

## Multiplicity in the Interpretation of Linear Kinetics \*

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Spectrophotometric investigations of multicomponent linear kinetics may lead to several possible interpretations when the spectra of the intermediates are unknown. This is illustrated for an investigation by Schläfer *et al.*<sup>1</sup> on the acidic aquation of the tris(ethylenediamine) to the *cis*-diaquobis(ethylenediamine)chromium(III) ion *via* an unknown intermediate.

Schläfer *et al.* consider only one of the two existing possibilities, *viz.* the one according to which the intermediate should exist in dominating amounts, and have approximately the same spectrum as the luteo ion. However, we are able to show that the other existing possibility, according to which the intermediate is found only in relatively small amounts, is the more probable in view of our results<sup>2</sup> on the aquation of the corresponding hexammine chromium ion and the requirements which the experiments place on the spectrum of the intermediate. This interpretation is further substantiated by Schläfer *et al.*'s experiments<sup>3</sup> on the racemization of the optically active luteo ion.

In our opinion the intermediate which is formed in acidic solution is simply an aquopentammine ion,  $\text{Cr en}_5(\text{enH})\text{H}_2\text{O}^{++++}$ , stabilized by the uptake of a hydrogen ion on the displaced amino group.

It has long been recognized that a system of first order partial reactions leads to a rate expression which is linear in exponential functions<sup>4</sup>. Several authors<sup>5-7</sup> have discussed such systems and one of the present authors has introduced non-orthogonal matrices for the treatment of data additively composed of the properties of the various species<sup>8</sup>.

The experimental data may be analyzed into a number of exponential functions, but the fixing of the proper sequence of the exponential coefficients requires additional information.

In a kinetic system of  $n$  components the time-dependence of the total property  $U = \tilde{u} x$ , where  $u$  is the property vector and  $x$  a concentration vector, can be described by

$$U = \tilde{u}_\lambda \{ \exp(-\lambda_1 t), \exp(-\lambda_2 t), \dots, \exp(-\lambda_{n-1} t), 1 \} \quad (1)$$

\* Presented in part at the International Conference on Coordination Chemistry, London 1959.

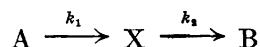
where  $u_\lambda$  is the coefficient vector. The exponential coefficients  $\lambda_i$  may be arranged in several different ways in relation to the reaction paths involved. Each arrangement leads to a requirement for the properties of the species, unique only for consecutive, irreversible reactions. In this case  $(n-1)!$  sets of properties,  $u$ , form the possibilities, and as there is only one proper sequence a choice must be made. The relationship between the property vector,  $u$ , and the coefficient vector,  $u_\lambda$ , is given by the previously derived expression<sup>8</sup>

$$u = (x_1^0)^{-1} \tilde{P} u_\lambda \quad (2)$$

where  $x_1^0$  is the initial concentration of the first component, and  $P$  a matrix constructed for the purpose.

The occasion for this paper is a discussion by Schläfer and Kling<sup>1</sup> on the properties of an intermediate shown to be formed as the first reaction product in the acidic hydrolysis of the tris(ethylenediamine)chromium(III) ion. Their discussion is based on the assumption that the spectrum of the intermediate which according to their calculations is formed in relatively high concentrations (up to  $\sim 80\%$ ) is very close to the spectrum of the luteo ion. For this reason they are forced to make improbable conclusions regarding the constitution of the intermediate. We have therefore reconsidered Schläfer's measurements with a view to an alternative explanation.

According to Schläfer and Kling, the family of spectral curves shows common isosbestic points and the liberation of one ethylenediamine molecule from the tris(ethylenediamine) chromium ion to be the first distinct step. The values of the rate constant calculated with this assumption show, however, a marked dependence on the progression of the aequation. Therefore, the reaction mechanism is proposed to be the following:



where the consecutive rate constants are denoted by  $k_1$  and  $k_2$ . A stands for the tris(ethylenediamine)chromium ion, and B for the *cis*-diaquobis(ethylenediamine) chromium ion, while X is the unknown intermediate.

