

Photochemical Studies of Chromium(III) Complexes.

Photoisomerization and Photochemical Ammine Ligand Aquation of the Isomeric Ammineaquachromium(III) Complexes

L. MØNSTED,^a and O. MØNSTED^b

^a Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark, and ^b Chemistry Department I, Inorganic Chemistry, University of Copenhagen, H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Photoinduced reactions of the eight different ammineaquachromium(III) complexes have been studied at 25 °C by irradiation at 366 nm and at 546 nm. The quantum yields for isomerization and loss of coordinated ammonia show no well defined wavelength dependence.

The reactivities of the tetraammines and the triammines are dominated by photoisomerization, and for both *cis*-tetraamminediaqua- and *fac*-triamminetriaquachromium(III) this is not in agreement with the simple empirical 'rule' which for these two species predicts the strong field ligand, *i.e.* ammonia, on an ammonia-water axis to be the leaving ligand.

Product distributions of the photochemical reactions are different from those of the thermal reactions at 60–80 °C. However, for competing reactions, that with the highest thermal activation energy is invariably more dominating photochemically than it is thermally, a result which does not support the common classification of photochemical reactions of chromium(III) as "anti-thermal".

A numerical method is given for the integration of the coupled first order differential equations which arise in a mathematical description of photochemical transformations. The application of this method to the determination of quantum yields by non-linear regression analysis for photolysis experiments with greater conversion of material is demonstrated in an appendix.

The photochemistry and photophysics of transition metal complexes has attracted great experimental and theoretical interest, but impor-

tant questions concerning reactivities of different excited states and reliable methods for predicting product distributions are still unanswered. Many complexes of chromium(III) have been studied in great detail and the results obtained have been the basis for several recent reviews.¹⁻³

The role played by different ligands has stimulated much research, and particular emphasis has been given to the rationalization of product distributions using ligand field based semi-empirical models.

Thermal reactions in solution of the various ammineaquachromium(III) isomers have been studied in some detail, and rates and activation parameters for thermal water exchange, for ammine ligand aquation and for isomerization have been determined.⁴⁻⁷ This set of ten different isomers is ideally suited for a detailed evaluation of the rôle of two different ligands in an octahedral environment, and the present work describes results for photochemical ammine ligand aquation and photoisomerization. A subsequent publication will deal with photochemical water exchange in the same series of complexes.

RESULTS AND DISCUSSION

Ammineaquachromium(III) complexes are photoactive, and when the complexes are irradiated in the ligand field bands in acid aqueous solution spectral changes and ion exchange chromatography show that loss of coordinated ammo-

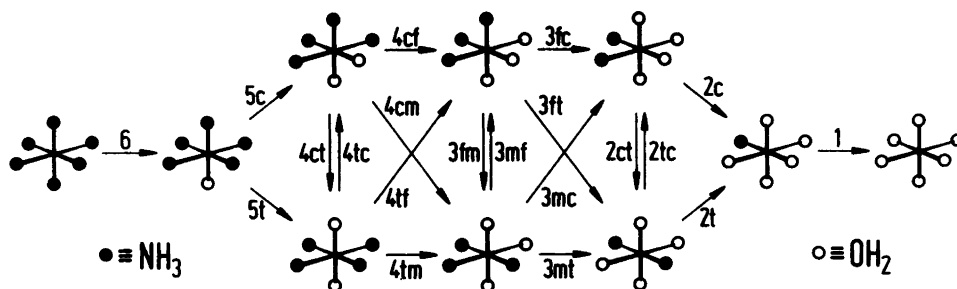


Fig. 1. Isomerization and ammonia ligand aquation reactions of ammineaquachromium(III) complexes in acid aqueous solution.

nia and isomerization occur. In sufficiently acid solution ammonia is lost irreversibly, and in sufficiently dilute solution polymerization does not occur. The experimental data can therefore be interpreted using a reaction scheme which only involves monomeric species, and this is shown in Fig. 1. An analysis within this reaction scheme of a series of experiments with each of the different ammineaquachromium(III) isomers alone as initial reactant gave the quantum yields

reported in Table 1. Fig. 2. shows the agreement between 'observed' and calculated concentrations for two typical experiments, started from the tetraamminediaquachromium(III) isomers.

