# Photoinduced Water Exchange of the Isomeric Ammineaquachromium(III) Complexes, and Mechanism of Solvent-Assisted Excited State Deactivation

L. Mønsted[a,*] and O. Mønsted[b]

[a]Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C and [b]Department of Inorganic Chemistry, the H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Mønsted, L. and Mønsted, O., 1986. Photoinduced Water Exchange of the Isomeric Ammineaquachromium(III) Complexes, and Mechanism of Solvent-Assisted Excited State Deactivation. – Acta Chem. Scand. A 40: 637–645.

Photoinduced water exchange of the eight possible ammineaquachromium(III) ions has been studied using oxygen-18 labelling. The measurements were made at 25 °C using an acidic 1 M perchlorate medium and irradiating at 546 nm. The photochemical reactivity is dominated by exchange of coordinated water, but the total reactivity falls off rapidly with increasing number of water ligands. The product distributions are best accounted for by an associative interchange mechanism and *trans*-attack of the entering water molecule to give a transition state with the geometry of a pentagonal bipyramid, for which ligand field model calculations show that the lowest quartet excited state, Q_E, is comparable in energy to the quartet ground state, Q_G, and has significantly lower energy than the lowest doublet state, D. This suggests the following simplified mechanism for the solvent-assisted excited state deactivation process:

$$Q_E(O_h) \searrow \atop \downarrow \atop D(O_h) \nearrow\ Q_E(D_{5h}) \rightleftharpoons Q_G(D_{5h}) \rightarrow Q_G(O_h)$$
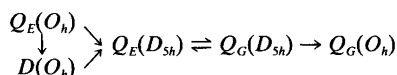
Product distribution ratios are different for the photochemical and corresponding thermal reactions, but for competing reactions with positive differences in enthalpies of activation, ΔH^*, the ratio of the quantum yields, φ, is always larger than that of the thermal rate constants, i.e.:

$$\varphi_a/\varphi_b > k_a/k_b \quad \text{when} \quad \Delta H_a^* > \Delta H_b^*$$

This result is also rationalized by the above mechanism. Product distributions show that: (*i*) Attack of the entering water molecule occurs predominantly in the plane of the octahedral complex with the greatest number of water ligands. (*ii*) Attack occurs predominantly in a position *cis* to ammonia ligands, and (*iii*) water is predominantly the leaving ligand.

Ammineaquachromium(III) complexes are photochemically active and isomerization and loss of coordinated ammonia have been investigated previously.[1] Both of these types of reactivities diminish rapidly as the number of coordinated water ligands is increased. Whether this apparently greater photoinertness is real or is the result of increased competitive photochemical exchange of coordinated water has, however, not been resolved.

---

*To whom correspondence should be addressed.

Knowledge concerning photoinduced water exchange reactions in general is sparse, and for chromium(III), only data for the hexaaquachromium(III) ion have previously been reported;[2] the quantum yields reported here for water exchange in all the possible ammineaquachromium (III) isomers supplement both this limited information and earlier thermal and photochemical data on this group of complexes. This has permitted a critical evaluation of current empirical and semi-empirical rationalizations of the photostereochemistry of chromium(III) complexes.

Results and discussion

Ammineaquachromium(III) complexes are photochemically active. In acidic solution, coordinated ammonia is substituted for solvent water and isomerization takes place. These processes have been investigated in detail previously.[1] In order to monitor the total photochemical reactivity of complexes of this type they have all been prepared coordinated with oxygen-18 labelled water. When such complexes are irradiated in the ligand field bands, coordinated water is exchanged for solvent water by a photochemical process. This is demonstrated in Fig. 1 for pentaammineaqua- and the isomeric tetraamminediaquachromium(III) ions.

Interpretation of these data is complicated by significant competitive thermal water exchange under the conditions necessary for well-defined photochemical conversion. Thus, for the pentaammineaquachromium(III) ion (data in Fig. 1) about half the release of coordinated oxygen-18 labelled water is the result of a thermal process. The previously published method for determining quantum yields, based partly upon numerical integration of the coupled first-order photochemical differential equations,[1] was therefore modified to take into account also thermal reactions. This is described in Appendix I.

