

# Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. VIII. The Acid Hydrolysis and Isomerization of *cis*- and *trans*-Tetraaquadichloridochromium(III) Ions in Aqueous Perchloric Acid

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The acid hydrolysis and isomerization of the *cis*- and *trans*-tetraaquadichloridochromium(III) cations in acid perchlorate solution has been investigated. The experiments were carried out in the temperature and hydrogen ion concentration ranges 20–50 °C and 0.25–1.00 M, respectively, and the ionic strength was adjusted to 1.00 M by the addition of sodium perchlorate.

The following reaction rate constants at 25 °C and activation energies were found:

For the hydrolysis reactions:

$$(cis): (1.53 \pm 0.15) \times 10^{-5} \text{ s}^{-1},$$

$$103 \pm 5 \text{ kJ mol}^{-1}$$

$$(trans): (4.53 \pm 0.11) \times 10^{-5} \text{ s}^{-1},$$

$$98.2 \pm 1.3 \text{ kJ mol}^{-1}$$

and for the isomerization reactions:

$$(cis \rightarrow trans): (1.5 \pm 0.3) \times 10^{-5} \text{ s}^{-1},$$

$$111 \pm 7 \text{ kJ mol}^{-1}$$

$$(trans \rightarrow cis): (1.97 \pm 0.14) \times 10^{-5} \text{ s}^{-1},$$

$$117 \pm 4 \text{ kJ mol}^{-1}$$

In an appendix the application of nonlinear regression analysis to the parametrization of kinetic data, within reaction schemes composed of an arbitrary number of first and second order reactions, is described in some detail.

Reactions of the isomeric tetraaquadichloridochromium(III) complexes have been the subject of a number of publications during the past twenty years, but it was not until ten years ago that the importance of the isomerization reactions was fully realized.<sup>1</sup> Examples of isomerization reactions of chromium(III) complexes are not numerous, and in

most of the cases so far discovered they constitute only minor contributions to the total reactivity of the complexes. As a result accurate characterization of such processes is usually lacking. However, for the isomeric tetraaquadichloridochromium(III) species isomerization competes favourably with aquation at 35 °C,<sup>1</sup> and it should therefore be possible to obtain well defined activation parameters for the isomerization reactions of these two complexes. The system was originally investigated by ion exchange chromatography of quenched reaction mixtures, but this is a tedious method if many kinetic experiments have to be carried out. Recently multi-wavelength absorption spectroscopy has been successfully applied to the far more complicated series of reactions involved in the hydrolysis of hexaamminechromium(III) to yield ultimately hexa-aquachromium(III).<sup>2</sup> A brief description of the numerical background for this method has been given previously,<sup>3</sup> but in view of the advantages and the potential of such modern numerical methods it was thought worthwhile to publish the method in somewhat greater detail and also to demonstrate its application to a system which has already been investigated in a more traditional manner.

## EXPERIMENTAL

*Chemicals.* *trans*-[CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]Cl·2H<sub>2</sub>O (Riedel de Haën AG) was recrystallized,<sup>4</sup> and (NH<sub>4</sub>)<sub>2</sub>[CrCl<sub>5</sub>(OH<sub>2</sub>)] was prepared<sup>5</sup> according to literature methods. The source of the other chemicals

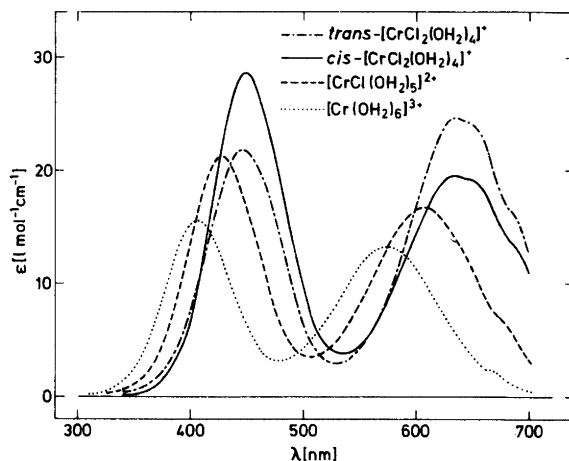


Fig. 1. Visible absorption spectra of complexes prepared and purified as described in the text, cf. Table 1.