The data in Table 1 show no well defined wavelength dependence, and are in acceptable agreement with literature data for pentaammineaqua^{9,10} and *trans*-tetraamminediaquachromium(III),¹¹ particularly when the different methods for evaluating the quantum yields, *cf.*

Table 1. Quantum yields, mol Einstein⁻¹ for ammonia ligand aquation and isomerization of ammineaquachromium(III) complexes in 0.5 M HClO₄+0.5 M NaClO₄ at 25 °C, *cf.* Fig. 1.

Reactant	Reaction	$\phi(546 \text{ nm}) \pm \sigma(\phi)$	$\phi(366 \text{ nm}) \pm \sigma(\phi)$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	6		0.443(15) ^b
$[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$	5c	0.175(6)	0.175(8)
	5t	0.020(6)	0.023(8)
<i>cis</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	4ct	0.141(6)	0.127(6)
	4cf	0.031(6)	0.024(4)
	4cm	0.027(7)	0.034(5)
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	4tc	0.310(4)	0.342(6)
	4tm	0.012(7)	0.022(9)
	4t ^{m'}	0.013(6)	0.008(7)
	3fm	0.146(5)	0.165(13)
<i>fac</i> - $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$	3fc	0.041(5)	0.041(9)
	3ft ^a	0.012(5)	0.006(10)
	3mf	0.064(4)	0.054(7)
	3mc	0.011(3)	0.012(5)
<i>mer</i> - $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$	3mt ^a	0.000(3)	0.000(7)
	2ct ^a	0.0000(10)	0.0029(19)
	2c	0.00192(17)	0.0025(2)
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$	2tc	0.051(2)	0.047(3)
	2t	0.0041(8)	0.0008(8)
$[\text{Cr}(\text{NH}_3)(\text{OH}_2)_5]^{3+}$	1 ^a	0.00004(8)	0.00027(9)

^a $\phi_{av} - 3\sigma(\phi) \leq 0$ at both wavelengths: these reactions are therefore not definitely established. ^b Data from Refs. 8 and 9.

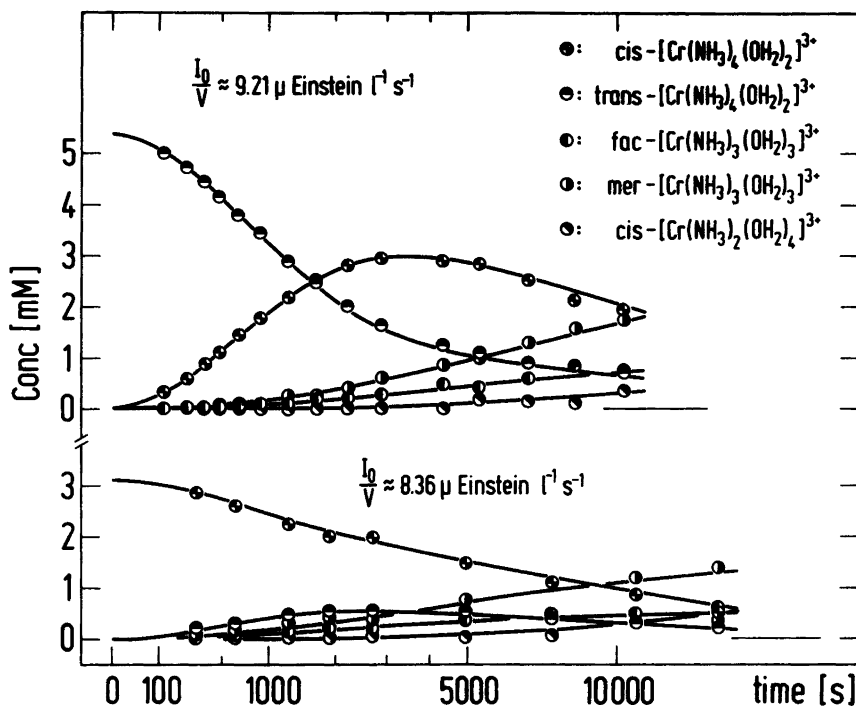


Fig. 2. Two photolysis experiments started from the isomeric tetraamminediaquachromium(III) complexes. The experimental points are calculated from the visible absorption spectra of the photolyzed solutions, and the solid curves are calculated from the quantum yields in Table 1, and molar absorption coefficients at 366 nm.

the Appendix, are considered.