A detailed interpretation of the experimental data is further made difficult by the multitude of possible reaction paths available for most of the complexes studied. Thus, while water exchange of the pentaammineaquachromium(III) ion is simple, for the isomeric pairs of tetraamminediaqua-, triamminetriaqua- and diamminetetraaquachromium(III) both stereoretentive and stereomobile processes must be considered; in *mer*-
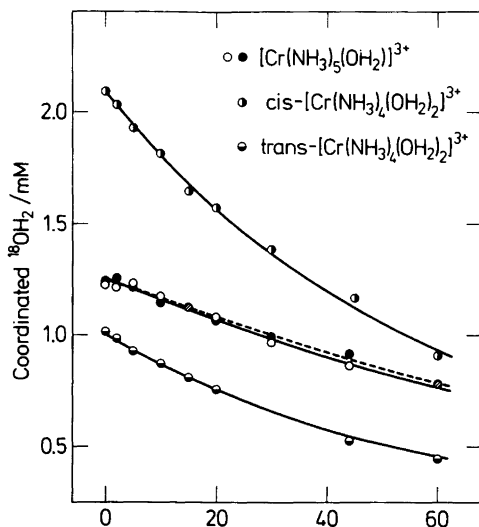

Fig. 1. Photolysis experiments started from oxygen-18 labelled pentaammineaqua- and the isomeric tetraamminediaquachromium(III) complexes. The experimental points are obtained from the mass spectrometric measurements and the solid curves are calculated from the quantum yields in Table 1, the concentrations of coordinated oxygen-18 at time = 0 and of chromium(III), the light intensities and the molar absorption coefficients at 546 nm. The differences in the two pentaammineaquachromium(III) experiments are caused by the use of different light intensities, viz. 9.09 and 8.20 μeinstein l^{-1} s^{-1}.

triamminetriaqua-, *cis*-diamminetetraaqua- and amminepentaaquachromium(III) the issue is further complicated by the presence of two different types of coordinated water ligands.

Stereochemical change in chromium(III) complexes of simple ligands in solution seems predominantly to be the result of intermolecular reactions with solvent. Intramolecular rearrangements are usually not observed, or contribute only little to the total reactivity. The present data accord with this predominantly intermolecular nature of the isomerization processes, since the total quantum yield for water exchange is always greater than, or equal to, the quantum yield for isomerization. It should be stressed, however, that the present experiments do not allow an unambiguous mechanistic assignment on this point, and the data in Table 1 are obtained by assuming that the isomerization reactions are accompanied by solvent exchange.

638

Table 1. Quantum yields and estimated standard deviations (mol complex einstein^{-1}) for the photochemical reactivities of ammineaquachromium(III) complexes in 0.5 M HClO$_4$ + 0.5 M NaClO$_4$ at 25 °C irradiated at 546 nm. The reported data are: φ(exch) for apparently stereotentive water exchange, φ(isom) for stereomobile water exchange, φ(NH$_3$) for ammonia ligand substitution and φ(total) for the total photochemical reactivity.

Reactant complex	φ(exch)[a]	φ(isom)[a,b]	φ(NH$_3$)[b]	φ(total)
[Cr(NH$_3$)$_6$]$^{3+}$	–	–	0.443(15)[c]	0.443(15)[c]
[Cr(NH$_3$)$_5$(OH$_2$)]$^{3+}$	0.078(10)	–	0.195(8)	0.273(13)
cis-[Cr(NH$_3$)$_4$(OH$_2$)$_2$]$^{3+}$	0.057(9)	0.141(6)	0.058(9)	0.256(15)
trans-[Cr(NH$_3$)$_4$(OH$_2$)$_2$]$^{3+}$	0.001(3)	0.310(4)	0.025(8)	0.336(9)
fac-[Cr(NH$_3$)$_3$(OH$_2$)$_3$]$^{3+}$	0.040(16)	0.146(5)	0.053(7)	0.239(17)
mer-[Cr(NH$_3$)$_3$(OH$_2$)$_3$]$^{3+}$	~0.12(3)[d]	0.064(4)	0.011(5)	0.19(3)
cis-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$	~0.179(15)[d]	0.000(1)	0.0019(2)	0.181(15)
trans-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$	0.072(16)	0.051(2)	0.0041(8)	0.127(18)
[Cr(NH$_3$)(OH$_2$)$_5$]$^{3+}$	~0.057(4)[d]	–	0.0000(1)	0.057(4)
[Cr(OH$_2$)$_6$]$^{3+}$	0.019(2)[e]	–	–	0.019(2)

[a]This work. [b]Ref. 1. [c]λ$_{irr}$ = 366 nm: Refs. 3 and 4. [d]These values contain contributions from different types of coordinated water ligands (see text). [e]Ref. 2 (see Appendix II).

