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PHOTOISOMERIZATION OF RHODIUM(III) AMINE COMPLEXES. THE DEDUCTION OF AN EXCITED STATE REACTION MECHANISM

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CONTENTS

A. INTRODUCTION

Certain types of experimental results are required, or are at least highly desirable, for the interpretation of kinetic data in terms of intimate reaction mechanisms [1]. For the photochemical reactions of transition metal complexes, access to such information, which is necessary for mechanistic

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classifications, is greatly hampered by the difficulties often encountered in the proper characterization or even identification of the reactive species generated by the absorption of a light quantum [2 -4]. Structural information concerning the reactive and short-lived excited state metal complex must be inferred indirectly from photophysical and photochemical behaviour, and thermodynamic data for the actual reactant and possible reaction intermediates must be compiled by the same indirect methods. Excited state absorption spectra and measurement of emission are most valuable tools for the photophysical characterization, and time-resolved spectral data, following excitation, have revealed that photochemical reactions of transition metal complexes, although fast, are far from instantaneous, and that excited state kinetic analyses are meaningful [3], affording information which is relevant to mechanistic assignments.

(i) Excited state properties and photochemistry

Electronic transitions in transition metal complexes have energies which in general are very large compared with activation energies for most reactions of transition metal complexes. The absorption of a light quantum supplies energy in excess for a large selection of reactions from the initial Franck–Condon state generated by light absorption or even from the thermally relaxed excited states [5]. Yet photochemical reactions are selective; accordingly, photochemical behaviour represents an important source of information on excited state selection rules and excited state energetics, provided that macroscopic observations of photochemistry are successfully interpreted in terms of microscopic transition states along excited state reaction coordinates.

Series of compounds for which the chemical reactions activated or driven by light yield reaction products different from those obtained in thermally activated reactions are of particular interest in the elucidation of photochemical reaction mechanisms. A difference in stereoselectivity between ground state reactions and excited state reactions is often the first indication of a shift in reaction mechanism between reactions in the electronic ground state and the relevant excited state.

(ii) Photochromic rhodium(III) complexes

Aquaaminerhodium(III) and acidoaminerhodium(III) complexes represent such cases. They are octahedral complexes with a low spin d^6 electronic configuration, and thermal ligand substitution in these mixed-ligand complexes is slow in aqueous solution and proceeds largely without stereochemical rearrangements. For the same series of complexes, ligand substitution

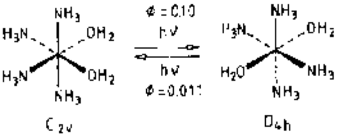


Fig. 1. Photochromism is a reversible light-induced chemical change, and for a doubly photochromic system, the reaction is light induced in both directions [6]. Isomeric amineaquarhodium(III) complexes are inorganic examples of doubly photochromic systems, among which the isomeric diaquatetraamminerhodium(III) ions have been studied in greatest detail [7–11]. Continuous 366 nm irradiation of an acidic solution at 25 ° C of either isomer of this latter complex thus results in the formation of a photostationary state which consists of 12% of the *cis* isomer and 88% of the *trans* isomer [7] (ϕ is the isomerization quantum yield (mol einstein^{-1})).

resulting from activation with light is efficient and shows extensive rearrangement concomitant with photosubstitution. These observations have provided a strong incentive to include an increasing number of isomeric pairs of rhodium(III) complexes in the study of their "antithermal" behaviour.

Moreover, isomeric aquaaminerhodium(III) complexes constitute rare inorganic examples of doubly photochromic systems which, besides being of intrinsic interest in terms of photochemical phenomena [6], have provided a means of estimating energy differences between excited state isomers (see Fig. 1).

The first part of the following treatment attempts to systematize the photochemical results obtained for these series of isomeric rhodium(III) complexes with the aim of illustrating how in a favourable case an excited state reaction mechanism can be deduced from patterns of photochemical reactivity and product distribution. Isotopic labelling experiments have been important in this context as they have shown that the photoisomerizations leading to the photostationary states for the doubly photochromic aquaaminerhodium(III) complexes are initiated by water ligand exchange. Subsequent analyses of reaction quantum yields and product distributions have pointed towards a dissociative reaction mechanism for the water exchange as well as for other photosubstitutions in the reactive excited state of these series of rhodium(III) complexes. Photoisomerization is thus initiated by ligand dissociation.

Photoreaction yields and photoisomerization yields for aquaaminerhodium(III) and acidoaminerhodium(III) complexes have been found to display well-defined pressure and temperature dependences. In the second part of this review, these effects are interpreted in terms of the deduced dissociative reaction mechanism for excited state ligand substitution. A transition state analysis seems justified also by the fact that the effect of either increasing pressure or increasing temperature on reaction yields, although small, is different and in general larger than the effect on photophysical processes such as radiative deactivation of the reactive excited states.

The reactive excited state rhodium(III) complexes generated by light absorption are good examples of what has been termed "electronic isomers" of their own ground states [3,12]. Although unstable, they can be treated as ordinary reactants which have chemistries different from those of their ground states. For rhodium(III) complexes, this applies in particular to isomerization reactions.

B. PHOTOISOMERIZATION OF RHODIUM(III) AMINES

The characterization of well-defined series of the very robust rhodium(III) coordination compounds goes back a century to Jørgensen [13,14]. These coordination compounds are sensitive to light, as noted by Delépine [15], and in solution, absorption of light results in rather efficient ligand exchange, i.e. in aqueous solution aquation results, with the formation of well-defined products or mixtures of products.

Chloropentaamminerhodium(III) was the first rhodium(III) complex to be subjected to more detailed photochemical investigations. Moggi [16] and later Kelly and Endicott [17] identified aquapentaamminerhodium(III) as the photoproduct when $[Rh(NH_3)_5Cl]^{2+}$ was exposed to light in acidic aqueous solution. Subsequently, it has been demonstrated that an ammonia ligand is photoaquated in a competitive reaction [18] and, more recently [19], that both isomers of aquachlorotetraamminerhodium(III) are formed photochemically (see Fig. 2).

Early investigations of the substitutional photochemistry of rhodium(III) complexes, such as those of Kutal and Adamson [20], seemed to show that,

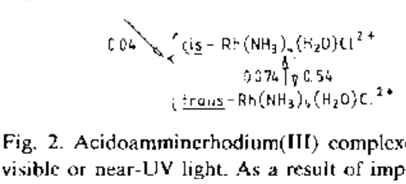


Fig. 2. Acidoamminerhodium(III) complexes yield well-defined products when exposed to visible or near-UV light. As a result of improved synthetic procedures and the utilization of new numerical methods, a more detailed knowledge of photoproduct distributions has gradually been obtained, as illustrated by the developments in the understanding of the photochemistry of $[Rh(NH_3)_5Cl]^{2+}$ [16–19]. The numerals on reaction arrows are quantum yields (mol einstein^{-1}) resulting from 366 nm excitation.

like the thermal substitutions, photosubstitutions in rhodium(III) amines are stereoretentive reactions. Muir and Huang [21] found, however, that the ethylenediamine complex *cis*-$[Rh(en)_2Cl_2]^+$ isomerized partly to *trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$ as a result of photoaquation of one of the chloro ligands.

As discussed in this review, it has now become clear that most photochemical ligand substitutions in rhodium(III) amine complexes result in complete or partial isomerization. The complex ion *cis*-$[Rh(NH_3)_4Cl_2]^+$, synthesized by Hancock in 1973 [22] and studied photochemically by Strauss and Ford [23], proved to be important in this connection. The observation of what was believed to be a complete photoisomerization concomitant with photoaquation to *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ and similar observations by Petersen and Jakse [24,25] on the photochemistry of bis(ethylenediamine) rhodium(III) complexes stimulated Vanquickenborne and Ceulemans [26] to undertake theoretical modelling of this type of rearrangement. Subsequently, these and other theoretical studies [27] have inspired further experimental work. In general, the reaction quantum yields have been found to be independent of excitation wavelength [12,19].

(i) Thermal and photochemical water exchange

Few rhodium(III) complexes allow a direct comparison between thermal and photochemical reactivity. However, the series of aquaaminerhodium(III) complexes given in Table 1 is of particular value in this connection. At the

TABLE 1

Acidity of coordinated water and water exchange in amineaquarhodium(III) complexes in acidic solution at 25.0 °C [a]

Complex	pK_a	k (s^{-1})	ϕ^* (mol einstein^{-1})	Ref.
$[Rh(NH_3)_5H_2O]^{3+}$	6.870	8.4×10^{-6}	0.43	29–31
cis-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	6.828	3.2×10^{-5}	0.44	32
trans-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	6.440	7.5×10^{-6}	0.33	32
cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	6.391 [b]	1.50×10^{-5} [c]	0.143 [c]	7, 8, 28
trans-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	4.860 [b]	1.42×10^{-8} [c]	0.025 [c]	7, 8, 28
cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	7.84	2.38×10^{-5}	0.66	28, 29, 33
trans-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	6.75	3.38×10^{-5}	0.39	28, 29, 33

[a] 1.0 M $(H,Na)ClO_4$, except for $[Rh(NH_3)_5H_2O]^{3+}$, for which complex, reaction media with ionic strength of 0.24 were employed for the water exchange studies. [b] $pK_{a,1}$, for which $\Delta H^0_{cis} = 45(2)$ kJ mol^{-1}, $\Delta S^0_{cis} = 28(5)$ J mol^{-1} K^{-1}; and $\Delta H^0_{trans} = 34(1)$ kJ mol^{-1}, $\Delta S^0_{trans} = 21(4)$ J mol^{-1} K^{-1}. [c] Based on complex concentration.