The present series of complexes is ideally suited for an evaluation of the influences of two different ligands on the stereochemistry of reaction products. Several empirical and semi-empirical models to predict leaving ligands and product stereochemistries can be found in the literature. The present data, however, do not support the simple hypothesis that the leaving ligand should be that of highest ligand field strength on the axis of the lowest average ligand field strength.¹² For both *cis*-tetraamminediaqua- and *fac*-triamminetriaquachromium(III) this 'rule' predicts ammonia, which has the higher ligand field strength, on an ammonia-water axis to be the leaving ligand. Clearly this prediction is in disagreement with the experimentally observed reactivities which are dominated by isomerization reactions for both these cations.

Much work has been devoted to clarify the detailed mechanism for photoinduced substitution reactions of transition metal ions, and many

speculative models attempting to account for the pronounced product distribution differences between thermal and photochemical reactions have been developed, *cf.* Refs. 1–3. This so-called 'anti-thermal' behaviour of the photoinduced reactions is also seen for almost all reactants in the present system. The significant contributions from *photoisomerization* reactions to the overall reactivity are particularly noteworthy since these reactions play only a minor rôle for the thermal reactivities. This difference should not be over-emphasized, however, since it is generally known, and as it also has been demonstrated for the *trans*-diamminetetraaquachromium(III) isomer in the present system,⁷ that stereomobile thermal reactions have higher activation energies than similar stereoretentive reactions of the same reactants. Stereomobility is therefore preferred also thermally but usually at higher temperatures than those normally used in kinetic investigations.

Theoretical models for transition metal photo-

chemistry would therefore probably benefit from the inclusion of the possibility of reactivity contributions from a vibrationally highly excited ground state, and this could be the basis for a unified treatment of photochemical and thermal reactions. The present data will be discussed in such a context in connection with presentation of data for photoinduced water exchange in several of the ammineaquachromium(III) isomers. This work is currently in progress.

EXPERIMENTAL

Chemicals. $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$,¹³ *cis*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$,¹⁴ *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)(\text{OH})]\text{Br}_2$,¹⁵ *fac*- $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$,¹⁶ *mer*- $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)\text{Cl}_2]\text{Cl}$,¹⁷ *cis*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$,¹⁸ *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$ ¹⁹ and $\text{Cs}[\text{Cr}(\text{NH}_3)(\text{OH}_2)_5](\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ²⁰ were prepared by literature methods. The sources of other chemicals have been described earlier.^{7,4}

Preparation of ammineaquachromium(III) solutions. *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$ solutions were prepared by directly dissolving the aquahydroxo compound in acid solution as this tetraammine ion is known to decompose on ion exchange resins.²¹ The other cations were purified by ion exchange chromatography on Sephadex SP-C-25 after being generated in aqueous solution by silver(I) accelerated removal of coordinated halide ions using silver(I)tosylate, *cf.* Refs. 4 and 5.

Photolysis experiments. The photolysis experiments were performed using an Osram HBO 100/2 high pressure mercury lamp and standard optical equipment from the firm *Spindler und Hoyer, Göttingen, BRD*. The experiments were carried out on solutions 3–5 mM in complex using 5 cm cylindrical cells thermostatted at 25 °C, at light intensities around 5 $\mu\text{Einstein min}^{-1}$. Under these conditions thermal reactions play no measurable rôle. The photolysis experiments were interrupted periodically for spectrophotometric measurement of the reaction mixtures using either a Cary 219 or a Cary 118 C. Light intensities were checked periodically by chemical actinometry: Ferrioxalate,²² $\phi \approx 1.21$ mol Einstein⁻¹ at 366 nm, and Reineckate,²³ $\phi \approx 0.282$ mol Einstein⁻¹ at 546 nm.

Method of calculation. The method of calculations follows closely that described in Ref. 24, except of course, that the differential equations were integrated using the method described in the appendix to this article. Visible absorption spectra of mixtures and pure components from

300 nm to 700 nm measured at 10 nm intervals were employed to calculate reactant- and reaction product concentrations in the photolyzed solutions. In the last step of the calculations data for all experiments at a particular wavelength of irradiation were processed simultaneously to give quantum yields, *cf.* Table 1, and initial reactant concentrations. It should perhaps be stressed that the wavelength calibration of even good quality UV-VIS spectrophotometers is seldom more accurate than ± 1 nm, and is frequently outside these limits. This means, of course, that spectra of mixtures containing even very few components cannot be expected to give precise information on component concentrations if pure component spectra measured on another spectrophotometer are used without accurate knowledge of the wavelength calibrations. It is therefore usually preferable to measure the spectra of pure components and reaction mixtures on the same spectrophotometer using identical instrument settings. This latter approach was adopted with the two spectrophotometers used in the present investigation. Uncertainties on individual component concentrations determined by this method are frequently rather large. However, these individual uncertainties are usually highly correlated, and provided the correlation terms are not neglected in the following calculations, accurate final parameters even for systems as complicated as that presented here still result.