The exchange data for the three ammineaquachromium(III) complexes with non-equivalent coordinated water ligands are all well accounted for by assuming only *one* photochemical exchange path. This could point towards the importance of reactivity contributions from solvent exchange reactions accompanied by scrambling of the coordinated water ligands (cf. Refs. 5 and 6). However, selective labelling experiments presently in progress will resolve this question.

From the data in Table 1 it can be seen that the reactivity of all these complexes, except for the pentaammineaquachromium(III) ion, is dominated by substitution of water ligands. Data for the *cis*-tetraamminediaqua- and *fac*-triamminetriaquachromium(III) ions are particularly noteworthy as they both contradict an empirical rule that states that the leaving ligand is that having the highest ligand field strength on the axis of lowest average ligand field:[7] for both these complexes application of this rule would predict ammonia ligand substitution to be dominant. More recent ligand field based models[8] also fail to predict correctly the leaving ligand in these complexes. Thus, for *cis*-[Cr(en)$_2$(OH$_2$)$_2$]$^{3+}$ (en = 1,2-ethanediamine), substitution of the equatorial amine is predicted (see Table 5 in Ref. 8). The minor difference in ligand field parameters between ammonia (σ$_{NH_3}$ ≈ 0.718 μm^{-1}, π$_{NH_3}$ ≈ 0 μm^{-1}) and 1,2-ethanediamine (σ$_{en}$ ≈ 0.728 μm^{-1}, π$_{en}$ ≈ 0 μm^{-1}; Table 1 in Ref. 8) does not change

this prediction for the *cis*-tetraamminediaquachromium(III) complex.

Table 2 shows data for competitive formation of the two tetraamminediaquachromium(III) isomers. The competition ratio is seen to depend upon the substrate, in clear contrast to what would be expected for dissociative activation such as demonstrated by many rhodium(III) systems, in which the photosubstitution processes are thought to proceed via an intermediate of reduced coordination number.[9] The absence of a stereoretentive water exchange path for the *trans*-tetraamminediaquachromium(III) ion is particularly illuminating, and in combination with the non-constant competition ratio it is further evidence in favour of the previously suggested mechanism[10] in which *trans*-attack of the entering water molecule gives a pentagonal bipyramidal transition state structure, as shown in Fig. 2.

Current theoretical approaches to the photochemical reactivity of chromium(III) complexes have focused upon transition state structures having reduced coordination numbers,[8] and little work has been done on seven-coordinated structures. For a pentagonal bipyramid, angular overlap model[11] calculations show that the lowest quartet excited state, Q_E, is close in energy to the quartet ground state, Q_G, and lies below the lowest doublet state, D, i.e.:

$$E(Q_G) \lesssim E(Q_E) < E(D).$$

639

Table 2. Quantum yields and estimated standard deviations (mol einstein^{-1}) for competitive formation of *cis*- and *trans*-tetraamminediaquachromium(III).

Reactant	φ_{cis}^a	φ_{trans}^a	$\dfrac{\varphi_{trans}}{\varphi_{cis}}$
$[Cr(NH_3)_5(OH_2)]^{3+}$	0.175(6)	0.020(6)	0.11(3)
cis-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.057(9)	0.141(6)	2.5(4)
trans-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.310(4)	0.001(3)	0.00(2)

^{a}Data from Ref. 1 and this work.

This ordering of energy levels is maintained for all chemically reasonable spectrochemical parameter values, and suggests a variation in ground state and lowest excited state energy levels along the reaction coordinate for the *trans*-attack mechanism, as shown in Fig. 3. Intersystem crossing to an excited quartet state of comparable or lower energy than that of the doublet state may clearly be an attractive path for the reactivity of this latter state. Fig. 3 is therefore also seen to combine the otherwise contrasting ideas of excited doublet state deactivation occurring either by back intersystem crossing to a reactive electronically excited quartet state[12] or by surface crossing to a reactive ground state intermediate.[13]

The predicted similarity between ground state thermal and excited state photochemical reactions, inherent in Fig. 3, is particularly interesting, especially since these latter reactions are frequently referred to as "antithermal". Few systems are known in which both competing thermal and photochemical reactions are well characterized. The data in Table 3 reveal, however, a clear correlation: the reaction which has the higher activation enthalpy is invariably more dominant photochemically than thermally, i.e.:

$$\varphi_a/\varphi_b > k_a/k_b, \quad \text{when} \quad \Delta H_a^* > \Delta H_b^*.$$

