

Photochemical water exchange in chromium(III) complexes, and mechanism of solvent assisted excited state deactivation

L. Mønsted and O. Mønsted.

Chemistry Department, Royal Veterinary and Agricultural University
and
Department of Inorganic Chemistry, University of Copenhagen.
Denmark.

Abstract - Photoinduced water exchange of a number of amine-aquachromium(III) complexes have been studied by ligand field band irradiation of oxygen-18 labelled complexes. The photochemical reactivity is dominated by exchange of coordinated water, but falls off rapidly with an increasing number of water ligands. Product distributions can be accounted for by an associative interchange mechanism and *trans*-attack of the entering water molecule. For competing reactions, labelled a and b, there is a clear correlation between thermal, k , and photochemical, ϕ , reactivities corresponding to:

$$\phi_a/\phi_b > k_a/k_b \text{ when } \Delta H_a^* > \Delta H_b^*.$$

Ligand field model calculations on reasonable transition state structures show that the lowest quartet excited state is comparable in energy to the quartet ground state and has significantly lower energy than the lowest doublet state. This suggests that the solvent assisted excited state deactivation of both excited quartet and doublet states predominantly take place via a quartet excited transition state close in energy and structure to the transition state of stereomobile thermal reactions.

In spite of the large efforts put into photochemical research of transition metal complexes during the last decades and the central role of an aqueous medium for the majority of this work, only very few investigations of photoinduced water ligand exchange have appeared. The photochemical reactivity of hexaaquachromium(III) was apparently the first to be studied [ref. 1] and was found to occur with a rather small quantum yield. Significant photochemical water ligand exchange was later demonstrated in pentaammine-aquarhodium(III) [ref. 2], but it was not until recently that water ligand exchange quantum yields for a significant number of chromium(III) [refs. 3,4,5] and rhodium(III) [refs. 6,7,8] complexes became available. A summary of the data for the aquachromium(III) complexes are given in Table 1.

Table 2 shows data for the competitive formation of tetraaminediaquachromium(III) isomers. The competition ratio is seen to depend heavily on the substrate in clear contrast to the dissociatively activated low charged rhodium(III) complexes which show constant competition ratios independent of substrate. One such recent example is the constant formation ratio for *cis*- and *trans*-tetraammineaquachlororhodium(III) isomers whether formed by water ligand exchange in the isomers or by chloride ligand substitution in the isomeric tetraamminedichlororhodium(III) isomers [ref. 6]. The absence of a stereoretentive water exchange path for both *trans*-tetraaminediaquachromi-

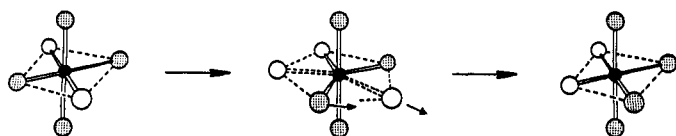


Fig. 1. *trans*-Attack of a water molecule in *trans*-tetraaminediaquachromium(III) forming the *cis* isomer stereospecifically.

TABLE 1. Quantum yields and estimated standard deviations (mol complex/einstein) for the photochemical reactivities of ammine- and (1,3-propanediamine)aquachromium(III) complexes in a 1 M perchlorate medium at 25°C irradiated at 546 or 366 nm. The reported data are: $\phi(\text{exch})$ for apparently stereoretentive water exchange, $\phi(\text{isom})$ for stereomobile water exchange and $\phi(N)$ for ammonia or amine ligand substitution [Refs. 1,3,4,5,9].

Reactant complex	$\phi(\text{exch})$	$\phi(\text{isom})$	$\phi(N)$
$[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$	0.078(10)	-	0.195(8)
<i>cis</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	0.057(9)	0.141(6)	0.058(9)
<i>cis</i> - $[\text{Cr}(\text{tn})_2(\text{OH}_2)_2]^{3+}$	0.066(12)	0.194(14)	0.0048(14)
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	0.001(3)	0.310(4)	0.025(8)
<i>trans</i> - $[\text{Cr}(\text{tn})_2(\text{OH}_2)_2]^{3+}$	0.000(10)	0.365(6)	0.012(2)
<i>fac</i> - $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$	0.040(16)	0.146(5)	0.053(7)
<i>mer</i> - $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$	0.12(3) ^a	0.064(4)	0.011(5)
<i>cis</i> - $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$	0.179(15) ^b	0.000(1)	0.0019(2)
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$	0.072(16) ^a	0.051(2)	0.0041(8)
$[\text{Cr}(\text{NH}_3)(\text{OH}_2)_5]^{3+}$	0.057(4)	-	0.0000(1)
$[\text{Cr}(\text{OH}_2)_6]^{3+}$	0.019(2)	-	-

a,b: These values contain contributions from different types of coordinated water ligands. b: For the *cis*-diammine-tetraaquachromium(III) ion selective labelling experiments indicate $\phi(\text{exch}) \approx 0.121(4)$ and $0.044(7)$ mol complex/einstein for water *trans* to water and ammonia, respectively [Ref. 10]. tn = 1,3-propanediamine.

um(III) isomers is particularly informative in a mechanistic context and furnishes further evidence for the earlier suggested *trans*-attack or edge-displacement mechanism [ref. 11]. This is shown in Fig.1.