APPENDIX

The coupled first order differential equations, which can be used to describe the photochemical transformations that may occur between ν species in a solution, which is irradiated with monochromatic light of intensity I_0 , travelling the distance l in a solution of volume V , can be written:

$$V \frac{d\xi_i(t)}{dt} = - \sum_{j=1}^{\nu} \phi_{ij} I_i + \sum_{j=1}^{\nu} \phi_{ji} I_j$$

with

$$I_i = I_0(1 - 10^{-A}) (A_i/A)$$

and:

$$A \equiv \sum_{i=1}^{\nu} A_i \equiv \sum_{i=1}^{\nu} \epsilon_i \xi_i l$$

ξ_i and ε_i are the concentration and molar absorption coefficient, respectively, of the i 'th species, and ϕ_{ij} is the quantum yield for transforming the i 'th species into the j 'th.

The above equations can also be written:

$$\frac{d\xi_i(t)}{dt} = \frac{I_0(1-10^{-A})}{VA} \sum_{j=1}^{\nu} (\phi_{ji}A_j - \phi_{ij}A_i) \quad i=1,2,\dots,\nu$$

and the integration can be performed by expressing $\xi_i(t)$ as a power series in $(t-t_0)$, eqn. (1),

$$\xi_i(t) = \xi_i(t_0) + \sum_{j=1}^{\infty} \gamma_{ij}(t-t_0)^j \quad i=1,2,\dots,\nu \quad (1)$$

with the t_0 -dependent coefficients γ_{ij} given by:

$$\gamma_{i0} = \xi_i(t_0) \quad t_0 \geq 0$$

and:

$$\gamma_{i,p+1} = \frac{\rho_{i,p+1}}{\alpha_0(p+1)}$$

with

$$\rho_{i,p+1} = \frac{I_0}{V} \left\{ \sum_{q=0}^p \beta_q \sum_{j=1}^{\nu} \kappa_{ij}^{qp} - \sum_{j=1}^{\nu} \kappa_{ij}^{0p} \right\} - \sum_{q=1}^p (p+1-q) \alpha_q \gamma_{i,p+1-q} \quad p=0,1,2,\dots$$

$$\alpha_q = \sum_{i=1}^{\nu} \varepsilon_i \gamma_{iq} l \quad q=0,1,2,\dots$$

$$\beta_0 = 10^{-a_0}$$

$$\beta_q = -\frac{\ln 10}{q} \sum_{i=0}^q (q-i) \beta_i \alpha_{q-i} \quad q=1,2,\dots$$

and:

$$\kappa_{ij}^{qp} = \phi_{ij} \varepsilon_i \gamma_{i,p-q} - \phi_{ji} \varepsilon_j \gamma_{j,p-q} \quad \begin{cases} i=1,2,\dots,\nu \\ j=1,2,\dots,\nu \\ p=0,1,\dots \\ q=0,1,\dots,p \end{cases}$$

This set of equations provide a convenient numerical approach to the integration of the coupled differential equations which arise in photochemistry, and the method is easily used as basis for the determination of quantum yields

from experimental data, by nonlinear regression analysis.

For this purpose differential quotients of the measured quantities with respect to the desired parameters are needed. For a general parameter, ψ , these differential quotients are given by eqn. (2).