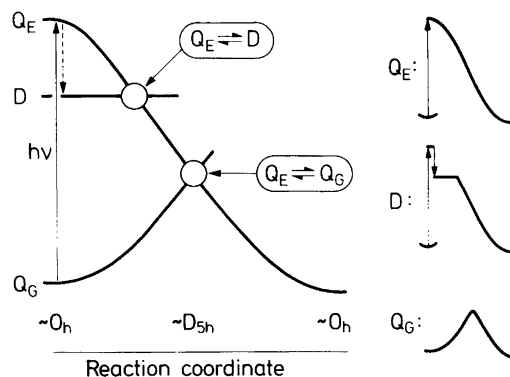Fig. 4 demonstrates, however, that the quantum yield ratio is not simply obtainable by "high-

Fig. 3. Variation of ground state and lowest excited state energy levels along the reaction coordinate for the *trans*-attack mechanism in Fig. 2. Inserts show energy variations along the reaction coordinate by reactions of the quartet, Q_E, and doublet, D, excited states and the quartet ground state, Q_G, respectively.

temperature" extrapolation of data for the thermal reactions, since the general trend of the data in Fig. 4 accords with the relationship

$$\varphi_a/\varphi_b \gtrsim (k_a/k_b)_T \exp((\Delta H_a^* - \Delta H_b^*)/RT).$$

It should be recalled, however, that there is probably a gradual change in mechanism with temperature: at lower temperatures reactions occur predominantly stereoretentively by a *cis*-attack of

Fig. 2. trans-Attack of a water molecule in *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ forming *cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ stereospecifically via a pentagonal bipyramidal transition state or intermediate.
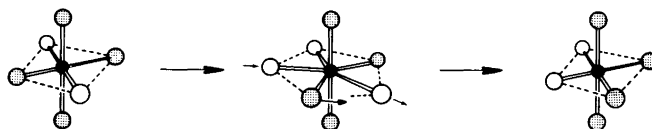
Table 3. Comparison of data for competitive photochemical and thermal reactions of some ammineaquachromium(III) complexes.

Reactant	Reaction products	φ^a/mol einstein^{-1}	$k(50\,°C)^b$/s^{-1}	ΔH^*/kJ mol^{-1}
trans-[Cr(NH₃)₂(OH₂)₄]³⁺	*trans*-[Cr(NH₃)₂(OH₂)₄]³⁺	0.071±0.012^c	$(89±3)\cdot 10^{-5}$ ^{c}	97.0±1.1
	cis-[Cr(NH₃)₂(OH₂)₄]³⁺	0.051±0.002	$(0.43±0.04)\cdot 10^{-6}$	113±4
	[Cr(NH₃)(OH₂)₅]³⁺	0.0041±0.0008	$(1.61±0.06)\cdot 10^{-6}$	107.2±1.6
fac-[Cr(NH₃)₃(OH₂)₃]³⁺	*fac*-[Cr(NH₃)₃(OH₂)₃]³⁺	0.040±0.016^c	$(366±15)\cdot 10^{-5}$ ^{c}	95.1±1.3
	cis-[Cr(NH₃)₂(OH₂)₄]³⁺	0.041±0.005	$(0.62±0.04)\cdot 10^{-6}$	112.6±2.4
cis-[Cr(NH₃)₄(OH₂)₂]³⁺	*cis*-[Cr(NH₃)₄(OH₂)₂]³⁺	0.078±0.010^c	$(250±16)\cdot 10^{-5}$ ^{c}	95.1±1.9
	fac-[Cr(NH₃)₃(OH₂)₃]³⁺	0.031±0.006	$(2.35±0.12)\cdot 10^{-6}$	104.7±2.0
[Cr(NH₃)₅(OH₂)]³⁺	[Cr(NH₃)₅(OH₂)]³⁺	0.078±0.010	$(137±6)\cdot 10^{-5}$	99.1±1.4
	cis-[Cr(NH₃)₄(OH₂)₂]³⁺	0.175±0.006	$(4.03±0.16)\cdot 10^{-6}$	110.5±1.6

^{a}Data from Ref. 1 and this work. ^{b}Extrapolated from data for 60–80 °C in Ref. 14 and data for 15–40 °C in Refs. 5 and 15. ^{c}These data are not statistically corrected but refer to the total reactivity of the complex. φ(complex) $= n\varphi$(OH₂) for a 'Cr(OH₂)$_n$'-complex, cf. Ref. 15.