Instead of the proper expression for the dependence of the optical density,  $E_t$ , on time,  $t$ , Schläfer and Kling use a pseudo-zero order rate law as a working hypothesis. In our opinion this is an incorrect simplification. Therefore, we have found it necessary to recalculate their data in terms of exponential functions. We have attempted to get the best representation of the data using (1) in the form

$$E_t = a_0 + a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) \quad (3)$$

where the coefficients  $a_0$ ,  $a_1$  and  $a_2$  are constants for each wavelength.

Table 1 contains in the first column the time in hours. In the second column are given Schläfer and Kling's experimental values for the optical densities,  $E_t$ , with the corresponding uncertainties. In the third column are given the values calculated from Schläfer's linear representations and the deviations from the experimental results. Similarly, the fourth column contains the values calculated from our linear combinations of exponential functions. It is seen

that our theoretical formulae with only one significant figure in the rate constants fit the experimental material at least as well as Schläfer and Kling's linear approximations. As the reaction proceeds, a further aqutation of the reaction products takes place. Consequently, we have disregarded all points past 63 h as being influenced by this further aqutation.

It is now possible to calculate the spectrum of the intermediate by means of the numerical values of  $a_0$ ,  $a_1$  and  $a_2$  in (3). Depending upon the choice of  $k_1$  and  $k_2$  between the rate constants, 0.06 and 0.008 h<sup>-1</sup>, we get two different

Table 1. Optical density,  $E_t$ , of 0.01 M tris(ethylenediamine) chromium(III) ion in 0.1 M HClO<sub>4</sub> as a function of time at 30°C. Experimental values and values calculated from Schläfer's linear representation (S) and from our sets of exponential functions (J).

	(S)	(J)	(J)
340 m $\mu$ :	0.507-0.001959t	0.174-0.351 exp(-0.008t)	-0.018 exp(-0.06t)
Hours	experimental	calculated(S)	calculated(J)
0	0.509 ( $\pm 0.001$ )	0.507 (-0.002)	0.507 (-0.002)
3	0.501 ( $\pm 0.001$ )	0.501 ( 0.000)	0.502 (+0.001)
6	0.494 ( $\pm 0.001$ )	0.495 (+0.001)	0.496 (+0.002)
9	0.490 ( $\pm 0.001$ )	0.489 (-0.001)	0.490 ( 0.000)
15	0.478 ( $\pm 0.001$ )	0.478 ( 0.000)	0.478 ( 0.000)
20	0.468 ( $\pm 0.001$ )	0.468 ( 0.000)	0.468 ( 0.000)
23	0.462 ( $\pm 0.001$ )	0.462 ( 0.000)	0.461 (-0.001)
27	0.452 ( $\pm 0.001$ )	0.454 (+0.002)	0.453 (+0.001)
33	0.441 ( $\pm 0.001$ )	0.442 (+0.001)	0.441 ( 0.000)
37	0.433 ( $\pm 0.001$ )	0.435 (+0.002)	0.433 ( 0.000)
41	0.425 ( $\pm 0.001$ )	0.427 (+0.002)	0.425 ( 0.000)
45	0.418 ( $\pm 0.001$ )	0.419 (+0.001)	0.418 ( 0.000)
48	0.411 ( $\pm 0.002$ )	0.413 (+0.002)	0.412 (+0.001)
51	0.406 ( $\pm 0.001$ )	0.407 (+0.001)	0.407 (+0.001)
54	0.402 ( $\pm 0.001$ )	0.401 (-0.001)	0.401 (-0.001)
58	0.393 ( $\pm 0.002$ )	0.393 ( 0.000)	0.394 (+0.001)
63	0.384 ( $\pm 0.002$ )	0.384 ( 0.000)	0.386 (+0.002)
	(S)	(J)	
390 m $\mu$ :	0.139+0.000715*t	0.261-0.124 exp(-0.008t)	
0	0.139 ( $\pm 0.001$ )	0.139 ( 0.000)	0.137 (-0.002)
3	0.140 ( $\pm 0.001$ )	0.141 (+0.001)	0.140 ( 0.000)
6	0.143 ( $\pm 0.001$ )	0.143 ( 0.000)	0.143 ( 0.000)
9	0.145 ( $\pm 0.001$ )	0.145 ( 0.000)	0.146 (+0.001)
15	0.149 ( $\pm 0.001$ )	0.150 (+0.001)	0.151 (+0.002)
20	0.153 ( $\pm 0.001$ )	0.153 ( 0.000)	0.155 (+0.002)
23	0.157 ( $\pm 0.001$ )	0.155 (-0.002)	0.158 (+0.001)
27	0.161 ( $\pm 0.001$ )	0.158 (-0.003)	0.161 ( 0.000)
33	0.166 ( $\pm 0.001$ )	0.163 (-0.003)	0.166 ( 0.000)
37	0.168 ( $\pm 0.001$ )	0.165 (-0.003)	0.169 (+0.001)
41	0.172 ( $\pm 0.001$ )	0.168 (-0.004)	0.172 ( 0.000)
45	0.174 ( $\pm 0.001$ )	0.171 (-0.003)	0.174 ( 0.000)
48	0.178 ( $\pm 0.002$ )	0.173 (-0.005)	0.177 (-0.001)
51	0.179 ( $\pm 0.001$ )	0.175 (-0.004)	0.179 ( 0.000)
54	0.182 ( $\pm 0.002$ )	0.178 (-0.004)	0.180 (-0.002)
58	0.184 ( $\pm 0.001$ )	0.180 (-0.004)	0.183 (-0.001)
63	0.188 ( $\pm 0.001$ )	0.184 (-0.004)	0.186 (-0.002)