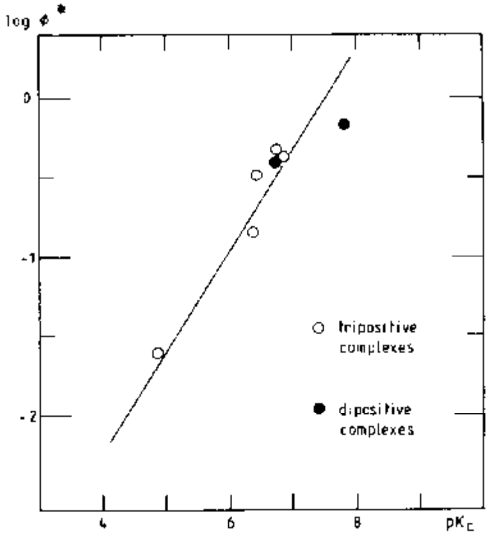


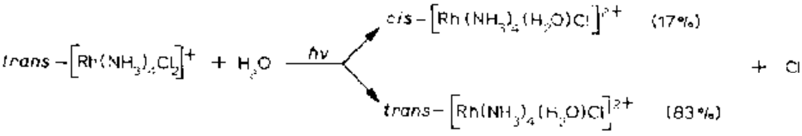
Fig. 3. Linear relationship between ground state pK_a of water ligand and log ϕ^*, where ϕ^* is the water exchange yield (mol einstein^{-1}). Data from Table 1.

present time, the series includes seven members of pentaamine and tetraammine complexes for which rate constants for the exchange of coordinated water with solvent water and quantum yields for the same process under identical conditions have been determined using ^{18}O isotopic labelling [7,28,30–33].

It is notable that for these complexes the ranking according to decreasing acidity (*trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ > *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ > *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ > *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ > *cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ ≈ $[Rh(NH_3)_5H_2O]^{3+}$ > *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$) finds an exact parallel in the increasing efficiency with which light induces water exchange, as shown in Fig. 3. For a given series of metal complexes, the acidity of coordinated water increases with the strength and polarization of the metal–oxygen bond, which is the same bond as that broken during water exchange. The noted correlation between acidity and photochemical water exchange efficiency is thus expected for an exchange mechanism in which bond breaking is more important than bond formation. A similar correlation is not found between the water ligand acidity and the thermal water exchange rate, and for this latter process, bond formation seems to be of greater importance during the activation.

(ii) Stereochemical consequences of photosubstitution

Thermal ligand substitutions in rhodium(III) complexes are largely stereoretentive processes, and the observation of isomerization concomitant with photochemical ligand substitution indicates, even more strongly than the noted correlation between acidity and water exchange yields, important mechanistic differences between thermal and photochemical ligand substitution reactions [10,11,34–39]. The relationship between substitution and isomerization is not simple, and the ratio between substitution and isomerization depends on the nature of the reacting complex, for example, see ref. 19:



A common feature of these photoreactions is, however, that substitution yields are larger than isomerization yields. Despite this fact, a model entailing a one-to-one ratio between isomerization yields and substitution yields for those rhodium(III) complexes which do isomerize has served as a useful working hypothesis [10,23–27,34–37]. This has helped to design the series of experiments which have clarified the interaction between substitution and isomerization. Deuterium isotope effects and product distributions have played key roles in this connection.

(a) Deuterium isotope effect on photoisomerization

Perdeuteration of ammine ligands in complexes such as $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_6]^{3+}$ leads to significant enhancements [18,40,41] of the photosubstitution yields in aqueous solution at ambient temperature, for example,

$$[Rh(NH_3)_6]^{3+} + H_3O^+ \rightarrow [Rh(NH_3)_5H_2O]^{3+} + NH_4^+ \qquad (1)$$
$$\phi = 0.080 \text{ mol einstein}^{-1}$$

$$[Rh(ND_3)_6]^{3+} + D_3O^+ \rightarrow [Rh(ND_3)_5D_2O]^{3+} + ND_4^+ \qquad (2)$$
$$\phi = 0.150 \text{ mol einstein}^{-1}$$

However, deuteration has a more varied effect on photoisomerization.

The vast difference in the proton exchange rate for coordinated ammonia and coordinated water in rhodium(III) complexes in acidic solution has permitted in situ creation of the four D/H isotopomers of each of the two geometric isomers of $[Rh(NH_3)_4(H_2O)_2]^{3+}$ and $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ [9]

TABLE 2

Deuterium isotope effect on the photoisomerization of amineaquarhodium(III) complexes in acidic perchlorate solution at 25 °C

Complex	Solvent	ϕ_{tc} [a] (mol einstein^{-1})	ϕ_{ct} [a] (mol einstein^{-1})	$E_a(\phi_{tc})$ [b] (kJ mol^{-1})	$E_a(\phi_{ct})$ [b] (kJ mol^{-1})	ΔH^0_{app} [c] (kJ mol^{-1})	ΔS^0_{app} [c] (J mol^{-1} K^{-1})	Ref.
$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	H_2O	0.276(12)	0.113(6)					32
$[Rh(en)_2(NH_3)(D_2O)]^{3+}$	D_2O	0.28(2)	0.12(2)					42
$[Rh(NH_3)_4(H_2O)_2]^{3+}$	H_2O	0.011(1)	0.102(4)	37(3)	4(3)	−33(4)	−90(15)	7, 42
$[Rh(NH_3)_4(D_2O)_2]^{3+}$	D_2O	0.016(2)	0.22(1)	30(3)	1(3)	−30(4)	−80(15)	9, 42
$[Rh(ND_3)_4(H_2O)_2]^{3+}$	H_2O	0.016(2)	0.123(6)	16(3)	2(3)	−14(4)	−28(15)	9, 42
$[Rh(ND_3)_4(D_2O)_2]^{3+}$	D_2O	0.018(3)	0.23(1)	20(3)	5(3)	−14(4)	−24(15)	9, 42
$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	H_2O	0.064(3)	0.52(1)					33
$[Rh(NH_3)_4(D_2O)Cl]^{2+}$	D_2O	0.054(5)	0.54(2)					9
$[Rh(ND_3)_4(H_2O)Cl]^{2+}$	H_2O	0.057(5)	0.60(2)					9
$[Rh(ND_3)_4(D_2O)Cl]^{2+}$	D_2O	0.066(4)	0.64(1)					9
$[Rh(NH_3)_4(H_2O)Br]^{2+}$	H_2O	0.018(1)	0.457(11)					43
$[Rh(NH_3)_4(D_2O)Br]^{2+}$	D_2O	0.034(2)	0.417(3)					43

[a] Photoisomerization yield. [b] Apparent activation energy calculated from temperature dependence of photoisomerization yields (15 – 44 °C). [c] ΔH^0_{app} and ΔS^0_{app} are the apparent reaction enthalpy and entropy respectively for *cis*-to-*trans* photoisomerization calculated from the temperature dependence (15–44 °C) of quantum yield ratios according to $\ln(\phi_{ct}/\phi_{tc}) = [(-\Delta H^0_{app}/T) + \Delta S^0_{app}]/R$.

and has allowed a direct comparison of the effect of selective deuteration of ammonia and water ligands on photoisomerization (Table 2). Photoisomerization quantum yields are rather insensitive to these deuterations, with the notable exception of the *cis*-to-*trans* isomerization yields for $[\mathrm{Rh(NH_3)_4(H_2O)_2}]^{3+}$ and $[\mathrm{Rh(ND_3)_4(H_2O)_2}]^{3+}$, which were both increased by a factor of ca. 2 by deuteration of water in either compound. For the photoisomerizations

$$cis\text{-}[\mathrm{Rh(NH_3)_4(H_2O)X}]^{z+} \underset{\Phi_{tc}}{\overset{\Phi_{ct}}{\rightleftarrows}} trans\text{-}[\mathrm{Rh(NH_3)_4(H_2O)X}]^{z+} \tag{3}$$

these observations, considered together with results from phosphorescence lifetime measurements, have established that deuterium isotope effects on photochemical processes in this class of compounds are unimolecular properties of the complex rather than properties of the solvent [18]. This led to the conclusion that the excited state rearrangement is competing with deactivation dominated by high frequency O–H promoting modes. For X = Cl, Br, the deactivation is almost undisturbed by deuteration, while for X = H_2O, deactivation through O–H modes is replaced with lower frequency O–D modes, rendering rearrangement more competitive. However, this conclusion provides an important link between water exchange and isomerization. For $[\mathrm{Rh(NH_3)_4(H_2O)Cl}]^{2+}$ and its isotopomers, the competitive high frequency O–H modes are lost prior to excited state rearrangement of a pentacoordinate intermediate. Water ligand dissociation is thus a distinct step prior to rearrangement.

A sensitive test of this photoisomerization mechanism for amineaquarhodium(III) complexes (which requires the presence of more than one water ligand in the coordination sphere before deuteration significantly affects the photoisomerization efficiencies) is at hand through the investigation of *cis*- and *trans*-$[\mathrm{Rh(en)_2(NH_3)(H_2O)}]^{3+}$ and comparison with the likewise tripositive complexes *cis*- and *trans*-$[\mathrm{Rh(NH_3)_4(H_2O)_2}]^{3+}$. No deuterium isotope effect was found for the pentaamines ($[\mathrm{Rh(en)_2(NH_3)(H_2O)}]^{3+}$ vs. $[\mathrm{Rh(en)_2(NH_3)(D_2O)}]^{3+}$ in Table 2), which confirms that a water ligand is lost prior to rearrangement also in these tripositive complexes.