the entering ligand, whereas at higher temperatures stereomobile reactions with higher activation enthalpies will dominate. A more accurate prediction of the quantum yield ratio for competitive stereomobile photochemical reactions would therefore necessarily have to be based upon thermal data which do not contain reactivity contributions from both stereoretentive and stereomobile paths. Fig. 4 may be seen as an illustration of this, since the horizontal difference between the fully drawn line and the "best" line through those experimental points for which the thermal *a*-reaction is known to be completely stereomobile could be interpreted as arising from a contribution of about 10 % of a stereomobile reaction to the corresponding *b*-reactions. An even smaller stereomobile reactivity contribution combined with a larger activation enthalpy for this type of reactivity than for the stereoretentive reactivity also correlates thermal and photochemical reactivities. For *cis*-diamminetetraaquachromium(III), selective labelling experiments have led to the estimate that less than (6±3) % of the total thermal water exchange proceeds by a stereomobile path.[5] This value is probably also a fair estimate of the upper limit for the complexes in Fig. 4. Contrary to common belief, therefore, "antithermal" behaviour of the photochemical reactions cannot be verified for the ammineaquachromium(III) complexes. Instead, Fig. 4 demonstrates a clear correlation between thermal and

photochemical data and Fig. 3 provides a mechanistic rationale for this behaviour.

The *trans*-attack mechanism illustrated in Fig. 2 clearly has important consequences for the stereochemical outcome of a photochemical reaction. Stereoretentive water exchange in *trans*-te-
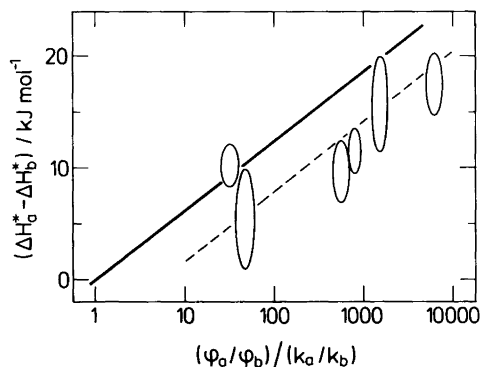

Fig. 4. Correlation between photochemical and thermal data for some competitive reactions of chromium(III). The solid line corresponds to $(\varphi_a/\varphi_b)/(k_a/k_b)_T = \exp((\Delta H_a^* - \Delta H_b^*)/RT)$, $T = 323$ K. The broken line is that having the same slope which "best" fits, in the least-squares sense, those points (see Table 3) for which the *a*-reaction is known to be completely stereomobile. The experimental data are shown as contour ellipses of the probability density function drawn at the 68 % level.
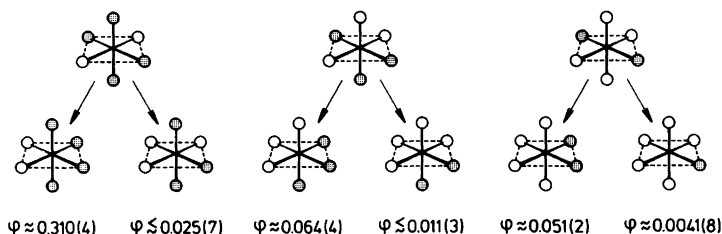
641

$\varphi \approx 0.310(4)$ $\varphi \lesssim 0.025(7)$ $\varphi \approx 0.064(4)$ $\varphi \lesssim 0.011(3)$ $\varphi \approx 0.051(2)$ $\varphi \approx 0.004(8)$

Fig. 5. Quantum yields (mol einstein^{-1}) for isomerization and substitution of coordinated ammonia of the *trans*-$\{(NH_3)_2(OH_2)_2\}$-plane for three different combinations of axial ligands (see text).

traamminediaquachromium(III) is clearly not possible, and the *trans*-tetraamminediaqua- to *fac*-triamminetriaquachromium(III) reaction and the reaction of the latter complex to give *trans*-diamminetetraaquachromium(III) are also impossible according to this mechanism; neither of these processes are observed experimentally.

The proposed model suggests that participation of the two ligands on the axis perpendicular to the reacting plane will be small. Close examination of the experimental data shows this expectation to be fulfilled, as illustrated for the reactions of the *trans*-$\{a_2aq_2\}$ plane (a = NH$_3$, aq = OH$_2$) in Fig. 5. Isomerization is seen to dominate over loss of coordinated ammonia irrespective of the *trans* ligands, and it is not unreasonable to assume a competition ratio for these two processes which is independent of the nature of the two axial ligands, especially when the minor uncertainties concerning reactivity contribu-

tions from the $\{a_4\}$ and $\{a_3aq\}$ planes in the *trans*-tetraamminediaqua- and *mer*-triamminetriaquachromium(III) isomers, respectively, are also taken into account. The total experimental material has been subjected to a similar analysis. Table 4 shows the relative reactivity contributions from the different planes of the octahedral complexes, and Table 5 gives competition ratios for the various reactions of those planes which may have more than one outcome. The quantum yields are described well by this model, as indicated by the value $\Sigma[(\varphi_{obs} - \varphi_{calc})^2/\sigma^2(\varphi)] \approx 7.0$ for five degrees of freedom, and all parameters except some related to the reactivity of the $\{a_3aq\}$ plane are reasonably well defined and have physically meaningful values.