\* This value is not calculated by Schläfer. It is estimated by means of the two other slopes.

Table 1. (Continued)

440 m $\mu$ :	(S)	(J)	
	0.633-0.002212t	0.251+0.406 exp(-0.008t)	-0.026 exp(-0.06t)
0	0.631 ( $\pm 0.001$ )	0.633 (+0.002)	0.631 ( 0.000)
3	0.625 ( $\pm 0.001$ )	0.626 (+0.001)	0.626 (+0.001)
6	0.619 ( $\pm 0.002$ )	0.620 (+0.001)	0.620 (+0.001)
9	0.616 ( $\pm 0.002$ )	0.613 (-0.003)	0.614 (-0.002)
15	0.602 ( $\pm 0.002$ )	0.600 (-0.002)	0.601 (-0.001)
20	0.590 ( $\pm 0.002$ )	0.589 (-0.001)	0.589 (-0.001)
23	0.582 ( $\pm 0.001$ )	0.582 ( 0.000)	0.582 ( 0.000)
27	0.572 ( $\pm 0.002$ )	0.573 (+0.001)	0.573 (+0.001)
33	0.560 ( $\pm 0.001$ )	0.560 ( 0.000)	0.559 (-0.001)
37	0.551 ( $\pm 0.002$ )	0.551 ( 0.000)	0.550 (-0.001)
41	0.543 ( $\pm 0.001$ )	0.542 (-0.001)	0.541 (-0.002)
45	0.533 ( $\pm 0.002$ )	0.533 ( 0.000)	0.533 ( 0.000)
48	0.524 ( $\pm 0.002$ )	0.527 (+0.003)	0.526 (+0.002)
51	0.520 ( $\pm 0.002$ )	0.520 ( 0.000)	0.520 ( 0.000)
54	0.513 ( $\pm 0.002$ )	0.514 (+0.001)	0.514 (+0.001)
58	0.506 ( $\pm 0.003$ )	0.505 (-0.001)	0.505 (-0.001)
63	0.495 ( $\pm 0.002$ )	0.494 (-0.001)	0.496 (+0.001)

spectra by insertion in (2), which takes on a very simple form in the present case. It corresponds to the second example of our previous paper<sup>8</sup>.

