Kinetics of Complex Formation

III *. The Rate of Decomposition of Hexammine Chromium(III) Ion

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The decomposition of hexammine chromium(III) ion in nitric acid solutions is followed by measuring the rate of dissolution of the hexammine nitrate. The aquation of the hexammine is independent of the hydrogen ion concentration and the following expression is found for the pseudo-unimolecular velocity constant

$$k_{-6} = 10^{12.3} \cdot e^{-26\,000/RT}$$

By spectrophotometric analysis it is proved that the hexammine decomposes by going through a series of lower ammines.

The complexity of the chromium(III)-ammines can apparently not be determined in aqueous ammonia-ammonium buffers. The ammines undergo various transformations and under certain conditions polynuclear salts may be formed [3]. Even in solutions with very high ammonium salt concentration a slow irreversible decomposition continues which sooner or later results in the separation of some basic precipitates. It may be mentioned that a hexammine chromium(III) solution of the composition: $C_{Cr} = 0.006$ M, $C_{NH_3} = 2$ M, $C_{NH_4NO_3} = 5$ M, which was kept in the dark at 68°, remained completely homogeneous for two days, but on the third day nearly all the chromium had separated as a basic precipitate. Fig. 1a shows how the absorption spectrum of this solution changes with time at 25° and 68° C. An experiment in which charcoal was added to the same solution (see Fig. 1a) shows that heterogeneous catalysis, contrary to what is found [4] for corresponding transformations of cobalt(III)-ammines, only plays a minor role in the decomposition reactions of chromium(III)-ammines. Day-light catalyzes the decomposition to some extent, and for this reason all solutions were kept in dark bottles.

Fig. 1b shows how the absorption spectra of acidic hexammine chromium(III) nitrate solutions change with time at 50°. The family of curves shows directly that the transformations proceed independent of the hydrogen