The data in Table 4 are particularly informative and show unambiguously dominant relative reactivity contributions from planes with a greater number of water ligands. This may clearly be cor-

Table 4. Relative photochemical reactivity contributions and estimated standard deviations for the different square-planar subunits of the octahedral ammineaquachromium(III) complexes (see text). a = NH$_3$ and aq = OH$_2$.

| Complex | Square planes | | | | | |
	$\{a_4\}$	$\{a_3\,aq\}$	*cis*-$\{a_2\,aq_2\}$	*trans*-$\{a_2\,aq_2\}$	$\{a\,aq_3\}$	$\{aq_4\}$
[Cr a$_6$]$^{3+}$	1	–	–	–	–	–
[Cr a$_5$ aq]$^{3+}$	?	?	–	–	–	–
cis-[Cr a$_4$ aq$_2$]$^{3+}$	–	0.27(15)	0.73(15)	–	–	–
trans-[Cr a$_4$ aq$_2$]$^{3+}$	0.00(3)	–	–	1.00(3)	–	–
fac-[Cr a$_3$ aq$_3$]$^{3+}$	–	–	1	–	–	–
mer-[Cr a$_3$ aq$_3$]$^{3+}$	–	0.08(6)	–	0.35(2)	0.57(7)	–
cis-[Cr a$_2$ aq$_4$]$^{3+}$	–	–	0.00(1)	–	1.00(1)	–
trans-[Cr a$_2$ aq$_4$]$^{3+}$	–	–	–	0.43(12)	–	0.57(12)
[Cr a aq$_5$]$^{3+}$	–	–	–	–	0.00(17)	1.00(17)
[Cr aq$_6$]$^{3+}$	–	–	–	–	–	1

Table 5. Competition ratios and estimated standard deviations for photochemical reactions of the square-planar subunits of the octahedral ammineaquachromium(III) complexes (see text). $a = NH_3$ and $aq = OH_2$.

Reactant plane	Products plane	Relative reactivity contribution
$\{a_3\,aq\}$	*cis*-$\{a_2\,aq_2\}$: *trans*-$\{a_2aq_2\}$: $\{a_3\,aq\}$	? : 0.24(8) : 1
trans-$\{a_2\,aq_2\}$	$\{a\,aq_3\}$: *cis*-$\{a_2\,aq_2\}$	0.084(16) : 1
cis-$\{a_2\,aq_2\}$	$\{a\,aq_3\}$: *cis*-$\{a_2\,aq_2\}$: *trans*-$\{a_2\,aq_2\}$	0.25(4) : 0.20(10) : 1
$\{a\,aq_3\}$	$\{aq_4\}$: $\{a\,aq_3\}$	0.011(2) : 1

related with the relative energies of the individual components of the $^4T_2(O_h) \leftarrow\,^4A_2(O_h)$ transition in lower symmetry, which are rather accurately given by the average spectroscopic Δ-value for the four ligands in the plane of the electronic transition. The pattern of reactivity can clearly be accounted for by reactions of both quartet and doublet excited states, as shown in Fig. 3. The intimate mechanism favouring reactivity in the plane of the greatest number of water ligands is different, however: for the quartet state it is favoured by internal conversion to the lowest excited quartet state prior to reaction, but for the doublet state it is favoured by back intersystem crossing to that quartet state which distortions and attack of the entering water molecule most readily make comparable in energy to the doublet state.

Fig. 6 shows the total photochemical reactivity of the ammineaquachromium(III) complexes, which is clearly seen to increase significantly as a function of the number of ammonia ligands. Furthermore, those complexes with significant reactivity contributions from more than one type of plane (see Table 4) fall below the linear correlation between the total quantum yields and the number of ligands of one type which is seen in the diagram for the other complexes. Several possible explanations for this behaviour may be suggested but at present these are all at the speculative level.