(b) Stereomobile and stereoretentive photosubstitution

The water exchange yield for each aquaaminerhodium(III) complex has invariably been found to be larger than the isomerization yield (see Tables 1 and 2), and stereomobile and stereoretentive water exchange can be treated kinetically as competitive processes. Moreover, the selective deuterium isotope effect indicates that competition between the formation of the two products follows an initial water dissociation step. For isomeric complexes with two water ligands, this leads to reaction schemes for the interrelated

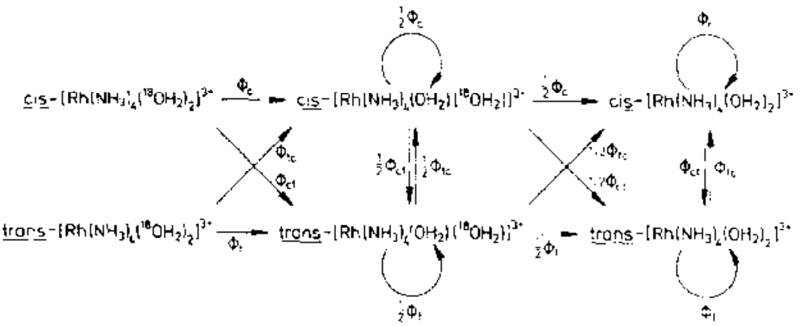


Fig. 4. Stereoretentive and stereomobile photochemical water exchange are competitive processes, and the total water exchange yields are the sum of the isomerization yield and the yield for stereoretentive water exchange: $\phi^*_{cis} = \phi_c + \phi_{ct}$ and $\phi^*_{trans} = \phi_t + \phi_{tc}$ (see Table 3). (Figure reproduced with the permission of Acta Chemica Scandinavica [7].)

water-exchange and isomerization processes similar to that shown in Fig. 4, which has been used for the interpretation of the aqueous solution photochemistry of *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ [7]. In Table 3, the quantum yields for the water exchange in the three *cis–trans* pairs included in Table 1 have accordingly been divided into quantum yields for competitive stereomobile and stereoretentive processes:

$$\begin{aligned} \phi^*_{cis} &= \phi_{ct} + \phi_c \\ \phi^*_{trans} &= \phi_{tc} + \phi_t \end{aligned} \tag{4}$$

They are further compared with the quantum yields for the likewise competitive stereomobile and stereoretentive chloro-ligand photoaquations of the analogous chloro complexes.

In acidic aqueous solution, *trans*-$[Rh(NH_3)_4Cl_2]^+$ undergoes photoaquation, and *cis*-$[Rh(NH_3)_4Cl_2]^+$ reacts in a similar fashion, also producing a *trans–cis* mixture of $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ [19,33]. However, the ratio between the quantum yield for the formation of the *trans* product and that for the formation of the *cis* product for the two dichloro complexes is identical (R_{tc} in Table 3). Moreover, the latter *trans*-to-*cis* ratio is identical with the *trans*-to-*cis* product ratio found for the water exchange of the isomeric $[Rh(NH_3)_4(H_2O)Cl]^{2+}$. The common *trans*-to-*cis* ratio, independent of both the nature of the leaving ligand (H_2O or Cl^-) and the reactant stereochemistry, provides further evidence for a photoisomerization mechanism, with ligand dissociation and rearrangement as distinct steps in the reactive excited state. This model [34,44] has been elaborated in Fig. 5 for the isomeric $[Rh(NH_3)_4Cl_2]^+$ and $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ complexes.

TABLE 3

Ligand photosubstitution quantum yields and product stereochemistry for pentaaminerhodium(III) and tetraaminerhodium(III) complexes in aqueous 0.50 M $HClO_4$ + 0.50 M $NaClO_4$ at 25°C [a]

Reactant	Product	ϕ [b] (mol einstein^{-1})	R_{tc} [c]	Ref.
cis-$[Rh(en)_2(NH_3)Cl]^{2+}$	*cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	0.071(2) 0.0042(10)	0.060(16)	32
trans-$[Rh(en)_2(NH_3)Cl]^{2+}$	*cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	0.075(3) 0.000(4)	0.00(5)	32
cis-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ [d]	*cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	0.33(2) 0.113(6)	0.35(3)	32
trans-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ [d]	*cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$	0.276(12) 0.05(2)	0.18(8)	32
cis-$[Rh(NH_3)_4Cl_2]^{+}$	*cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.063(7) 0.328(9)	5.3(5)	19, 33
trans-$[Rh(NH_3)_4Cl_2]^{+}$	*cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.025(9) 0.122(9)	5(2)	19, 33
cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ [d]	*cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.12(3) 0.543(14)	4.5(6)	33
trans-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ [d]	*cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.074(2) 0.33(4)	4.5(6)	33
cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ [d]	*cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	0.041(4) 0.102(4)	2.5(4)	7
trans-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ [d]	*cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	0.0111(7) 0.0143(11)	1.3(2)	7

[a] Excitation of lowest energy multiplicity-allowed ligand field transition. [b] Quantum yields have been found to be independent of excitation wavelength in all cases (see the relevant references). [c] R_{tc} is the ratio between the quantum yield for the formation of *trans* products and that for the formation of *cis* products. [d] Water exchange, as studied by ^{18}O labelling.

A key feature of this model is that kinetically the photoisomerizations can be treated as a series of consecutive processes and reactions, some of which are expected to display distinct temperature and pressure dependences. (i) For either the *cis* or *trans* hexacoordinate complex ($[Rh(NH_3)_4Cl_2]^+$ or $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ in Fig. 5), initial absorption of a photon ($h\nu$) produces an electronically excited molecule. (ii) From this reactive state, ligand dissociation (H_2O or Cl^-) produces a pentacoordinate square-pyramidal species ($[Rh(NH_3)_4Cl]^{2+}$) of either basal or apical coordination geometry.

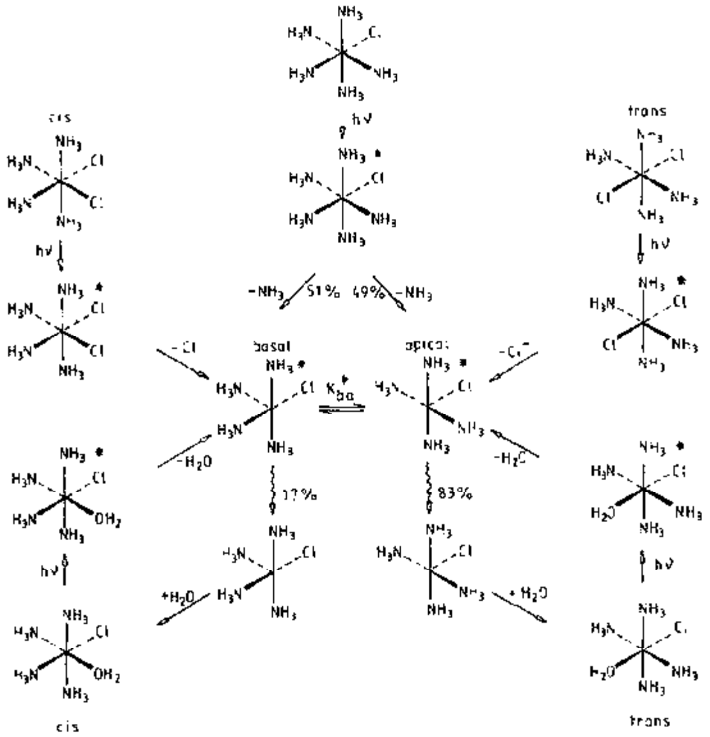


Fig. 5. The limiting photosubstitution mechanism for rhodium(III) amine complexes. Photochemical water exchange in *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ yields the same *trans*-to-*cis* product ratio as chloride photoaquation in *cis*- and *trans*-$[Rh(NH_3)_4Cl_2]^+$. Ammine photoaquation in $[Rh(NH_3)_5Cl]^{2+}$ to produce $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ occurs to an equal extent from the axial and equatorial positions.

(iii) Two alternatives are available to these excited-state reaction intermediates: deactivation to the ground state or basal–apical rearrangement. (iv) The competitive deactivation of either isomer produces ground state intermediates as precursors for the photoproduct, in effect determining the *trans*-to-*cis* photoproduct ratio.

Included in Fig. 5 is the ammonia photoaquation reaction of $[Rh(NH_3)_5Cl]^{2+}$, the stereochemistry of which has been studied using ^{15}N labelling [45] and which yields the same $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ photoproduct as the tetraammine complexes shown in Fig. 5. The chloride photoaquation is the major photoreaction of $[Rh(NH_3)_5Cl]^{2+}$ (see Fig. 2); however, the isotopic labelling has shown that two competitive processes of almost equal importance account for the minor ammonia photoaquation in this pentaammine complex (Table 4).