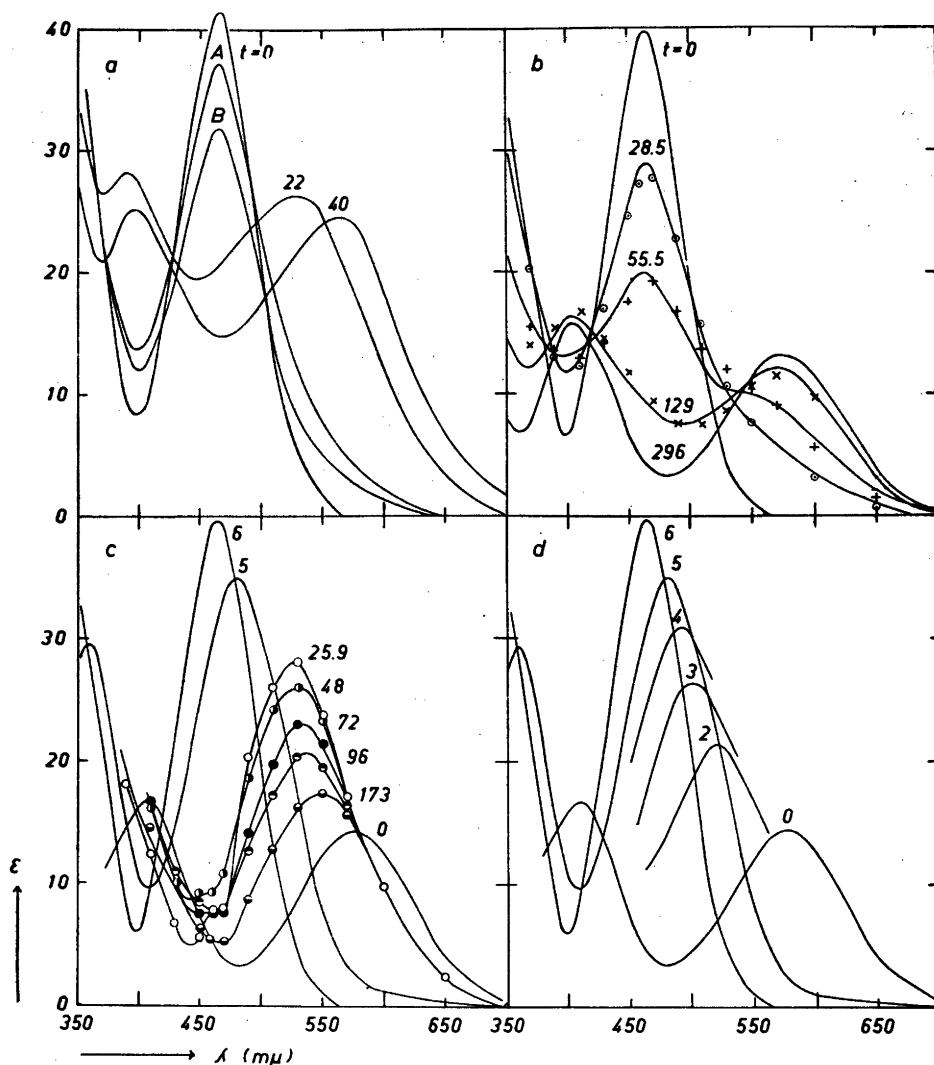---

* For the earlier papers in this series, see Refs. [1,2].

Fig. 1. Molar extinction coefficients versus wavelength in mμ.

a: A solution of the composition: $C_{Cr} = 0.006$ M, $C_{NH_3} = 2$ M, $C_{NH_4NO_3} = 5$ M followed in time. Curve A: 100 hrs at 25° C. Curve B: 100 hrs at 25°, but with 2 g "Norite" per 100 ml. Curves after 22 and 40 hrs at 68.5° are also given.

b: Acidic 0.005 M hexammine chromium (III) nitrate solutions followed in time at 50° C. In 1 M HNO_3 after 0, 28.5, 55.5, 129 and 296 hrs (full-drawn curves). In 0.5 M HNO_3 after 29 hrs (o-points), 54.5 hrs (+ points), and in 2 M HNO_3 after 127.5 hrs (× -points).

c: Absorption spectra of reaction products. ε_R, λ-curves at 40° corresponding to the experiment given in Table 1. For comparison is also given the absorption of hexammine, aquopentammine and hexaquo chromium (III) ions (curves 6, 5 and 0, respectively).

d: Absorption spectra of aquoammine chromium (III) ions at room temperature. Hexammine and hexaquo in 1 M HNO_3 (curves 6 and 0). Aquopentammine in 0.1 M $HClO_4$ (curve 5) according to measurements of C. E. Schäffer. Diaquotetrammine, triaquotriammine and tetraquodiammine in water (curves 4, 3 and 2) according to Colmar and Schwartz [5].

Table 1. Velocity of decomposition of hexammine chromium (III) ion in 1 M HNO₃
at 40° C.

t_{hours}	0	25.92	48.0	72.25	95.75	172.6
C_{NH_3}	0.1763	0.1976	0.2152	0.2359	0.2618	0.3311
$C_{NH_3} - C_{NH_3}^o$	0	0.0213	0.0389	0.0596	0.0855	0.1548
$10^8 \cdot \dfrac{d\ C_{Cr}}{d\ t_{sec.}}$	—	3.81	3.75	3.82	4.13	4.15
$10^6 \cdot k_{-6}$ (sec.$^{-1}$)	—	1.30	1.28	1.30	1.40	1.41

k_{-6}(av.) $= 1.34 \cdot 10^{-6}$

ion concentration in 0.5, 1 and 2 *M* nitric acid solution. After about 300 hours the absorption curve has reached an appearance which is very similar to that of the hexaquo chromium(III) ion (see Fig. 1d, where also absorption curves [5] for the intermediate chromium(III) ammines are given). The extinction coefficients in the maxima are somewhat higher than for the hexaquo ion, but polynuclear latently basic compounds perhaps exist in the solution [6].

The velocity of decomposition of the hexammine chromium(III) ion was determined directly by measuring the rate of dissolution of luteo nitrate in nitric acid solutions. Solvent and salt were vigorously shaken in a thermostat, and samples were taken from time to time, and the increase in concentration as well as the optical density at various wavelengths were determined. For convenience, the total ammonia concentration $C_{NH_3} = 6C_{Cr}$ instead of the chromium was determined by a micro-Kjeldahl distillation. Denoting the molar saturation concentrations for luteo salt with C_{Cr}^o and $C_{NH_3}^o$, respectively, we have:

$$\frac{d\ C_{Cr}}{d\ time} = \frac{C_{NH_3} - C_{NH_3}^o}{6 \cdot time} = k_{-6} \cdot \frac{C_{NH_3}^o}{6}$$

and for the velocity constant

$$k_{-6} = \frac{C_{NH_3} - C_{NH_3}^o}{C_{NH_3}^o \cdot time}$$

Saturation is reached in a few minutes, and the data given in Table 1 show that it is possible by this method to get fairly constant values for the rate constant.