employed has been described earlier.<sup>3</sup>

**Preparation of solutions.** *trans*-[CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]-Cl·2H<sub>2</sub>O dissolved in water, (NH<sub>4</sub>)<sub>2</sub>[CrCl<sub>5</sub>(OH<sub>2</sub>)] aged in water solution at room temperature for 5 min and *trans*-[CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]-Cl·2H<sub>2</sub>O aged in acidified water solution at 25 °C for 1½ h were used as the initial materials for the preparation of the *trans*-[CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>, *cis*-[CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> and [CrCl(OH<sub>2</sub>)<sub>5</sub>]<sup>2+</sup> ions, respectively, in solution.

Purification of solutions obtained in this way was carried out by ion exchange chromatography as follows: A volume of solution containing about 0.25 mequiv. of chromium(III) was charged on to a 1 × 10 cm column packed with Sephadex SP C-25 cation exchange resin. The column was operated at 0 °C, and anionic and neutral species were first removed by elution with water. Next the monopositive tetraaquadichloridochromium(III) species were displaced with 0.05 M sodium perchlorate solution acidified with perchloric acid to pH ~3. Spectrophotometric monitoring of the eluate showed that fresh solutions of recrystallized green chromic chloride contained the *trans* isomer exclusively. In an analogous fashion aged solutions of aquapentachloridochromate(III) ions were found

to contain both the *cis* and the *trans* isomer. Usually, however, the *trans* isomer comprised less than about 10 % of the monopositive species in such solutions, and the pure *cis* isomer was therefore readily obtained in solution by the chromatographic technique described above. After removal of monopositive species the dipositive pentaquachloridochromium(III) ion could be eluted free from other species with acidified, pH ~3, 0.35 M sodium perchlorate solution.

Visible absorption spectra of solutions prepared in this way are given in Fig. 1 and Table 1.

**Kinetic measurements**, and the **Methods of analysis** were essentially as described previously,<sup>3</sup> except for the use of a modified Cary 118C spectrophotometer.

**Method of calculation.** The numerical treatment of the experimental material was conveniently divided into a number of distinct steps. The initial step is characteristic of the type and the mode of operation of the spectrophotometer employed and will consequently not be described. The results of these calculations are mean values and variances of absorptivities of the quenched reaction mixtures and of the pure components which constitute these reaction mixtures at a series of wavelengths. Absorp-

Table 1. Spectral characteristics of solutions of complexes prepared and purified as described in the text and diluted with perchloric acid to yield a 0.5 M perchloric acid solution.

Complex	$\lambda_1$ max [nm]	$\epsilon_1$ max [l mol <sup>-1</sup> cm <sup>-1</sup> ]	$\lambda_2$ max [nm]	$\epsilon_2$ max [l mol <sup>-1</sup> cm <sup>-1</sup> ]	$\epsilon_1$ max/ $\epsilon_2$ max
<i>cis</i> -[CrCl <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	635	19.4	450	28.7	0.675
<i>trans</i> -[CrCl <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	635	24.8	448	21.8	1.134
[CrCl(OH <sub>2</sub> ) <sub>5</sub> ] <sup>2+</sup>	608	16.7	430	21.2	0.793

tion spectra in the range 290–700 nm measured at 10 nm intervals were employed in this work.

The next three steps of the calculations were all carried out within the framework of nonlinear regression analysis. This technique is excellently described in a number of textbooks on statistical methods and will therefore not be described here.