Thermal and photochemical reactions of chromium(III) complexes often result in different reaction products, and this is frequently taken to be indicative of a general 'antithermal' behaviour of the photochemical processes. This was early reported for pentaamminechromium(III) which thermally releases chloride, apparently with retention of configuration, to give pentaammineaquachromium(III) but photochemically gives *cis*-tetraammineaquachlorochromium(III) [ref. 12] probably as the result of aquation of the ammonia ligand in *trans* position to the chloride ligand in the reactant complex [ref. 13]. It is now known that stereoretentive thermal reactions of chromium(III) have generally lower energies of activation than reactions in which a stereochemical change occur. The availability of data for both photochemical [refs. 3,4] and thermal water ligand exchange [refs. 4,5,14,15,16] and amine ligand aquation [refs. 4,5,9,17,18,19] has provided data for competitive reactions with rate constants differing up to four orders of magnitude having well defined activation enthalpy differences. From these

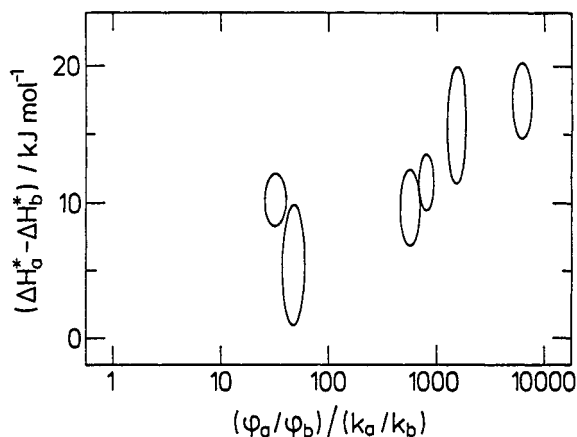


Fig.2. Correlation between photochemical and thermal data for some competitive reactions of chromium(III). The experimental data are shown as contour ellipses of the probability density function drawn at the 68% level.

TABLE 2. Quantum yields and estimated standard deviations (mol complex/einstein) for competitive formation of *cis*- and *trans*-tetraaminediaquachromium(III) [refs. 3, 4, 5, 9].

Reactant complex	$\phi(cis)$	$\phi(trans)$	R^a
$[Cr(NH_3)_5(OH_2)]^{3+}$	0.175(6)	0.020(6)	0.11(3)
<i>cis</i> - $[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.057(9)	0.141(6)	2.5(4)
<i>trans</i> - $[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.310(4)	0.001(3)	0.00(2)
<i>cis</i> - $[Cr(tn)_2(tnH)(OH_2)]^{4+}$	0.118(6)	0.053(5)	0.45(5)
<i>cis</i> - $[Cr(tn)_2(OH_2)_2]^{3+}$	0.066(12)	0.194(14)	2.9(5)
<i>trans</i> - $[Cr(tn)_2(OH_2)_2]^{3+}$	0.365(6)	0.000(10)	0.00(5)

a: $R = \phi(trans)/\phi(cis)$.

data it is clear that for two competitive reactions labelled a and b the reactions with the higher activation enthalpy is invariably more dominating photochemically than thermally, i.e. in qualitative terms:

$$\phi_a/\phi_b > k_a/k_b \text{ when } \Delta H_a^* > \Delta H_b^*.$$

This is further demonstrated in Fig. 2 and it obviously invalidates a classification of photochemical reactions as 'antithermal'.

Attempts to rationalize the photochemical reactivities of transition metal complexes have both been purely empirical and based on the use of ligand field models at various degrees of sophistication. The present data for *cis*-tetraaminediaquachromium(III) are particularly informative in relation to these rationalizations. The data in Table 1 show preferred water ligand substitution over substitution of coordinated ammonia, and this is neither in agreement with the leaving ligand being that of the highest ligand field strength on the axis of lowest average ligand field strength [ref. 20], nor with more elaborate ligand field calculations [ref. 21], since these treatments both predict that ammonia ligand photosubstitution should be the preferred reaction in disagreement with the experimental findings.

Detailed information on transition states for ligand substitution reactions is at present only indirectly available through various theoretical approaches. The general trends for substitution at an octahedral chromium(III) complex obtained through angular overlap model [Ref. 22] calculations can be summarized as follows:

- (i) Ligand field effects cannot discriminate between associative and dissociative transition states or intermediates. Energy variations caused by the ligand field are very similar for the two modes of activation. Strong discrimination is, however, seen between stereoretentive reactions, *cis*-attack or a square pyramidal transition state, and reactions accompanied by stereochemical change, *trans*-attack or a trigonal bipyramidal transition state.
- (ii) The ligand field gives a positive contribution to the enthalpy of activation for substitution reactions in the electronic ground state. The magnitude of the contributions is greater for greater ligand field strength of the involved ligands and is considerably smaller for stereoretentive reactions than for reactions accompanied by stereochemical change.