Table 5 shows "product" distribution ratios for reactions of the planes of the octahedral complexes. Qualitatively, the reactivity pattern seems consistent and can be summarized as follows: Firstly, substitution of coordinated water is preferred to substitution of coordinated ammonia. Secondly, major movement of an ammonia ligand (see Fig. 2) is preferred to movement of a water ligand, and thirdly, attack at an ammonia-ammonia or ammonia-water edge is preferred to attack at a water-water edge. Further work is definitely needed to quantify these trends but it should be noted that the first point is in agreement with predictions based upon the suggested correlation with the thermal data, and both the second and third points may be rationalized by noting that the stabilization of the lowest quartet
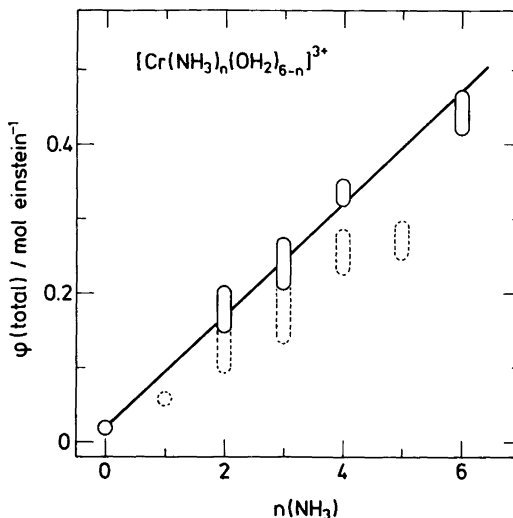

Fig. 6. Correlation between total photochemical reactivity and number of coordinated ammonia ligands (see Table 1). Solid points are those for which $\varrho - 3\sigma(\varrho) > 0.9$, where ϱ is the dominant relative reactivity contribution from a square-planar subunit of the octahedral complex (see Table 4) and $\sigma(\varrho)$ is the estimated standard deviation of this quantity. Data for the remaining complexes are shown as dashed points, and the experimental data are drawn with an extent corresponding to $\pm 2 \times$ e.s.d.

643

excited state by angular ligand movements in the simple approximation is proportional to the spectroscopic Δ-values of the ligands.

Work currently in progress will attempt to generalize the above rationalizations to include also other ligands.

Experimental

Chemicals,[1] preparation of oxygen-18 enriched aquachromium(III) complexes,[5,6,15] methods of analyses,[16] mass spectrometric measurements[15] and *photolysis experiments[17]* have all been described previously.

The method of calculation follows that outlined in Refs. 1 and 15, except that the coupled first-order differential equations for the photochemical and thermal processes were integrated by the method described in Appendix I. Mass spectrometric δ-values were converted to concentrations of coordinated oxygen-18, $[^{18}O_c]$, and estimated standard deviations, $\sigma([^{18}O_c])$, and the quantity

$$\sum_i \sum_t \{([^{18}O_c]_{obs} - [^{18}O_c]_{calc})^2 / \sigma^2([^{18}O_c])\}$$

where the summations extending over all experiments, i, and all times, t, were minimized as a function of the degree of oxygen-18 labelling in the individual experiments and of all quantum yields for water exchange. Examples of the agreement between observed and calculated curves are shown in Fig. 1 for four of the experiments, and the quantum yields determined are given in Table 1. The previously determined quantum yields for substitution of coordinated ammonia and for isomerization were regarded as being constant during the minimization, but a numerical differentiation of the "new" quantum yields with respect to those determined previously and to the thermal rate constants was performed. This was used for more realistic error estimates for the quantum yields for water exchange than those obtained by simply keeping the known parameters constant.

Appendix I

The appendix in Ref. 1 describes a quite general method for integration of the coupled first-order differential equations describing a system in which photochemical transformations between v species may take place. The method is quite easily extended to take also thermal reactions into account and only a few additional terms need to be introduced in some of the equations given previously. In order to avoid unnecessary duplication of the earlier work, only those equations which are altered and the new terms are given below. The coupled first-order differential equations are now written as

$$\frac{d\xi_i(t)}{dt} = [\text{Ref. 1}] + \sum_{j=1}^{v} (\tau_{ji}\xi_j - \tau_{ij}\xi_i)$$

$$i = 1,2,\dots, v$$

where τ_{ij} is the thermal rate constant for transformation of the i'th species into the j'th by a first-order process. This addition simply adds new terms to $\varrho_{i,p+1}$ and $\partial\varrho_{i,p+1}/\partial\psi$ which now become

$$\varrho_{i,p+1} = [\text{Ref. 1}] + \sum_{l=0}^{p} \alpha_l \sum_{j=1}^{v} (\tau_{ji}\gamma_{j,p-l} - \tau_{ij}\gamma_{i,p-l})$$