TABLE 4

Stereochemical origin of photoaquated ammonia in pentaamminerhodium(III) complexes, $[Rh(NH_3)_5X]^{2+}$ [a]

X^-	ν_{max} [b] (μm^{-1})	Lowest energy triplet	$\phi(X^-)$ [c] (mol einstein^{-1})	$\phi(NH_3)$ [c] (mol einstein^{-1})	ϕ_{eq}/ϕ_{ax} [d]	Ref.
Br	2.79	^3E	$\leqslant 0.02$	0.18	0.15	43
Cl	2.89	^3E	0.15	0.04	1.0	45
CN^-	3.48	^3A	— [e]	0.086	19	46

[a] Determined by ^{15}N labelling in acidic aqueous solution at ambient temperature. [b] Lowest energy (singlet) ligand field absorption band. [c] Photoaquation quantum yields. [d] Ratio between released NH_3 from equatorial and axial positions. [e] Cyanide photoaquation not detected.

Three different ratios are to be distinguished in a discussion of the stereochemical consequences of photosubstitution in pentaammine and tetraammine complexes. For the *trans–cis* photoisomerizations, the final *trans*-to-*cis* product ratio depends on the relative absorptivity at the wavelength of irradiation and the isomerization yields. For monochromatic light, it is given by [6,10]

$$c^{\infty}_{trans}/c^{\infty}_{cis} = (\phi_{ct}/\phi_{tc})(\epsilon^{irr}_{cis}/\epsilon^{irr}_{trans}) \qquad (5)$$

This ratio, which is conveniently determined as illustrated in Fig. 6 for $[Rh(NH_3)_4(H_2O)_2]^{3+}$, is in general different from the ratio R_{tc} given in Table 3, the latter ratio being defined as $R_{tc} = \phi_{ct}/\phi_c$ for *cis* reactants and as $R_{tc} = \phi_t/\phi_{tc}$ for *trans* reactants [19]. Furthermore, for the pentaammine complexes, both of these ratios are, in general, different from ϕ_{eq}/ϕ_{ax}, the

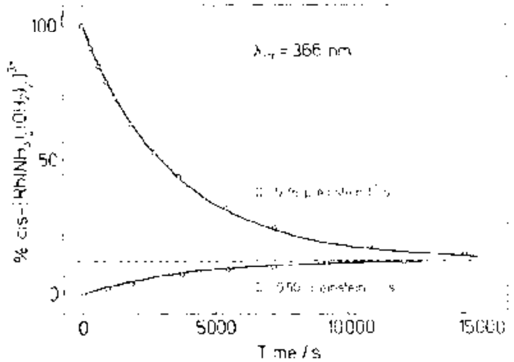


Fig. 6. Kinetics for the formation of a photostationary state for the doubly photochromic complexes *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ (see Fig. 1). (Figure reproduced with the permission of Acta Chemica Scandinavica [7].)

TABLE 5

ϕ_{ct}/ϕ_{tc} [a] isomerization quantum yield ratios for photochromic aquatetraaminerhodium(III) complexes, $[RhA_4(H_2O)X]^{z+}$, in aqueous solution at 25 °C

Complex	Tetraammine [b]	Ref.	Bis(ethylenediamine) [c]	Ref.	Bis(1,3-propanediamine) [d]	Ref.
$[RhA_4(H_2O)_2]^{3+}$	9.3	7	>140	48	2.9	49
$[RhA_4(NH_3)(H_2O)]^{3+}$			0.41	32		
$[RhA_4(H_2O)(OH)]^{2+}$	< 0.01	10	0.083	48	0.033	49
$[RhA_4(H_2O)Cl]^{2+}$	8.1	19	55	39	9.1	38
$[RhA_4(H_2O)Br]^{2+}$	25	43	90	39	22	38
$[RhA_4(H_2O)(CN)]^{2+}$	< 0.02	47				

[a] See Fig. 1 and eqn. (5). [b] $A_4 = (NH_3)_4$. [c] $A_4 = (en)_2$. [d] $A_4 = (tn)_2$.

ratio between equatorial and axial ammonia photolabilization. While the composition of photostationary states has been determined for several isomeric pairs and, according to eqn. (5), has provided the ratio between the isomerization yields, ϕ_{ct}/ϕ_{tc} (Table 5), the ratios R_{tc} and ϕ_{eq}/ϕ_{ax} have been determined only for the few complexes listed in Tables 3 and 4. Compared with ϕ_{ct}/ϕ_{tc}, the last two ratios are, however, more valuable for mechanistic assignments since they are directly related to excited state properties. The isotope labelling work required to obtain this information for other isomeric pairs should be encouraged.

(c) The dissociative limit for photosubstitution

The common product ratio for the isomeric $[Rh(NH_3)_4Cl_2]^+$ and $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ (Fig. 5) has provided circumstantial evidence for dissociative ligand substitution in the photochemistry of rhodium(III) amines. For water exchange in *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ and *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$, the intermediates generated should deactivate according to this model, also forming $[Rh(NH_3)_4(H_2O)_2]^{3+}$ in a common *trans*-to-*cis* ratio. Unfortunately, R_{tc} for the isomeric diaqua complexes is badly defined (Table 3), mainly owing to the low efficiencies with which these complexes exchange water. However, the results are not in disagreement with the model which postulates the formation of common excited state intermediates of reduced coordination number, i.e. $[Rh(NH_3)_4(H_2O)]^{3+}$. For the pentaamine complexes $[Rh(en)_2(NH_3)Cl]^{2+}$ and $[Rh(en)_2(NH_3)(H_2O)]^{3+}$, the stereochemical results show a puzzling difference between the chloro and the aqua complexes, especially when considered together with the lack of deuterium isotope effect for the latter complexes.

Chloride photoaquation in the isomeric $[Rh(en)_2(NH_3)Cl]^{2+}$ yields almost exclusively the *cis* isomer (Table 3) and the R_{tc} ratio is within experimental uncertainty the same for the two reactants. R_{tc} for the chloro photoaquation is, however, different from R_{tc} for the water exchange in $[Rh(en)_2(NH_3)(H_2O)]^{3+}$, and it has been suggested that this difference indicates a gradual change to an associative mechanism [32]. The observation of some *trans* products in the photolysis of *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ would argue for such an associative contribution, although the noted substantial fraction of *trans* product in the photolysis of *cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ is disturbing, since an associative mechanism is expected to favour stereoretention as it does in the thermal reactions of rhodium(III).

In conclusion, the photosubstitutions in rhodium(III) amine complexes are best understood on the basis of a dissociative mechanism. For the tripositive complexes $[Rh(NH_3)_4(H_2O)_2]^{3+}$ and $[Rh(en)_2(NH_3)(H_2O)]^{3+}$, the behaviour might be complicated by stronger ion pairing and the formation of perchlorate complexes as transient photoproducts in the 1.0 M perchlorate medium used in these investigations, since the observations on deuterium isotope effects also for these species are best accommodated within the limiting dissociative model.

C. ENERGETICS AND DYNAMICS OF EXCITED STATE REARRANGEMENT

The limiting dissociative reaction mechanism for photosubstitution in rhodium(III) amine complexes, deduced from observations on photostereochemistry, gains strong support from the bonding properties evaluated spectroscopically for the ligand field excited states [26,27,50]. When the available kinetic and spectroscopic information is combined, a consistent model which accounts for both the energetic and dynamic aspects of the photoisomerizations seems to emerge [11,44,51,52]. The key excited state processes including the initial light absorption, to be discussed separately, are shown in Fig. 7. Some of these have been probed as functions of systemic parameters, providing an increasing understanding of the chemical properties of the short-lived electronically excited states.

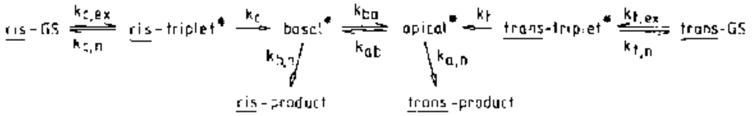


Fig. 7. Kinetic model of *cis*-to-*trans* and *trans*-to-*cis* photoisomerization of rhodium(III) amine complexes in solution (see Fig. 5). The ground state molecules (GS) form under conditions of continuous illumination the lowest energy triplet excited state in a steady state concentration. The latter triplet states are reactive states which, as a result of ligand dissociation, form triplet intermediates of reduced coordination number, capable of apical–basal rearrangement competitive with deactivation.

