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Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. IV. Reaction Products of the Acid Hydrolysis of Pentaammineaquachromium(III)

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The authors of two recent papers^{1,2} on the aquation in acid solution of the pentaammineaquachromium(III) ion disagree about the nature of the reaction products. The discrepancies between the reported results are summarized in Table 1. No quantitative error limits are given for the reaction rate constants of Ref. 2, but it is stated that the *trans*-tetraammineaquachromium(III) ion is a significant reaction product. Contrary to this result the

Table 1. Comparison between reaction rate constants at 75°C in a 1 M perchlorate medium for formation of *cis*- (k_{sc}) and *trans*-tetraammineaquachromium(III) (k_{st}) from pentaammineaquachromium(III).

	$10^6 \times k_{sc}$ (s ⁻¹)	$10^6 \times k_{st}$ (s ⁻¹)	$10^6 \times (k_{sc} + k_{st})$ (s ⁻¹)
Ref. 1	83.1 ± 1.4	0.0 ± 0.8	83.1 ± 1.4
Ref. 2	~ 60	~ 15	77, 78

trans-tetraammine ion was not found in detectable amounts according to Ref. 1.

Different experimental approaches to the kinetic investigation were employed in the two papers. In Ref. 1, changes in the visible absorption spectra of a series of quenched reaction mixtures were directly converted into reaction rate constants. In Ref. 2, however, the overall reaction rate constant for disappearance of the pentaammine ion was obtained after separation of unreacted pentaammine ions from the quenched reaction mixtures by ion exchange chromatography in basic solution. This total reaction rate constant was then separated into *cis* and *trans* isomer contributions by analysis of the spectral characteristics, in a narrow region around the maximum of the first spin allowed absorption band, of a tetraammine mixture obtained by ion exchange chromatography in basic solution of a hydrolysed solution of pentaammineaquachromium(III) ions.

As the agreement between the overall reaction rate constant in the two papers must be considered satisfactory we have made further experiments on the behaviour of the isomeric tetraammine ions by elution on Dowex 50W X8 columns with strong sodium hydroxide solution.

As reported in Ref. 2 the molar absorption coefficient around 500 nm of the acidified tetraammine eluate obtained from hydrolysed pentaammineaquachromium(III) solutions is intermediate between those of the two pure tetraammine isomers. However, for the same solutions a molar absorption coefficient at the maximum of the second spin allowed absorption band lower than those of both tetraammine isomers was also observed. This latter observation is obviously in disagreement with formulation of the column eluate as a mixture of the isomeric tetraammines only. As resin induced complex decomposition is sometimes encountered authentic samples of the two tetraammine isomers were subjected to the sodium hydroxide elution used for the separation of the pentaammine reaction mixtures. For both isomers such resin induced decomposition was found as judged by the visible absorption spectra of acidified column eluates.

For the visible absorption spectra of both tetraammine isomers lower molar absorption

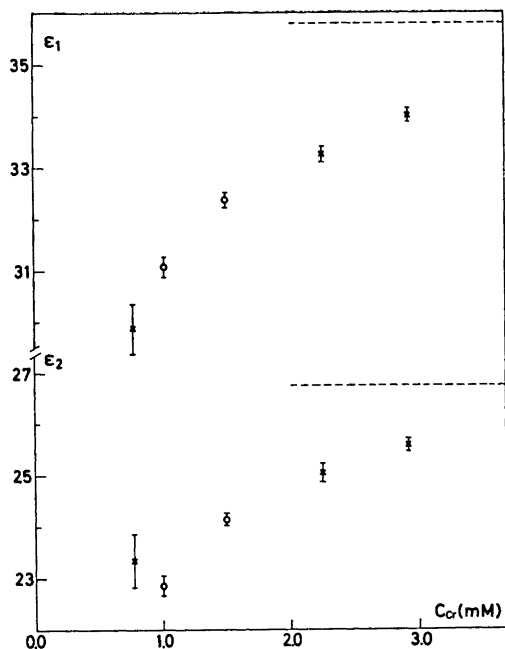


Fig. 1. Molar absorption coefficients at the maxima of the two first spin allowed bands of acidified tetraammine eluates as function of the chromium(III) concentration. \times , initially pure *cis*-tetraamminediaquachromium(III) solution; \circ , hydrolysed pentaammineaquachromium(III) solution; ---, absorptivity of authentic *cis*-tetraamminediaquachromium(III) (Ref. 3). The indicated error limits are drawn as \pm twice the estimated standard deviations upon the molar absorption coefficients.

coefficients at the two absorption maxima and a higher molar absorption coefficient at the absorption minimum were invariably found. Molar absorption coefficients for the eluted chromium(III) species were not reproducible, but depended upon the chromium(III) concentration in the eluate. This is shown in Fig. 1 for the two absorption maxima of eluates of initially pure *cis*-tetraamminediaquachromium(III) isomer.

The acidified *cis* isomer eluate was subjected to a 0.5 M sodium perchlorate elution on a SP-Sephadex C-25 cation exchange resin. This revealed four bands of which the first two were not completely separated. First a minor amount of a pink species was eluted. Next the major constituent of the solution was displaced and from the spectral characteristics of this species it was identified as the unchanged *cis* tetraammine isomer. After this species a slowly moving reddish violet band was seen, and at the column top a greyish green species remained

The close similarity between the spectral characteristics of the two types of chromium eluates, that of the initially pure *cis*-tetraammine isomer and that of the tetraammine mixture formed from the pentaammineaquachromium(III), is shown in Fig. 1 and suggests to us that evidence in favour of production of the *trans*-tetraamminediaquachromium(III) isomer from the pentaammineaquachromium(III) ion is still lacking. Consequently, in agreement with our earlier work (Ref. 1), only the *cis*-tetraamminediaquachromium(III) isomer has yet been found as a primary hydrolysis product of the pentaammineaquachromium(III) ion in acid perchlorate solution.

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