$$\frac{\partial\varrho_{i,p+1}}{\partial\psi} = [\text{Ref. 1}] + \sum_{l=0}^{p} \left[\frac{\partial\alpha_l}{\partial\psi} \sum_{j=1}^{v} (\tau_{ji}\gamma_{j,p-l} - \tau_{ij}\gamma_{i,p-l}) \right.$$

$$\left. + \alpha_l \sum_{j=1}^{v} \left(\tau_{ji}\frac{\partial\gamma_{j,p-l}}{\partial\psi} - \tau_{ij}\frac{\partial\gamma_{i,p-l}}{\partial\psi} \right) \right]$$

$$p = 0, 1, 2, \dots$$

while the remaining expressions in Ref. 1 are unchanged.

This provides a method of integrating the differential equations. If solvent exchange is investigated, however, then usually only the concentration of "label" is followed with time and the general formulation will thus require a transformation of the calculated concentrations, ξ, into a smaller set, ξ'. If this transformation is written in matrix notation as

$$\xi \to \xi' : c' = T_c \, c$$

then differential quotients for the regression analysis are obtained from

$$\frac{\partial c'}{\partial \psi} = T_c \frac{\partial c}{\partial \psi}$$

where $\partial c / \partial \psi$ is the column vector calculated previously.[1]

Appendix II

Photoinduced exchange of coordinated water in hexaaquachromium(III) has been investigated previously for an aqueous solution of 0.1 M Cr $(ClO_4)_3$ in 0.1 M $HClO_4$.[2] During the present work with the ammineaquachromium(III) complexes we attempted to reproduce this earlier work, but with chromium(III) concentrations at the millimolar level and in 1.0 M $(Na,H)ClO_4$. This gave a poorly-defined result for the quantum yield but nevertheless indicated a significantly lower value, i.e. 0.000(2) mol H_2O einstein^{-1} at 7–25 °C and 0.1–0.5 M H^+, to be compared with average values of: 0 °C, 0.0031(4); 10 °C, 0.014(3) and 27 °C, 0.017(3) mol H_2O einstein^{-1}, respectively, in Ref. 2.

There are seemingly no obvious explanations for this discrepancy. It should be remembered, however, that at the higher temperatures about 80–90 % of the observed exchange occurs by the thermal path. The significantly higher light intensities necessitated by the greater chromium(III) concentrations in Ref. 2 could, therefore, possibly have produced such a temperature distribution in the photolyzed samples that the average sample temperature cannot be used accurately to correct for the large thermal reactivity. The reported apparent activation energy for the process is also abnormally high for a photochemical reaction of chromium(III) (see Table 1 in Ref. 18). It was therefore chosen to use the value for 0 °C

from Ref. 2: 0.0031(4) mol H_2O einstein^{-1} ≡ 0.019(2) mol $[Cr(OH_2)_6]^{3+}$ einstein^{-1} in Table 1 of the present work.

References

1. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 38* (1984) 679.
2. Plane, R. A. and Hunt, J. P. *J. Am. Chem. Soc. 79* (1957) 3343.
3. Kirk, A. D., Frederick, L. A. and Wong, C. F. C. *Inorg. Chem. 18* (1979) 448.
4. Krause, H. H. and Wasgestian, F. *Inorg. Chim. Acta 29* (1978) 231.
5. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 36* (1982) 365.
6. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 36* (1982) 555.
7. Adamson, A. W. *J. Phys. Chem. 71* (1967) 798.
8. Vanquickenborne, L. G. and Ceulemans, A. *Coord. Chem. Rev. 48* (1983) 157 and references therein.
9. Mønsted, L. and Skibsted, L. H. *Acta Chem. Scand., Ser. A 38* (1984) 535 and references therein.
10. Kirk, A. D. *Mol. Photochem. 5* (1973) 127.
11. Schäffer, C. E. *Struct. Bonding (Berlin) 14* (1973) 69.
12. Linck, N. J., Berens, S. J., Magde, D. and Linck, R. G. *J. Phys. Chem. 87* (1983) 1733 and references therein.
13. Ramasami, T., Endicott, J. F. and Brubaker, G. R. *J. Phys. Chem. 87* (1983) 5057 and references therein.
14. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 28* (1974) 569.
15. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 34* (1980) 259.
16. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. 27* (1973) 2121.
17. Mønsted, L. and Skibsted, L. H. *Acta Chem. Scand., Ser. A 37* (1983) 663.
18. Kirk, A. D. *Coord. Chem. Rev. 39* (1981) 225.