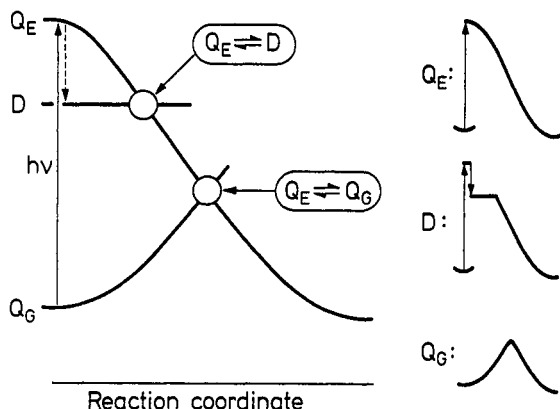


Fig. 3. Variation of ground state and lowest excited state energy levels along the reaction coordinate for the *trans*-attack mechanism in Fig. 1. Inserts show energy variations along the reaction coordinate by reactions of the quartet and doublet excited states and the quartet ground state, respectively.

- (iii) There is a negative contribution to enthalpies of activation for reactions of the lowest excited quartet state. The numerical value of this contribution is greater for ligands of high ligand field strength and is numerically smallest for stereoretentive reactions.
- (iv) There is only a minor contribution to enthalpies of activation for reactions of the lowest doublet state.

These general trends provide a fair rationale of the change in stereochemistry for chromium(III) substitution reactions: the ground state reactions are predominantly stereoretentive and the excited state reactions are accompanied by stereochemical change.

A simplified view of the general trends of the variations in ground state and lowest excited state energy levels for the *trans*-attack mechanism depicted in Fig. 1 is shown in Fig. 3. Intersystem crossing to an excited quartet state of comparable or lower energy than that of the excited doublet state may clearly be an attractive path for the reactive deactivation of this state. Interpreted in this way Fig. 3 is seen to combine the views of excited doublet state deactivation occurring either by back intersystem crossing to a reactive quartet state [ref. 23] or by surface crossing to a reactive ground state intermediate [ref. 24].

Ligand field model calculations suggest that influences from the ligands on the axis perpendicular to the 'reacting plane', cf. Fig. 1, are small. This is verified experimentally by a more extensive analysis of the product distributions in the ammineaquachromium(III) system [ref. 3]. This analysis shows unambiguously dominant relative reactivity contributions from 'planes' with a greater number of water ligands, and it is tempting to correlate this preference with the relative energies of the individual components of the first spin-allowed absorption band, which are rather accurately given by the average ligand field strength of the four ligands in the plane of the transitions.

REFERENCES

1. R.A. Plane and J.P. Hunt, *J. Amer. Chem. Soc.* 79 3343 (1957).
2. P.C. Ford and J.D. Petersen, *Inorg. Chem.* 14 1404 (1975).
3. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A40 637 (1986).
4. L. Mønsted and O. Mønsted, *Proc. XXVI I.C.C.C., Porto, Portugal*, B45 (1988).
5. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* To be submitted.
6. L. Mønsted and L.H. Skibsted, *Acta Chem. Scand.* A37 663 (1983).
7. L. Mønsted and L.H. Skibsted, *Acta Chem. Scand.* A40 590 (1986).
8. L. Mønsted, O. Mønsted and L.H. Skibsted, *Acta Chem. Scand.* 43 128 (1989).
9. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A38 679 (1984).
10. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* To be submitted.
11. A.D. Kirk, *Mol. Photochem.* 5 127 (1973).
12. H.F. Wastgestian and H.L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)* 57 282 (1968).
13. E. Zinato, P. Riccieri and A.W. Adamson, *J. Amer. Chem. Soc.* 96 375 (1974).
14. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A34 259 (1980).
15. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A36 365 (1982).
16. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A36 555 (1982).
17. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* 27 2121 (1973).
18. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A28 23 (1974).
19. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* A28 569 (1974).
20. A.W. Adamson, *J. Phys. Chem.* 71 798 (1967).
21. L.G. Vanquickenborne and A. Ceulemans, *Coord. Chem. Rev.* 48 157 (1983) and references therein.
22. C.E. Schäffer, *Struct. Bonding* 6 68 (1968).
23. N.J. Linck, S.J. Berens, D. Magde and R.G. Linck, *J. Phys. Chem.* 87 1733 (1983).
24. T. Ramasami, J.F. Endicott and G.R. Brubaker, *J. Phys. Chem.* 87 5057 (1983) and references therein.