(i) *Light absorption and emission*

The multiplicity-allowed ligand field transitions of the low spin d^6 rhodium(III) centers ($^1T_1 \leftarrow {}^1A_1$ and $^1T_2 \leftarrow {}^1A_1$, assuming octahedral symmetry) are, at least for complexes with aliphatic amines, energetically well separated from other electronic transitions, and the absorption of visible or near-UV light produces metal-centered singlet excited states. Early investigations have shown that electronic excitation of haloamine complexes leads to weak emission from the lowest energy ligand field state ($^3T_1 \rightarrow {}^1A_1$) in the microsecond range at 77 K and formally characterized as phosphorescence [53,54]. At ambient temperature, the emission decay is bi-exponential and an almost temperature-independent fast fluorescence component in the picosecond region has been traced to vibronically unrelaxed singlet states [55]. The total quantum yields for emission have been estimated as being in the range $10^{-7} < \phi_r < 10^{-6}$, and the bromo complexes are generally brighter emitters than the analogous chloro compounds [11,56]. The triplet state considered responsible for the slower component of the emission in the nanosecond region at ambient temperature has been concluded to be the same as the photoreactive state [18,58–60]. For the photoisomerization, this provides us with two important tools for the characterization of the reactive state of each isomer. These are the Stokes shift determined from low temperature

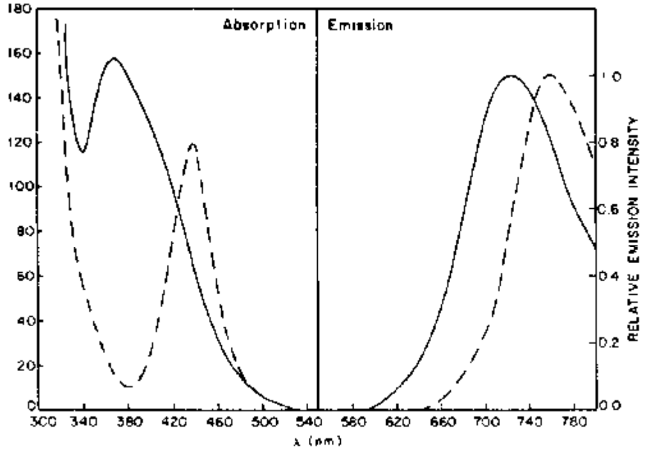


Fig. 8. Absorption spectra of the lower energy ligand field band (298 K, aqueous solution) and the normalized emission spectra (77 K, KBr pellets) of the 1,3-propanediamine compounds *cis*-$[Rh(tn)_2Br_2]ClO_4$ (solid line) and *trans*-$[Rh(tn)_2Br_2]ClO_4$ (broken line). The Stokes shift is larger for the *cis* isomers than for the *trans* isomers of rhodium(III) amine complexes. (Figure reproduced with the permission of Acta Chemica Scandinavica [61].)

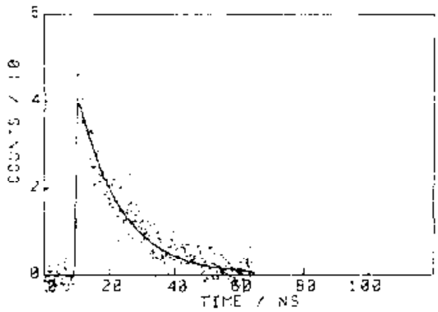


Fig. 9. Phosphorescence decay for *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$ in dilute aqueous solution at 25 °C as determined by time-correlated single-photon detection. The solid line is the best fit for an exponential decay corresponding to a lifetime of 13.0 ns. The analogous *cis* complex is significantly shorter lived with a lifetime of 2.1 ns. (Figure reproduced with the permission of Acta Chemica Scandinavica [57].)

emission, as shown in Fig. 8 for the 1,3-propanediamine (tn) complexes *cis*- and *trans*-$[Rh(tn)_2Br_2]^+$, and the lifetime of the reactive triplet states determined from emission decay in aqueous solution under conditions similar to those used for the photochemical investigations, as shown in Fig. 9 for *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$.

From investigations using sensitization techniques and from the lack of wavelength dependence of photoreaction yields, it has further been concluded that haloaminerhodium(III) complexes form the reactive, lowest energy triplet states from the initially populated singlet states with intersystem crossing (isc) yields of approximately unity [18,59,60]. With $\phi_{isc} \approx 1$, and on the additional assumption of intersystem crossing to the reactive triplet made fast by spin orbit coupling relative to the deactivation of the latter state to the ground state, the steady state approximation introduced by Bergkamp et al. [18,58] allows the transformation of quantum yields (ϕ_i) and phosphorescence lifetimes (τ) into individual rate constants (k_i) for radiative deactivation (k_r), non-radiative deactivation (k_n) and excited state ligand dissociation (k_x):

$$\phi_i = \frac{k_i}{k_x + k_r + k_n} = k_i\tau \tag{6}$$

The phosphorescence efficiency is small ($\phi_r < 10^{-6}$) and consequently $k_r \ll k_x + k_n$, allowing the evaluation of k_x and k_n from substitution quantum yields and lifetimes measured under identical conditions [18,58]:

$$k_x = \phi_x\tau^{-1} \tag{7}$$

$$k_n = \tau^{-1} - k_x \tag{8}$$

TABLE 6

Luminescence lifetimes and rate constants for halide dissociation and non-radiative deactivation from lowest energy ligand field excited state for isomeric chloropentaaminerhodium(III), aquachlorotetraamminerhodium(III), dichlorotetraaminerhodium(III) and dibromotetraaminerhodium(III) complexes in dilute aqueous solution at 25 °C

Complex	Tetraammine [11,18,56] $A_4 = (NH_3)_4$			Bis(ethylenediamine) [39,57] $A_4 = (en)_2$			Bis(1,3-propanediamine) [38] $A_4 = (tn)_2$		
	τ (ns)	k_x (s^{-1})	k_n (s^{-1})	τ (ns)	k_x (s^{-1})	k_n (s^{-1})	τ (ns)	k_x (s^{-1})	k_n (s^{-1})
trans-$[RhA_4(NH_3)Cl]^{2+}$	14.2	1.6×10^7	5.7×10^7	13.0	5.8×10^6	6.7×10^7			
cis-$[RhA_4(NH_3)Cl]^{2+}$				2.1	3.5×10^7	4.7×10^8			
trans-$[RhA_4(H_2O)Cl]^{2+}$	2.2	1.8×10^{8} [a]	2.7×10^8						
cis-$[RhA_4(H_2O)Cl]^{2+}$	2.4	2.8×10^{8} [a]	1.4×10^8						
trans-$[RhA_4Cl_2]^+$	1.8	8×10^7	5×10^8	2.2	2.5×10^7	4.3×10^8	1.4	5.7×10^7	6.6×10^8
cis-$[RhA_4Cl_2]^+$	1.3	3×10^8	5×10^8	2.5	1.9×10^8	2.1×10^8	0.9	6.2×10^8	4.9×10^8
trans-$[RhA_4Br_2]^+$	1.5	6.3×10^7	6×10^8	2.2	2.1×10^{7} [b]	4.3×10^{8} [c]	0.67	8.2×10^7	1.4×10^9
cis-$[RhA_4Br_2]^+$	1.0	2.4×10^8	7×10^8	2.5	1.4×10^8	2.6×10^8	0.30	2.1×10^9	1.2×10^9

[a] Aqua ligand dissociation. [b] $\Delta H_x^{\neq} = 24$ kJ mol^{-1}, $\Delta S_x^{\neq} = -24$ J mol^{-1} K^{-1} [62]. [c] $\Delta H_n^{\neq} = 8.6$ kJ mol^{-1}, $\Delta S_n^{\neq} = -51$ J mol^{-1} K^{-1} [62].

The first-order rate constant for the decay of the reactive triplet state has been evaluated for several series of complexes, and the examples shown in Table 6 are available for a discussion of isomerization.

(ii) Ligand dissociation

Photosubstitution quantum yields have been found to increase with increasing temperature despite the fact that increasing temperature reduces the emission lifetimes [18,62]. In a few favourable instances (e.g. *trans*-$[Rh(en)_2Br_2]^+$, a complex which has a relatively strong emission and a small substitution yield [62]) quantitative data on the temperature dependence of the deduced triplet-state rate constants have permitted activation parameters to be calculated according to transition state theory (see footnotes to Table 6). The photosubstitution process and the non-radiative decay are characterized by distinctly different activation parameters, which indicates that the two processes are passing through different transition states out of the reactive triplet. For *trans*-$[Rh(en)_2Br_2]^+$, and also for $[Rh(NH_3)_5Br]^{2+}$, the enthalpy of activation for the non-radiative decay is smaller than the enthalpy of activation for the ligand dissociation. It has been concluded that the excited electronic states with ambient temperature lifetimes even shorter than 1 ns represent true metastable species with thermally activated chemistries which are notably different from those of the ground states of the same molecules. The different values for the energy barriers for the non-radiative decay and the ligand dissociation distinguish the model given in Fig. 7 from an alternative model including a single barrier crossing from the triplet into a "hot ground state" of fleeting existence and a subsequent branching decay either to the photosubstitution product or to the reactant ground state.

(iii) The reactive triplet state

Two possibilities are available for the reactive triplet, i.e. ligand dissociation or non-radiative decay. A negative entropy of activation for *trans*-$[Rh(en)_2Br_2]^+$ indicates that increased ordering is required to form the transition state of each of these processes, and especially for the non-radiative decay, a substantial rearrangement of, most likely, the surrounding solvent shell is required. However, as seen from Table 6, the ligand dissociation requires a more substantial enthalpy input than the dissipation of excitation energy to the medium by non-radiative processes. The results of ^{15}N-labelling studies of a series of pentaamine complexes, together with rate constants for the reactive triplet of the *cis* and *trans* isomers of three different series of tetraamine complexes, are available for further characterization of the triplet reactivities.