Denoting the optical density in general by D, and the optical density of pure hexammine in saturated solution by D_6^o, we get for the mean extinction coefficient of the reaction products formed by the decomposition:

$$\varepsilon_R = \frac{D - D_6^o}{(C_{Cr} - C_{Cr}^o) \cdot d} = \frac{6\ (D - D_6^o)}{(C_{NH_3} - C_{NH_3}^o) \cdot d}$$

where d is the thickness of the absorbing layer in cm. The mean extinction coefficients of reaction products found at various times in the experiment given in Table 1 are plotted in Fig. 1c. The family of curves is not far from having an isopiestic point in common with all the known aquo ammine

Table 2. Average values for the aquation velocity constant.

$$\log k_{-6} = 12.3 - \frac{26\ 000}{4.57\ T}$$

°C	$1/T°$	$C_{Cr}^{°}$ (solubility in 1 M HNO$_3$)	log k_{-6} (sec.$^{-1}$) obs.	calc.
25.0	0.003356	0.00964	−6.69	−6.8
40.0	0.003195	0.02938	−5.87	−5.85
63.8	0.002969	0.1260	−4.51	−4.6

chromium(III) ions except the pentammine ion (see Fig. 1d). It is, therefore, far from certain that aquo pentammine is ever important among reaction products. It is qualitatively known from direct observations that this ion is decomposed to lower ammines at a much higher rate than the luteo ion. On the other hand the relatively strong displacement of the maximum of the ε_R-curves towards red seems to exclude the possibility that the simple ammines are the only reaction products.

The mean values for k_{-6} determined at 25°, 40° and 63.8° C are shown in Table 2. By graphic interpretation of the data the activation energy E is estimated to 26 kcal/mole, and the frequency factor $Z'_{-6} = Z_{-6} \cdot C_{aq}$ to $10^{12.3}$. The values for the velocity constant computed from these values for the Arrhenii constants are also given in the table.

EXPERIMENTAL

Preparation of salts. With minor modifications the complex salts used were prepared according to methods described in the literature. Hexammine chromium(III) nitrate was prepared from the luteo chloride, which was prepared by the Christensen method from anhydrous chromium(III) chloride and liquid ammonia [7]. The hexammine nitrate was purified by repeated reprecipitations with nitric acid; the product was washed with alcohol and air-dried at 60° C, and prepared in this way it could be kept unchanged for months in a dark bottle with a tight fitting stopper. *Anal.* Calc. for Cr(NH$_3$)$_6$(NO$_6$)$_3$: Cr 15.3; N 37.1. Found: Cr 15.1; N 37.1. The solubility of the salt at 18.6° C was found to be 0.0117 M in 0.5 M HNO$_3$, 0.00543 M in 1.0 M HNO$_3$, and 0.00314 M in 2.0 M HNO$_3$.

Technique. The measurements of the rate of dissolution of the hexammine nitrate were made in a water thermostat with an arrangement for effective horizontal shaking of a bottle. At various times during an experiment the shaking was stopped for a short time, and a measured amount of the saturated solution drawn up through a glass filter, adequately diluted and cooled. In order to avoid precipitation during the transference of the saturated solution the pipette was surrounded by a glass mantle containing water at the thermostat temperature.

The optical densities were measured at a Beckman DU. Cells of 1, 2 and 5 cm were used according to wavelength and dilution.

The total ammonia concentrations of the solutions were determined by a micro-Kjeldahl distillation in a Parnas-Wagner apparatus. The solution was transferred with a syringe pipette, and the ammonia was steam-distilled into an excess of 0.01 N HCl. The back titration was made with a 0.01 N borax solution, and methylred was used as indicator. A blank was run to correct for traces of ammonia in the Kjeldahl lye.

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