With the terms of eqn (3) the molar extinction coefficients,  $\epsilon$ , are the following:

$$\begin{aligned}\epsilon_A &= 100(a_0 + a_1 + a_2) \\ \epsilon_B &= 100a_0 \\ \epsilon_X &= 100(a_0 + a_2(k_1 - k_2)/k_1)\end{aligned}$$

The calculated values of  $\epsilon_x$  at the three wavelengths examined by Schläfer and Kling are given in Table 2 and plotted in Fig. 1, which also gives the spectra of the tris(ethylenediamine) ion (A) and the *cis*-diaquobis(ethylenediamine)chromium ion (B). If the suggestion of Schläfer and Kling, *viz.*  $k_1 > k_2$  is correct, one would expect a spectrum of the intermediate nearly identical with that of the luteo ion. However, if on the other hand  $k_1 < k_2$ , nothing need to be said *a priori* about the absorption spectrum of the intermediate. In the latter case the intermediate compound also accumulates to a much smaller extent so the requirement is less rigorous.  $k_1 = 0.06$  and  $k_2 = 0.008 \text{ h}^{-1}$  leads to a maximum amount of 73 % of the intermediate while the other sequence only involves 10 %.

Table 2. Molar extinction coefficients for the tris(ethylenediamine) chromium ion (A), the *cis*-diaquobis(ethylenediamine) chromium ion (B) and for the unknown intermediate (X).

wavelength	340 m $\mu$	390 m $\mu$	440 m $\mu$	
$\epsilon_A$	50.7	13.7	63.1	
$\epsilon_X$	$\left\{ \begin{array}{l} k_1 > k_2 \\ k_1 < k_2 \end{array} \right.$	47.8	15.4	60.3
		29.1	26.1	42.0
$\epsilon_B$	17.4	26.1	25.1	

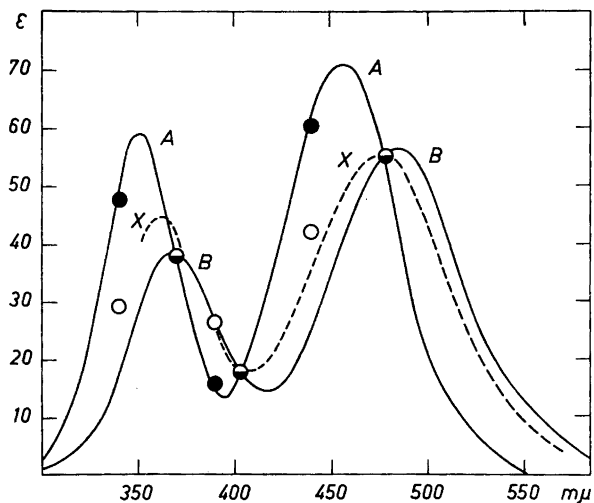


Fig. 1. The spectra of the tris(ethylenediamine) and the *cis*-diaquobis(ethylenediamine) chromium(III) ions (curves A and B) in 0.1 M HClO<sub>4</sub> according to Schläfer and Kling<sup>1</sup>. The dashed curve is an estimate of the spectrum of the intermediate complex (X) based on the similarity with the ammine complexes in Fig. 2.

- — calculated molar extinction coefficient of X in the case  $k_1 < k_2$ .  
 ● — calculated molar extinction coefficient of X in the case  $k_1 > k_2$ .