(a) Pentaamminerhodium(III)

A σ antibonding e_g orbital is populated on promotion of an electron from the t_{2g}^6 ground state, and when symmetry is lowered from pure O_h as in $[Rh(NH_3)_6]^{3+}$ to C_{2v} as in pentaammine complexes, the emitting ^3T triplet splits into ^3E and ^3A levels. For pentaammine complexes in which the heteroligand is of stronger field than the ammine ligand, the ^3E state has the lower energy corresponding to the one-electron configuration $(d_{xz}, d_{yz})^4(d_{xy})^1(d_{x^2-y^2})^1(d_{z^2})^0$, and the antibonding e_g orbital is concentrated in the equatorial plane. In contrast, for pentaammines with a weak-field heteroligand, the excitation is concentrated along the tetragonal axis. For pentaamminerhodium(III) complexes, the importance of ammonia photoaquation relative to photoaquation of the heteroligand depends on the nature of the latter ligand (see Fig. 2). Moreover, the stereochemical origin of the photoaquated ammonia in $[Rh(NH_3)_5CN]^{2+}$, $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Br]^{2+}$ correlates with the antibonding electron distribution in the lowest energy triplet state, as seen from the data in Table 4, which have been obtained using ^{15}N labelling [43,45,46]. For $[Rh(NH_3)_5Cl]^{2+}$, in which the difference in energy between ^3A and ^3E is less significant, equatorial and axial ammonia are labilized in a temperature-independent ratio close to unity, as shown in Fig. 5 [45].

(b) Isomeric tetraaminerhodium(III)

The *cis* dihalotetraammine complexes have partial molar volumes very similar to those of the corresponding pentaammines, whereas the *trans* dihalotetraammine complexes are ca. 18 cm^3 mol^{-1} larger [63]. This decrease in volume of the less symmetrical *cis* isomers has been ascribed to a stronger specific solvation. For each isomeric pair investigated [11,38,39,61], the *cis* isomer has invariably been found to display the larger Stokes shift (Fig. 8). This indication of a larger distortion of the emitting excited state relative to the ground state for the *cis* isomer is paralleled by a faster ligand dissociation for this latter isomer. The non-radiative deactivation is less influenced by the coordination geometry, as may be seen from the rate constants calculated according to eqns. (7) and (8) for the deactivation of the reactive triplets of the isomeric pentaamine and tetraamine complexes shown in Table 6.

Even minor changes in ligand properties have proven to have a strong influence on excited state dynamics. The halide dissociation rate constants for the three series of closely related tetraamine complexes in Table 6 provide us with a rare opportunity to explore the influence of steric and electronic factors on the most common unimolecular chemical reaction by which excited states of metal complexes are deactivated. In agreement with the spectrochemical series, ethylenediamine seems, from the relative position of the ligand field transitions, to be a significantly stronger σ-donor than both ammonia and 1,3-propanediamine for rhodium(III) complexes [38,39,48,49], and the halide dissociation rate constants prove to be smaller for the ethylenediamine complexes than for both the ammonia and the 1,3-propanediamine analogues. An exception is the pentaammine complex *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$ from which, in contrast to what has been found for *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$, chloride dissociates faster than from $[Rh(NH_3)_5Cl]^{2+}$ in the triplet state [57]. The ratio between the rate constants for the same dissociation process in the ethylenediamine and the ammonia complexes depends on the stereochemistry but not on whether the leaving ligand is chloride or bromide: $k^{en}_{Cl}/k^{NH_3}_{Cl} = k^{en}_{Br}/k^{NH_3}_{Br} = 0.3$ for the *trans* isomers; $k^{en}_{Cl}/k^{NH_3}_{Cl} - k^{en}_{Br}/k^{NH_3}_{Br} = 0.6$ for the *cis* isomers [39]. Neither ammonia nor ethylenediamine have any π-bonding capabilities, and the lack of influence of the leaving ligand on the relative rate confirms the correlation between the σ-donor strength of the non-reacting amine ligand and the halide dissociation rate. This is because if steric factors were the more important in determining the difference in reactivities between the ammonia and the ethylenediamine complexes, then the ratio should depend also on the bulkiness of the halide. Moreover, the fact that halide dissociation is accelerated twice as much for the *trans* as for the *cis* complexes upon changing ethylenediamine for ammonia, identifies the *cis* ligand as being the more important in determining the relative halide dissociation rates in the triplet state.

In rhodium(III) complexes, the donor strength of ammonia and 1,3-propanediamine is surprisingly similar, as demonstrated by the ligand field spectra [38,49]. Accordingly, any differences in halide dissociation rates help to identify effects stemming from other than purely electronic factors. In contrast to what is the case for the chloro complexes, bromide dissociation is accelerated for both stereochemistries of the 1,3-propanediamine complexes relative to the ammonia (and the ethylenediamine) complexes. For the *cis* complex, the two adjacent voluminous bromides, in combination with an already crowded coordination sphere created by the bulky 1,3-propanediamine ligands, accelerate the bromide dissociation dramatically. The increased rate approaches the rate suggested for the intersystem crossing process that populates the reactive triplet [64]. Notably, this implies that the steady state approximation also approaches the limits for its validity for these *cis* complexes. However, the internal consistency of the conclusions regarding the influence of electronic and steric factors on the excited state reactivities for these three series of tetraamine complexes adds strong support to the applicability of the steady state approximation originally introduced by Bergkamp et al. [18,58].

Few complexes allow a comparison between ligand substitution rates in the ground state and the triplet excited state. However, the isomeric $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ provides a direct comparison of the water exchange rate constants for the two different electronic states (Tables 1 and 6), revealing for both isomers a rate acceleration of 10^{13} as a result of the promotion of an electron from a non-bonding to a σ-antibonding orbital [7,56].

(iv) A steady state approximation for rearrangement

The fate of the pentacoordinate excited state intermediates created by ligand dissociation determines the extent of isomerization observed. Although no direct information is available concerning the actual lifetimes of these basal and apical intermediates, they are expected to be very reactive, and a steady state approximation for their concentrations seems warranted. In agreement with the reaction scheme in Fig. 7, a *cis* reactant leads to the following steady state concentrations during illumination:

$$[\text{basal}^*]_{ss} = \frac{k_c(k_{a,n} + k_{ab})}{(k_{ba}k_{a,n} + k_{b,n}k_{a,n} + k_{b,n}k_{ab})}[\textit{cis}\ \text{triplet}^*] \tag{9}$$

$$[\text{apical}^*]_{ss} = \frac{k_c k_{ba}}{(k_{ba}k_{a,n} + k_{b,n}k_{a,n} + k_{b,n}k_{ab})}[\textit{cis}\ \text{triplet}^*] \tag{10}$$

Since the rate of formation of the *cis* and *trans* products respectively is proportional to these steady state concentrations

$$\frac{\mathrm{d}[\textit{cis}\ \text{product}]}{\mathrm{d}t} = k_{b,n}[\text{basal}^*]_{ss} \tag{11}$$

$$\frac{\mathrm{d}[\textit{trans}\ \text{product}]}{\mathrm{d}t} = k_{a,n}[\text{apical}^*]_{ss} \tag{12}$$

then the following relation between quantum yields and excited state rate constants is obtained:

$$\frac{\Phi_c}{\Phi_{ct}} = \frac{\mathrm{d}[\textit{cis}\ \text{product}]}{\mathrm{d}[\textit{trans}\ \text{product}]} = \frac{k_{b,n}(k_{a,n} + k_{ab})}{k_{a,n}k_{ba}} \tag{13}$$

A similar relation is obtained for the isomeric *trans* complex as reactant:

$$\frac{\Phi_{tc}}{\Phi_t} = \frac{k_{b,n}k_{ab}}{k_{a,n}(k_{b,n} + k_{ba})} \tag{14}$$

The basal and the apical intermediates appear, however, to be sufficiently long lived for equilibrium to be attained between the two isomers ($k_{ab} \gg k_{a,n}$ and $k_{ba} \gg k_{b,n}$). Evidence for this is also provided by the observation of ammonia scrambling in $[Rh(NH_3)_5Cl]^{2+}$ as a result of chloride photoaquation [45]. Accordingly, the ratio between *trans* and *cis* product (R_{tc} in Table 3) for both *cis* reactants (ϕ_{ct}/ϕ_c) and for the isomeric *trans* reactants (ϕ_t/ϕ_{tc}) can be expressed as

$$R_{tc} = \frac{\phi_{ct}}{\phi_c} = \frac{\phi_t}{\phi_{tc}} = \frac{k_{a,n}k_{ba}}{k_{b,n}k_{ab}} = \frac{k_{a,n}}{k_{b,n}} K^*_{ba} \tag{15}$$

in which latter relation the excited state equilibrium constant $K^*_{ba} = k_{ba}/k_{ab}$ has been introduced (see Fig. 5). The product ratio is seen to depend both on the energy difference between the apical and the basal isomers and on the relative rates of non-radiative deactivation for the two isomers. The rate of non-radiative deactivation of the hexacoordinate precursors for the intermediates of reduced coordination number shows little dependence on the stereochemistry, as is evident from the rate constants given in Table 6, and applying this further assumption ($k_{b,n} = k_{a,n}$) to eqn. (15) for the pentacoordinate intermediates, R_{tc} is identical with K^*_{ba}.

(a) Stereochemical preference

Only the few examples given in Table 3 are available for this direct comparison between R_{tc} and a theoretically calculated K^*_{ba}. However, the observed "preference" for either stereochemistry might also be expressed in terms of the isomerization yields. The combination of eqns. (4) and (15) yields

$$\phi_{ct} + \frac{k_{b,n}}{k_{a,n}} K^{*\,-1}_{ba} \phi_{ct} = \phi^*_{cis} \tag{16}$$

$$\phi_{tc} + \frac{k_{a,n}}{k_{b,n}} K^*_{ba} \phi_{tc} = \phi^*_{trans} \tag{17}$$

from which it is further seen that

$$\frac{\phi_{ct}}{\phi_{tc}} = \frac{\phi^*_{cis}}{\phi^*_{trans}} \frac{k_{a,n}}{k_{b,n}} K^*_{ba} \tag{18}$$

The stereochemical preference of the doubly photochromic aqua complexes, expressed as ϕ_{ct}/ϕ_{tc} and known for an increasing number of isomeric pairs, is thus a composite quantity. It is controlled by three factors: (i) the relative magnitudes of the water exchange yields of the two isomers; (ii) the relative rates of deactivation of the two pentacoordinate intermediates; (iii) the equilibrium constant between the latter two isomers.