$$\frac{\partial \xi_i(t)}{\partial \psi} = \frac{\partial \xi_i(t_0)}{\partial \psi} + \sum_{j=1}^{\infty} \frac{\partial \gamma_{ij}}{\partial \psi} (t-t_0)^j \quad i=1,2,\dots,\nu \quad (2)$$

with:

$$\frac{\partial \gamma_{i0}}{\partial \psi} = \frac{\partial \xi_i(t_0)}{\partial \psi} \quad t_0 \geq 0 \quad (3)$$

and:

$$\frac{\partial \gamma_{i,p+1}}{\partial \psi} = \frac{1}{\alpha_0(p+1)} \frac{\partial \rho_{i,p+1}}{\partial \psi} - \frac{\gamma_{i,p+1}}{\alpha_0} \frac{\partial \alpha_0}{\partial \psi}$$

with

$$\frac{\partial \rho_{i,p+1}}{\partial \psi} = \frac{I_0}{V} \left\{ \sum_{q=0}^p \left[\frac{\partial \beta_q}{\partial \psi} \sum_{j=1}^{\nu} \kappa_{ij}^{qp} + \beta_q \sum_{j=1}^{\nu} \frac{\partial \kappa_{ij}^{qp}}{\partial \psi} \right] - \sum_{j=1}^{\nu} \frac{\partial \kappa_{ij}^{0p}}{\partial \psi} \right\} - \sum_{q=1}^p (p+1-q) \left[\frac{\partial \alpha_q}{\partial \psi} \gamma_{i,p+1-q} + \alpha_q \frac{\partial \gamma_{i,p+1-q}}{\partial \psi} \right] \quad p=0,1,2,\dots$$

$$\frac{\partial \alpha_q}{\partial \psi} = \sum_{i=1}^{\nu} \varepsilon_i l \frac{\partial \gamma_{iq}}{\partial \psi} \quad q=0,1,2,\dots$$

$$\frac{\partial \beta_0}{\partial \psi} = -\ln 10 \beta_0 \frac{\partial \alpha_0}{\partial \psi}$$

$$\frac{\partial \beta_q}{\partial \psi} = -\frac{\ln 10}{q} \sum_{i=0}^q (q-i) \left[\frac{\partial \beta_i}{\partial \psi} \alpha_{q-i} + \beta_i \frac{\partial \alpha_{q-i}}{\partial \psi} \right] \quad q=1,2,\dots$$

$$\frac{\partial \kappa_{ij}^{qp}}{\partial \psi} = \varepsilon_i \left[\frac{\partial \phi_{ij}}{\partial \psi} \gamma_{i,p-q} + \phi_{ij} \frac{\partial \gamma_{i,p-q}}{\partial \psi} \right]$$

$$- \varepsilon_j \left[\frac{\partial \phi_{ji}}{\partial \psi} \gamma_{j,p-q} + \phi_{ji} \frac{\partial \gamma_{j,p-q}}{\partial \psi} \right] \quad \begin{cases} i=1,2,\dots,v \\ j=1,2,\dots,v \\ p=0,1,\dots \\ q=0,1,\dots,p \end{cases}$$

Differential quotients with respect to quantum yields, ϕ_{ij} , and initial concentrations, ξ_i^0 , or functions of initial concentrations, are needed for a parametrization of an experimental material, and both these types are readily calculated from the previous equations by noting that:

$$\frac{\partial \xi_i}{\partial \xi_j^0} = \delta_{ij} = \begin{cases} 1 & i=j \\ 0 & i \neq j \end{cases} \quad \text{at } t_0=0$$

and:

$$\frac{\partial \xi_i}{\partial \phi_{jk}} = 0 \quad \text{at } t_0=0$$

in eqn. 3.

A method analogous to the present has previously been used to interpret kinetic data in systems with many consecutive and competitive thermal first order kinetic processes.²⁴ The method presented for photochemical processes can also be extended to allow for thermal reactions during the photolysis.

Eqns. 1 and 2 have been tested with various upper limits for the summations, and with various values of $(t-t_0)$. A polynomial in $(t-t_0)$ of degree 5 in combination with an adjustment of $t-t_0$ so as to make the last term in the series expansion insignificant compared to those terms already summed up, seems to be the most effective in terms of computer time.

The quite general equations given in this appendix are easily applied to actual systems, and general computer programs, which can handle suitably written reaction schemes are readily constructed. Such programs have provided a very flexible tool for the interpretation of photoche-

mistry in several complicated multicomponent systems. Recently it has thus been possible to characterize new minor reaction paths in the photochemistry of some tetraamminerhodium(III) complexes,²⁵ paths which were not detected by the short time photolysis earlier necessitated by older, less satisfactory numerical methods for evaluating quantum yields.

Acknowledgements. This research was supported by a grant from *Carlsbergfondet* (to LM). The authors also wish to thank B. Øby for technical assistance.

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Received February 17, 1984.