In the first step the absorption spectrum of a quenched reaction mixture,  $A = A(\lambda)$ , was expressed as a linear combination of the absorption spectra of the components in the reaction mixture,  $\varepsilon = \varepsilon(\lambda)$ . This was performed by minimization of:

$$s_1^2 = \sum_{\lambda} [(A_{\lambda} - \mathbf{c}^T \boldsymbol{\varepsilon}_{\lambda})^2 / (V(A_{\lambda}) + \mathbf{c}^T \mathbf{V}(\boldsymbol{\varepsilon}_{\lambda}) \mathbf{c})]$$

where  $A_{\lambda}$  is the mean value of the absorptivity of the reaction mixture at wavelength  $\lambda$  and  $V(A_{\lambda})$  is the variance of this mean value.  $\boldsymbol{\varepsilon}_{\lambda}$  is the column vector of mean values of the molar absorptivities of the pure components and  $\mathbf{V}(\boldsymbol{\varepsilon}_{\lambda})$  is the matrix of variances of these mean values. Finally,  $\mathbf{c}$ , the result of the computation, is the column vector of mean values of component concentrations in the reaction mixture, and  $\mathbf{V}(\mathbf{c})$ , which is obtained simultaneously, is the matrix of variances of and covariances between these concentration mean values.

In the second step of the calculations, rate constants for the individual kinetic experiments were computed by minimization of:

$$s_2^2 = \sum_i [(\mathbf{c}_i - \mathbf{c}(t, \mathbf{c}_0, \mathbf{k}))^T \{\mathbf{V}(\mathbf{c}_i)\}^{-1} (\mathbf{c}_i - \mathbf{c}(t, \mathbf{c}_0, \mathbf{k}))]$$

where  $\mathbf{c}_i$  and  $\mathbf{V}(\mathbf{c}_i)$  are the quantities determined in the previous step of the calculations, now supple-

mented with an index to distinguish different reaction times.  $\mathbf{c}(t, \mathbf{c}_0, \mathbf{k})$  is the column vector of calculated concentrations at time  $t$  as function of the column vectors of initial concentrations,  $\mathbf{c}_0$ , and rate constants,  $\mathbf{k}$ , obtained as described in the appendix. An example of the agreement found between calculated,  $\mathbf{c}(t, \mathbf{c}_0, \mathbf{k})$ , and observed concentrations,  $\mathbf{c}_i$ , is shown in Fig. 2.

In the third step of the calculations all sets of mean values of reaction rate constants were assembled to yield activation parameters by minimization of:

$$s_3^2 = \sum_{T, [\text{H}^+]} [(\mathbf{k} - \mathbf{k}([\text{H}^+], T))^T \{\mathbf{V}(\mathbf{k})\}^{-1} (\mathbf{k} - \mathbf{k}([\text{H}^+], T))]$$

where  $\mathbf{V}(\mathbf{k})$  is the matrix of variances of and covariances between the reaction rate constants. For the present system, and within the range of hydrogen ion concentrations investigated, the hydrogen ion concentration dependence of the calculated rate constants is given by:

$$\mathbf{k}([\text{H}^+], T) = \mathbf{k}_0(T) + \frac{1}{[\text{H}^+]} \mathbf{k}_1(T)$$

For each term in the above two column vectors of calculated rate constants the temperature dependence is assumed to follow an expression of the form:

$$k(T) = \frac{RT}{Nh} \exp\{\Delta S^\ddagger / R - \Delta H^\ddagger / RT\}$$

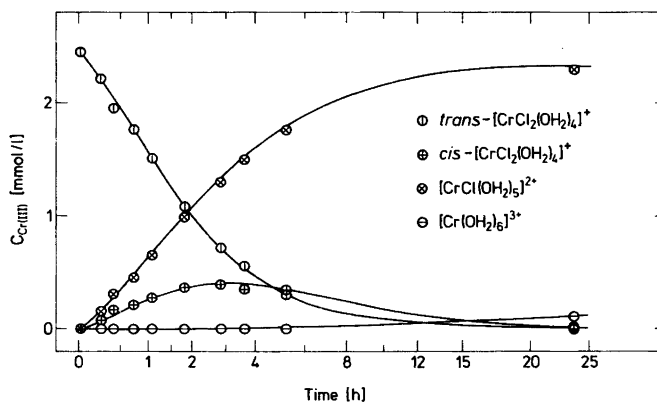


Fig. 2. Reaction kinetic experiment at 30.0 °C with  $[\text{H}^+] = 0.992 \text{ M}$ , started from *trans*-tetraaquadichloridochromium(III). Experimental points are calculated from measured visible absorption spectra of a series of quenched reaction mixtures, and the solid curves are calculated from the parameters of Table 2. The improvement in the agreement between experimental points and calculated curves, which is obtained if rate constants calculated for this particular kinetic experiment are used, is too small to be seen clearly on the figure.