(b) Comparison between kinetic and spectroscopic models

The spectroscopic model of Vanquickenborne and Ceulemans, based on the angular overlap model [26,50], provides a method for estimating the energy difference between the triplet apical and basal isomers. In the crudest approximation, the energy difference for tetraamine complexes can be expressed as

$$E(\text{apical}) - E(\text{basal}) = -\tfrac{3}{4}(\sigma_N - \sigma_X) \tag{19}$$

in which σ_N and σ_X are the σ-donor strengths of the amine ligand and the hetero ligand respectively. This energy difference relates directly to K^*_{ba}:

$$\tfrac{3}{4}(\sigma_N - \sigma_X) = RT \ln K^*_{ba} \tag{20}$$

which, when the approximations discussed above are included, can be identified with R_{tc}. For $[Rh(NH_3)_4Cl]^{2+*}$, R_{tc} is found to be approximately five (Table 3), whereas $K^*_{ba} \approx 10^4$ as calculated from eqn. (20), while $R_{tc} \approx 2$ and $K^*_{ba} \approx 10^6$ are found for $[Rh(NH_3)_4H_2O]^{3+*}$. These calculations are only approximate, as the ligand donor parameters have been obtained from spectroscopic data for chromium(III) complexes [26,65]. The noted disagreement between the spectroscopically calculated K^*_{ba} and the observed R_{tc} probably reflects the substantial approximations invoked in both the kinetic model and the purely spectroscopic model. However, the situation is not too discouraging. The spectroscopically calculated energy difference between the two excited state intermediates is rather similar to the observed energy difference, especially in relation to the large total excitation energy, and the qualitative selection rules for the photostereochemistry of rhodium(III) amines, which can directly be deduced from eqn. (20), have been found to have great predictive power [35].

Thus for a given amine, the preference for the *trans* configuration of the photoproduct $[RhA_4(H_2O)X]^{z+}$ increases according to eqn. (19) in the order of decreasing σ-donor strength of the heteroligand X. The stereochemical preference expressed as the quantum yield ratio ϕ_{ct}/ϕ_{tc} in Table 5 follows the order $X = Br^- > Cl^- > H_2O > NH_3 > OH^- \approx CN^-$ for each of the three tetraamine series, with the single exception of $Rh(en)_2(H_2O)_2^{3+}$, and in agreement with decreasing σ-donor strength. Moreover, for a given ligand X, eqn. (19) predicts that the *trans* preference should increase with increasing σ-donor strength of the amine. Notably, the ratio ϕ_{ct}/ϕ_{tc} is invariably larger for the ethylenediamine complexes than for the ammonia and 1,3-propanediamine complexes for which last two series the quantum yield ratios are surprisingly similar. This is in agreement with the very similar σ-donor strength of the two amines. It should be noted, however, that ϕ_{ct}/ϕ_{tc} depends on at least three factors (see eqn. (18)), and when R_{tc} becomes available for other isomeric pairs, a more quantitative treatment should be possible, which should also help to unify the kinetic and spectroscopic models for photoisomerizations of low spin d^6 metal complexes.

(v) Pressure and temperature effect on photoisomerization

The temperature dependence of photoisomerization quantum yields is available for the four H/D isotopomers of the isomeric diaquatetraamminerhodium(III) complexes [42]. However, caution should be exercised against making too strong a mechanistic inference from the apparent thermodynamic parameters given in Table 2 for the photoisomerization of $[Rh(NH_3)_4(H_2O)_2]^{3+}$ and the deuterated analogs:

$$\textit{cis-}\left[Rh(NH_3)_4(H_2O)_2\right]^{3+} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} \textit{trans-}\left[Rh(NH_3)_4(H_2O)_2\right]^{3+} \tag{21}$$

since the composite quantity ϕ_{ct}/ϕ_{tc} in eqn. (18), rather than $R_{tc}(\approx K^*_{ba})$, has been used for their deduction. However, a consistent pattern is seen, and the *trans* preference observed for these complexes (see Table 5) is paralleled by a significant exothermicity for the net *cis*-to-*trans* photoisomerization. The negative sign of ΔS° can likewise find its explanation in each of three factors in eqn. (18) or a combination thereof.

The apparent energy of activation for ϕ_{ct} is very small and, notably, the magnitude of this latter quantum yield is sensitive to deuteration of the water ligands. The opposite is true for ϕ_{tc}, which shows a relatively large apparent energy of activation and a less significant effect of water ligand deuteration. The following expression, obtained from a combination of eqns. (6) and (16)

$$\phi_{ct} = \frac{k_c}{k_c + k_{c,n}} \times \frac{1}{(k_{b,n}/k_{a,n})K_{ba}^{*-1} + 1} \tag{22}$$

shows, as does the analogous equation for ϕ_{tc}, the formidable experimental task that it would be to assign these temperature and deuterium isotope effects on photoisomerization with certainty to individual rate constants. However, the fact that a small temperature effect follows a large deuterium isotope effect for ϕ_{ct} (and vice versa for ϕ_{tc}) strongly suggests a different balance between strong and weak coupling for the non-radiative deactivation competing with rearrangement for the two isomers. At the so-called weak coupling limit, excited state distortions are small, and deactivation is dominated by high frequency vibrations with large deuterium isotope effects and small temperature dependences. In contrast, when excited state distortions are large, the non-radiative deactivation requires significant thermal activation, and deuterium isotope effects are small [40,66,67]. It is tempting to suggest a different balance between weak and strong coupling for the two isomers and consequently a larger excited state distortion for the *trans* isomer. However, the Stokes shifts are larger for the *cis* isomers [61], indicating a larger distortion for the emitting hexacoordinate *cis* triplet than for the hexacoordinate *trans* triplet. This apparent inconsistency does, however, disappear if it is assumed that differences in the sensitivity of $k_{a,n}$ and $k_{b,n}$, the rate constants for non-radiative deactivation of the apical and basal excited states to their respective ground states, are responsible for the observed effect on photoisomerization. The larger distortion of the excited state apical isomer, which is indicated by a significant strong coupling component for the *trans* isomer, requires a larger enthalpy input for ligand dissociation in its hexacoordinate precursor, and this enthalpy barrier may also account for the slower dissociation rates invariably found for the *trans* isomers relative to the *cis* isomers. However, a thorough understanding of the individual deactivation paths for the different ligand field excited states requires an extension of the theoretical work on ligand dissociation [26,27] to include the vibronic coupling between excited states and ground states.

From the pressure dependence of photoisomerization quantum yields, which has been determined for a few rhodium(III) complexes including *cis*-$[Rh(NH_3)_4Cl_2]^{+}$ and *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ and their bromo analogs [63], apparent volumes of activation have been calculated according to

$$\frac{\partial\{\ln[\phi_{isom}/(1-\phi_{isom})]\}}{\partial P} = -\frac{\Delta V^{\neq}_{isom}}{RT} \tag{23}$$

This activation parameter is likewise a composite quantity, since it depends on the pressure dependences of the individual rate constants (see eqn. (22)). $\Delta V^{\neq}$ is relatively positive for stereoretentive photosolvolysis of rhodium(III) complexes, in agreement with the dissociative substitution mechanism [63,67,68]. For photoisomerization, $\Delta V^{\neq}_{isom} = 0.0$ cm^3 mol^{-1} for *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ and $V^{\neq}_{isom} = -1.0$ cm^3 mol^{-1} for *cis*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$, and a more detailed interpretation of the effect of pressure on photoisomerization reactions such as that in eqn. (21) will have to await the determination of pressure effects on R_{tc}.

(vi) pH dependence of photochromicity

The composition of the photostationary state for the doubly photochromic aquaaminerhodium(III) complexes depends on the balance of the ligand field in the pentacoordinate excited state intermediates (see Fig. 7). For diaquatetraaminerhodium(III) complexes, this leads to a significant pH dependence of the *cis*-to-*trans* ratio in the photostationary state, since the dissociation of a proton from an aqua ligand increases the σ-strength sufficiently to make this heteroligand a stronger σ-donor than the amines.

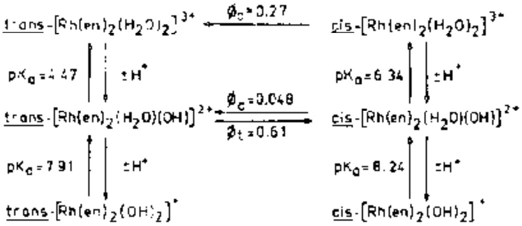


Fig. 10. Aqueous solution photochemistry of *cis*- and *trans*-diaquabis(ethylenediamine)rhodium(III). Photoisomerization of diaquatetraaminerhodium(III) complexes and their conjugate bases results in photostationary states with *cis*-to-*trans* ratios which are strongly dependent on solution pH. (Figure reproduced with the permission of Acta Chemica Scandinavica [48].)