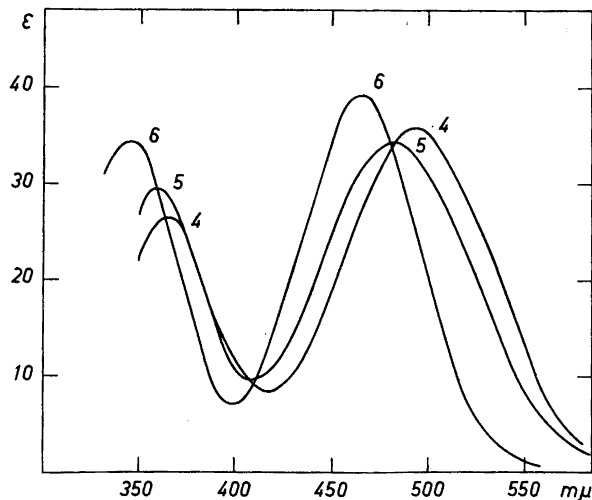


Fig. 2. The spectra of the hexammine, aquopentammine and diaquotetrammine chromium(III) ions (curves 6, 5 and 4) in acidic solution according to Jørgensen and Bjerrum<sup>2</sup>.

In our investigation of the aquation of chromium(III) amines<sup>2</sup> we found at 40°C for the rate constants of the hexamine and aquopentamine the values 0.0051 and 0.085 h<sup>-1</sup>, respectively. Properly corrected for the difference in temperature (a conversion factor of 0.25) the values directly comparable with the present rate constants, 0.006 and 0.08 h<sup>-1</sup>, are 0.0013 and 0.021 h<sup>-1</sup>, respectively.

It is interesting to note that the tris(ethylenediamine) complex reacts more rapidly than the corresponding hexamine ion. The activation energies are 24.3 and 26.0 kcal, respectively. This suggests a considerable tension in the chelate ring, and makes it probable that the first step is simply an opening of the ring followed by the uptake of a proton. Professor R. G. Inskeep\* has shown that the rate of aquation of the tris(ethylenediamine)chromium ion is practically independent of the hydrogen ion concentration in the range from 0.1 to 1 M HClO<sub>4</sub>. Furthermore it is remarkable that the hexamine chromium(III) ion aquates 16 times slower than the aquopentamine chromium(III) ion, and most probably this evidence can be taken as a support for the case  $k_1 < k_2$ . It is, however, still more indicative to compare the requirements placed on the spectrum of the intermediate with the spectrum actually found in the ammonia system. The spectra of the hexamine (6), aquopentamine (5) and diaquotetrammine (4) chromium ions are shown in Fig. 2. The shape and the position of the spectra of the hexamine and the tetrammine chromium ions are well known to be very similar to those of the tris(ethylenediamine) and bis(ethylenediamine) chromium ions. This argument applied to the spectrum of the pentamine chromium ion would predict a spectrum for the corresponding complex in the ethylenediamine system as outlined in Fig. 1 (the dashed curve). This curve is seen to fit quite well to the points calculated for the sequence of rate constants assumed by us. At the wavelength, 390 mμ, one of the exponential terms in (3) vanishes (see Table 1). Here, X and B seem to have an isosbestic point (see Table 2).

The existence of the pentamine as intermediate is further proved by Schläfer and Seidel's<sup>3</sup> investigations on the racemization of the active luteo ion. The rate-determining constant, 0.00814 h<sup>-1</sup>, is equal to the slow one found in the hydrolysis reaction, and the peculiar irregularity in the beginning of the experiment points towards two steps with reaction probabilities of approximately 1 h<sup>-1</sup>. In Schläfer's interpretation, one of these fast reactions must be due to the racemization of the luteo ion, and the slow rate-determining step is the racemization of the never isolated intermediate through aquation. Our interpretation places the slow racemization on the aquation of the luteo ion, while the partially hydrolyzed species racemize fast. This is in agreement with the fact that the luteo ion can only racemize through intramolecular rearrangement while the lower complexes have the possibility of racemization through water exchange.

Thus it seems to us that it has been possible unequivocally to correlate the experimental facts with the assumption that the first reaction product in the hydrolysis of the tris(ethylenediamine) chromium ion in acidic solution

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is an aquopentammine ion,  $\text{Cr en}_2(\text{enH})\text{H}_2\text{O}^{++++}$ , stabilized by the uptake of a hydrogen ion on the displaced amino group.

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