The parameters thus computed are characterized by very strong correlation between activation enthalpies and entropies associated with the same reaction. Consequently it is frequently desirable to represent the reduced data in a form characterized by less strong correlation between parameters of temperature dependent and independent terms. The smallest possible correlation is obtained by choosing parameters,  $k', E$ , according to:

$$k(T) = k' \exp\{-E(1/RT - 1/RT_0)\},$$

where  $T_0$  is the average temperature of all the kinetic experiments considered.

## RESULTS AND DISCUSSION

It was early shown that green crystalline chromium(III) chloride contains a tetraaquadichlorido-chromium(III) species.<sup>7</sup> Various pieces of indirect evidence concerning the detailed geometry of this ion were subsequently presented until the question was finally answered by two crystal structure analyses<sup>8,9</sup> which showed the species to be the *trans* isomer. The corresponding *cis* isomer has so far only been obtained in solution from products formed by heating green chromium(III) chloride. In this work a somewhat different method is used, but as can be seen from a comparison between Table 1 and Ref. 6 an identical species is obtained.

The first kinetic investigations of the reactions of the isomeric tetraaquadichloridochromium(III) species were all carried out with the implicit assumption that isomerization reactions were unimportant for the kinetics of the system. This hypothesis was finally shown to be incorrect<sup>1</sup> and evidence in favour of the reaction scheme shown in Fig. 3, with

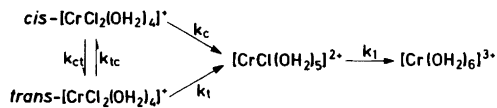


Fig. 3. Reaction scheme for isomerization and aquation of the isomeric tetraaquadichloridochromium(III) ions.

rate constants for the direct isomerization reactions comparable to those for the chloride ligand hydrolysis reactions and absence of isomerization *via* trichloridochromium(III) species, was presented.

In order to characterize the acid-independent paths of these reactions further, a number of kinetic experiments employing a 1.00 M perchlorate medium covering the hydrogen ion concentration and temperature ranges 0.25–1.00 M and 20–50 °C, respectively, were carried out. The final results obtained are shown in Table 2 and are compared in Table 3 with the earlier investigation which was carried out at 34.8 °C in 0.203 M perchloric acid.

As is usual with kinetic investigations of complicated reactions, the dominating reaction in the system, *i.e.* the hydrolysis of the *trans*-tetraaquadichloridochromium(III) ion, is well characterized, whereas the remaining reactions in the system are necessarily less well defined. Therefore conclusions about the reactions of the *cis* isomer are less certain than those which may be reached for the *trans* isomer, for which it is evident that the isomerization reaction must proceed *via* a transition state which differs from that for the chloride ligand hydrolysis reaction, since the activation energy for the latter process is significantly lower than that for the former.

Table 2. Rate constants at 35 °C and activation energies, mean values  $\pm$  standard deviations upon the mean values, and correlation coefficients for the acid independent reactions of *cis* and *trans*-tetraaquadichloridochromium(III) ions in aqueous 1.00 M perchlorate solution. Cf. Fig. 3.

Parameter symbol	Parameter values	Correlation coefficients							
$k_{tc}$	$(9.1 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$	—							
$k_t$	$(16.4 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$	+ .55	—						
$k_{ct}$	$(6.4 \pm 1.1) \times 10^{-5} \text{ s}^{-1}$	+ .42	+ .50	—					
$k_c$	$(5.8 \pm 0.6) \times 10^{-5} \text{ s}^{-1}$	-.19	-.61	-.81	—				
$E_{tc}$	$(117 \pm 4) \text{ kJ mol}^{-1}$	-.03	-.06	-.06	+ .10	—			
$E_t$	$(98.2 \pm 1.3) \text{ kJ mol}^{-1}$	+ .01	+ .21	+ .11	-.19	+ .50	—		
$E_{ct}$	$(111 \pm 7) \text{ kJ mol}^{-1}$	+ .03	+ .25	+ .29	-.44	+ .26	+ .42	—	
$E_c$	$(103 \pm 5) \text{ kJ mol}^{-1}$	-.03	-.03	-.34	+ .52	-.04	-.46	-.78	—

Table 3. Comparison with literature values of rate constants at 34.8 °C and  $[H^+] = 0.203$  M.