Accordingly, a simple change in solution pH can lead to dramatic differences in the photostereochemical properties of these diaqua complexes, as seen in Fig. 10 [48]. Moreover, the ground state pK_a of the diaqua complexes (Table 1) accounts quantitatively for the hydroxy/aqua complex distribution in the excited state, as judged from the *cis*-to-*trans* ratio in the photostationary state as a function of pH for each of the three diaquatetraamine complexes given in Table 5 [10,48,49]. This confirms that the time domain for the complete excited state rearrangement is orders of magnitude shorter than the Brønsted acid equilibration [10].

D. CONCLUSION

Rhodium(III) amine complexes have been most effective models for the widely studied ligand field photochemistry of d^6 metal ions [2,4,12]. Photostereochemistry has been one of the important tools in the investigation of the intimate reaction mechanisms of the process initiated by the absorption of a light quantum, and the details of the stereochemistry and dynamics of the reactions of ligand field excited states have provided critical tests of existing theoretical models [26,27,50]. Indeed, many questions are still unanswered, in particular in relation to the non-radiative deactivation processes. It is hoped that the results accomplished might provide part of the experimental basis for the next generation of models for ligand field excited state reactions of d^6 metal ions.

The application of the mechanistic results to other d^6 centers such as iron(II) and cobalt(III) [69] should be pursued, since they could help to understand the photochemistry of biologically important metal complexes. The use of the photoactivation of rhodium(III) complexes in the exploration of biomacromolecules such as nucleic acids is, in this connection, an interesting development [70,71].

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REFERENCES

1 M.L. Tobe, Inorganic Reaction Mechanisms, Nelson, London, 1972, pp. 4–10.
2 G.J. Ferraudi, Elements of Inorganic Photochemistry, Wiley, New York, 1988.
3 A.W. Adamson, Comments Inorg. Chem., 1 (1981) 33.
4 J.F. Endicott, T. Ramasami, R. Tamilarasan, R.B. Lessard, C.K. Ryun and G.R. Brubaker, Coord. Chem. Rev., 77 (1987) 1.
5 B.R. Hollebone, C.H. Langford and N. Serpone, Coord. Chem. Rev., 39 (1981) 181.
6 A.W. Adamson, in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, p. 413.
7 L. Mønsted and L.H. Skibsted, Acta Chem. Scand., Ser. A, 40 (1986) 590.
8 L.H. Skibsted, Acta Chem. Scand., Ser. A, 40 (1986) 364.
9 L.H. Skibsted, J. Chem. Soc., Chem. Commun., (1987) 779.
10 L.H. Skibsted and P.C. Ford, Inorg. Chem., 19 (1980) 1828.
11 D.A. Sexton, L.H. Skibsted, D. Magde and P.C. Ford, Inorg. Chem., 23 (1984) 4533.
12 P.C. Ford, D. Wink and J. DiBenedetto, Prog. Inorg. Chem., 30 (1983) 213.
13 S.M. Jørgensen, J. Pract. Chem., 25 (1882) 346.
14 S.M. Jørgensen, J. Pract. Chem., 44 (1891) 50.
15 M. Delépine, C.R., 240 (1955) 2468.
16 L. Moggi, Gazz. Chim. Ital., 97 (1967) 1089.
17 T.L. Kelly and J.F. Endicott, J. Phys. Chem., 76 (1972) 1937.
18 M.A. Bergkamp, J. Brannon, D. Magde, R.J. Watts and P.C. Ford, J. Am. Chem. Soc., 101 (1979) 4549.
19 L. Mønsted and L.H. Skibsted, Acta Chem. Scand., Ser. A, 38 (1984) 535.
20 C. Kutal and A.W. Adamson, Inorg. Chem., 12 (1973) 1454.
21 M.M. Muir and W.-L. Huang, Inorg. Chem., 12 (1973) 1831.
22 M.P. Hancock, Acta Chem. Scand., Ser. A, 29 (1975) 468.
23 D. Strauss and P.C. Ford, J. Chem. Soc., Chem. Commun., (1977) 194.
24 J.D. Petersen and F.P. Jakse, Inorg. Chem., 18 (1979) 1818.
25 J.D. Petersen and F.P. Jakse, Inorg. Chem., 18 (1979) 3394.
26 L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 17 (1978) 2730.
27 K.F. Purcell, S.F. Clark and J.D. Petersen, Inorg. Chem., 19 (1980) 2183.
28 L. Mønsted and O. Mønsted, Acta Chem. Scand., Ser. A, 38 (1984) 67.
29 L.H. Skibsted and P.C. Ford, Acta Chem. Scand., Ser. A, 34 (1980) 109.
30 T.W. Swaddle and D.R. Stranks, J. Am. Chem. Soc., 94 (1972) 8357.
31 P.C. Ford and J.D. Petersen, Inorg. Chem., 14 (1975) 1404.
32 L. Mønsted, O. Mønsted and L.H. Skibsted, Acta Chem. Scand., 43 (1989) 128.
33 L. Mønsted and L.H. Skibsted, Acta Chem. Scand., Ser. A, 37 (1983) 663.
34 L.H. Skibsted, D. Strauss and P.C. Ford, Inorg. Chem., 18 (1979) 3171.
35 L.H. Skibsted and P.C. Ford, J. Chem. Soc., Chem. Commun., (1979) 853.
36 S.F. Clark and J.D. Petersen, Inorg. Chem., 18 (1979) 3394.

37 S.F. Clark and J.D. Petersen, Inorg. Chem., 19 (1980) 2917.

38 L.H. Skibsted, M.P. Hancock, D. Magde and D.A. Sexton, Inorg. Chem., 23 (1984) 3735.

39 L.H. Skibsted, M.P. Hancock, D. Magde and D.A. Sexton, Inorg. Chem., 26 (1987) 1708.

40 J.D. Petersen and P.C. Ford, J. Phys. Chem., 78 (1974) 1144.

41 M.E. Frink and P.C. Ford, Inorg. Chem., 24 (1985) 1033.

42 L.H. Skibsted, to be published.

43 L.H. Skibsted, Acta Chem. Scand., Ser. A, 42 (1988) 189.

44 L.H. Skibsted, Coord. Chem. Rev., 64 (1985) 343.

45 L.H. Skibsted, Inorg. Chem., 24 (1985) 3791.

46 J.S. Svendsen and L.H. Skibsted, Acta Chem. Scand., Ser. A, 37 (1983) 443.

47 L.H. Skibsted and P.C. Ford, Inorg. Chem., 22 (1983) 2749.

48 K. Howland and L.H. Skibsted, Acta Chem. Scand., Ser. A, 37 (1983) 647.

49 B. Øby and L.H. Skibsted, Acta Chem. Scand., Ser. A, 38 (1984) 399.

50 L.G. Vanquickenborne and A. Ceulemans, Coord. Chem. Rev., 48 (1983) 157.

51 P.C. Ford, J. Chem. Educ., 60 (1983) 829.

52 J.D. Petersen, Inorg. Chem., 20 (1981) 3123.

53 T.R. Thomas and G.A. Crosby, J. Mol. Spectrosc., 38 (1971) 118.

54 T.R. Thomas, R.J. Watts and G.A. Crosby, J. Chem. Phys., 59 (1973) 2123.

55 D.A. Sexton, P.C. Ford, D. Magde, J. Phys. Chem., 87 (1987) 197.

56 D.A. Sexton, L.H. Skibsted, D. Magde and P.C. Ford, J. Phys. Chem., 86 (1982) 1758.

57 D. Magde and L.H. Skibsted, Acta Chem. Scand., Ser. A, 41 (1987) 208.

58 M.A. Bergkamp, R.J. Watts, P.C. Ford, J. Brannon and D. Magde, Chem. Phys. Lett., 59 (1978) 125.

59 T.L. Kelly and J.F. Endicott, J. Phys. Chem., 76 (1972) 1937.

60 M. Talebinasab-Savari, A.W. Zanella and P.C. Ford, Inorg. Chem., 19 (1980) 1835.

61 M.E. Frink, P.C. Ford and L.H. Skibsted, Acta Chem. Scand., Ser. A, 38 (1984) 795.

62 D. Magde, G.E. Rojas and L.H. Skibsted, Inorg. Chem., 27 (1988) 2900.

63 L.H. Skibsted, W. Weber, R. van Eldik, H. Kelm and P.C. Ford, Inorg. Chem., 22 (1983) 541.

64 T. Kobayashi and Y. Okashi, Chem. Phys. Lett., 86 (1982) 289.

65 J. Glerup, O. Mønsted and C.E. Schäffer, Inorg. Chem., 15 (1976) 1389.

66 R. Englman and J. Jortner, Mol. Phys., 18 (1970) 145.

67 P.C. Ford, in R. van Eldik (Ed.), Inorganic High Pressure Chemistry. Kinetics and Mechanisms, Elsevier, Amsterdam, 1986, p. 295.

68 W. Weber, R. van Eldik, H. Kelm, J. DiBenedetto, Y. Ducommun, H. Offen and P.C. Ford, Inorg. Chem., 22 (1983) 623.

69 C.H. Langford and A.Y.S. Malkhasian, J. Am. Chem. Soc., 109 (1987) 2682.

70 J.M. LaVelle and R.A. Krause, Mutat. Res., 172 (1986) 211.

71 M.R. Kirshenbaum, R. Tribolet and J.K. Barton, Proc. 196th ACS Nat. Meet., Los Angeles, CA, September 1988, Abstract INOR 92.