{-1}} & \frac{(k_{-1} - k_{-2})(k_{-1} - k_{-2'})}{k_{-2'}k_{-2} - w_{2'1}k_{-1}} & 0 \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

$$Q = \begin{bmatrix} \frac{(k_{-2} - w_{21})(k_{-2'} - w_{21})}{(k_{-2'} - k_{-2})(w_{21} - w_{2'1})} & -\frac{(k_{-2} - w_{21})(k_{-2'} - w_{2'1})}{(k_{-2'} - k_{-2})(w_{21} - w_{2'1})} & 0 & 0 \\ \frac{(k_{-2} - w_{21})(k_{-2'} - w_{2'1})}{(k_{-2'} - k_{-2})(w_{21} - w_{2'1})} & \frac{(k_{-2} - w_{21})(k_{-2'} - w_{21})}{(k_{-2'} - k_{-2})(w_{21} - w_{2'1})} & 0 & 0 \\ \frac{k_{-2'}(k_{-2} - w_{21})}{(k_{-2'} - k_{-2})(k_{-1} - k_{-2'})} & \frac{k_{-2}(k_{-2'} - w_{21})}{(k_{-2'} - k_{-2})(k_{-1} - k_{-2})} & \frac{k_{-2'}k_{-2} - w_{21}k_{-1}}{(k_{-1} - k_{-2'})(k_{-1} - k_{-2})} & 0 \\ \frac{k_{-1}(k_{-2} - w_{21})}{(k_{-2'} - k_{-2})(k_{-1} - k_{-2'})} & \frac{k_{-1}(k_{-2'} - w_{21})}{(k_{-2'} - k_{-2})(k_{-1} - k_{-2})} & \frac{k_{-2'}k_{-2} - w_{21}k_{-1}}{(k_{-1} - k_{-2'})(k_{-1} - k_{-2})} & 1 \end{bmatrix}$$

The property measured was the decrease of the hydrogen ion concentration during the reaction. Accordingly, the *property vector* and *coefficient vector* are the following:

$$\mathbf{u} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 2 \end{bmatrix} \quad \mathbf{u}_\lambda = x_1^0 \tilde{\mathbf{Q}} \mathbf{u} = x_1^0 \begin{bmatrix} \frac{(2k_{-1}-k_{-2}')(k_{-2}-w_{2'1})}{(k_{-2}'-k_{-2})(k_{-1}-k_{-2}')} \\ -\frac{(2k_{-1}-k_{-2})(k_{-2}'-w_{2'1})}{(k_{-2}'-k_{-2})(k_{-1}-k_{-2})} \\ -\frac{k_{-2}'-k_{-2}-w_{2'1}k_{-1}}{(k_{-1}-k_{-2}')(k_{-1}-k_{-2})} \\ 2 \end{bmatrix} = x_1^0 \begin{bmatrix} -a_1 \\ -a_2 \\ -a_3 \\ 2 \end{bmatrix}$$

Eqn. (8) gives

$$w_{2'1} = -(x_1^0)^{-1} \tilde{\mathbf{u}}_\lambda \{\lambda_1, \lambda_2, \lambda_3, \lambda_4\} = a_1 k_{-2}' + a_2 k_{-2} + a_3 k_{-1}$$

which of course can also be seen by direct calculation.

The experimental results in one way or other written as a sum of exponential functions are seen directly to give w_{10} and $w_{2'1}$. k_{-2}' and k_{-2} contain the remaining three reaction probabilities, and at least one further independent determination is necessary to calculate all of them.

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