Reaction (cf. Fig. 3)	Ref. 1 $10^5 \times (k_{obs})$ [s <sup>-1</sup> ]	This work $10^5 \times (k_0 + k_1/0.203)$ [s <sup>-1</sup> ]
$k_{tc}$	7.8	7.4
$k_t$	18.0	16.7
$k_{ct}$	6.2	8.5
$k_c$	8.3	7.0

In Table 4 data for the reactions of the tetraqua complexes investigated here have been compared with literature data for the corresponding tetraammine complexes. The most noteworthy feature is the absence of detectable isomerization for the latter two species. The explanation for this may be the same as that proposed to rationalize the differences in behaviour with respect to racemization of the *cis*-diaquabis(1,2-ethanediamine)-chromium(III) ion and the tris(1,2-ethanediamine)chromium(III) ion,<sup>12</sup> namely that changes in configuration are facilitated by exchange reactions of coordinated solvent molecules. Direct verification of this hypothesis is still lacking for the chromium(III) complexes cited here, but was obtained long ago for the isomerization of the *trans*-diaquabis(1,2-ethanediamine)cobalt(III) ion.<sup>13</sup>

Comparisons between the hydrolysis reactions of the tetraqua- and tetraammine complexes reveal the trend normally associated with chromium(III)

aquation reactions. For the pair of *cis* complexes the reactivity difference is dominated by the greater *trans* effect of coordinated ammonia than that of coordinated water. The pair of *trans* complexes is seen to react at roughly equal rates at 25 °C, but inspection of the activation parameters shows that this is accidental. The reaction of the tetraammine complex is described by significantly lower values of both activation enthalpy and activation entropy. Additional experimental data would evidently be of value for further elucidation, and the reactions of the remaining *trans*-dichlorido chromium(III) complexes of the general formula *trans*-[CrCl<sub>2</sub>(NH<sub>3</sub>)<sub>x</sub>(OH<sub>2</sub>)<sub>4-x</sub>]<sup>+</sup> ( $x=3$ , "*trans*"-2, "*cis*"-2, and 1) are therefore currently being studied.

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## APPENDIX

The coupled first order differential equations which may be used to describe the transformations occurring between  $p$  species in kinetic systems in solution, where both first and second order reactions take place, may be written:

$$\frac{d\xi_r(t)}{dt} = \sum_{j=1}^p [\gamma_{jr} + \sum_{s=r}^p \{\psi_{jrs} \xi_s(t)\}] \xi_r(t) \quad (\text{A.1})$$

Table 4. Kinetic parameters for chloride ligand hydrolysis and isomerization of some *cis*- and *trans*-dichlorido chromium(III) complexes.<sup>c</sup>

Complex	$10^5 k$ (25 °C) [s <sup>-1</sup> ]	$\Delta H^\ddagger$ [kJ mol <sup>-1</sup> ]	$\Delta S^\ddagger$ [J K <sup>-1</sup> mol <sup>-1</sup> ]	Ref.
<b>Hydrolysis</b>				
<i>cis</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	33.0 ± 0.15	84 ± 2	-25 ± 6	10
<i>cis</i> -[Cr(OH <sub>2</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	1.53 ± 0.15	101 ± 5	+1 ± 17	<sup>a</sup>
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	4.9 ± 0.2	87.9 ± 1.3	-33 ± 4	11 <sup>b</sup>
<i>trans</i> -[Cr(OH <sub>2</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	4.53 ± 0.11	95.7 ± 1.4	-7 ± 4	<sup>a</sup>
<b>Isomerization</b>				
<i>cis</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	Unobserved	—	—	10
<i>cis</i> -[Cr(OH <sub>2</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	1.5 ± 0.3	108 ± 7	+25 ± 25	<sup>a</sup>
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	Unobserved	—	—	11
<i>trans</i> -[Cr(OH <sub>2</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	1.97 ± 0.15	114 ± 4	+50 ± 13	<sup>a</sup>

<sup>a</sup> This work. <sup>b</sup> The values given here are calculated from  $k$  (45 °C) and the activation energy. <sup>c</sup> Numerical data are quoted as mean values ± standard deviations upon the mean values.

In this expression  $\xi_i(t)$  ( $i=1,2,\dots,p$ ) are the time dependent concentrations of the species, and  $\gamma_{ij}$  and  $\psi_{ijk}$  are quantities which are easily related to reaction rate constants.

The numerical integration of these coupled differential equations may be performed by expressing  $\xi_i(t)$  as a power series in  $(t-t_0)$ :

$$\xi_i(t) = \sum_{i=0}^{\infty} \mu_{ij}(t_0) (t-t_0)^i \quad (\text{A.2})$$

For this series expansion it is readily verified that the coefficients  $\mu_{ij}(t_0)$  may be obtained from:

$$\mu_{0j}(t_0) = \xi_j(t_0) \quad (i=0)$$

$$\mu_{ij}(t_0) = \frac{1}{i} \sum_{r=1}^p [\gamma_{jr} \mu_{i-1,r}(t_0) + \sum_{s=r}^p \psi_{jrs} \{ \sum_{u=0}^{i-1} \mu_{i-1-u,r}(t_0) \mu_{us}(t_0) \}] \quad (i>0)$$

This provides a convenient numerical method for the integration of the differential equations given by eqns. A.1, but in order to carry out a regression analysis differentials of  $\xi_i(t)$  with respect to all desired parameters, in particular  $\gamma_{ij}$  and  $\psi_{ijk}$ , are also necessary. To simplify the notation the subsequent derivations have been restricted to reaction schemes in which only first order reactions take place, i.e. for which  $\psi_{ijk}=0$ . In this case eqns. A.1 reduce to:

$$\frac{d\xi_i(t)}{dt} = \sum_{r=1}^p \gamma_{jr} \xi_r(t)$$

Eqns. A.2 may be differentiated to yield:

$$\frac{\partial \xi_i(t)}{\partial \gamma_{rs}} = \sum_{i=0}^{\infty} \frac{\partial \mu_{ij}(t_0)}{\partial \gamma_{rs}} (t-t_0)^i \quad (\text{A.3})$$

and the  $\mu$ -differentials may be computed from:

$$\frac{\partial \mu_{0j}(0)}{\partial \gamma_{rs}} = 0$$

$$\frac{\partial \mu_{0j}(t_0)}{\partial \gamma_{rs}} = \frac{\partial \xi_j(t_0)}{\partial \gamma_{rs}}$$

$$\frac{\partial \mu_{ij}(t_0)}{\partial \gamma_{rs}} = \frac{1}{i} \left[ \delta_{rj} \mu_{i-1,s}(t_0) + \sum_{k=1}^p \gamma_{jk} \frac{\partial \mu_{i-1,k}(t_0)}{\partial \gamma_{rs}} \right]$$

where  $\delta_{rj}$  is equal to 1 for  $r=j$  and equal to 0 otherwise.

Differentials with respect to other parameters may be evaluated analogously although at the present time only the inclusion of initial concentrations of one or more reactant species has been carried out.

In numerical calculations the summations in eqns. A.1 and A.3 must be restricted to a finite number of terms. In cases where comparisons with analytical solutions of the differential equations could be made it was found that a polynomial of degree 10 reproduced the analytical solution satisfactorily when combined with an adjustment of the step-length,  $t-t_0$ , so as to make the last term in the series expansion insignificant relative to those already summed.

The general equations given in this appendix may easily be applied to actual systems, and computer programs which handle suitably written reaction schemes are readily constructed. Such programs have provided a very flexible tool for the interpretation of the kinetics of a number of complicated multicomponent systems.<sup>2,14</sup>

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