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CHROMIUM(III) PHOTOCHEMISTRY AND PHOTOPHYSICS

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CONTENTS

INTRODUCTION

Studies of the photochemistry of Cr(III) complexes now date back about two decades. The first reviews of the topic appeared toward the end of that first decade and various aspects of the subject have been reviewed periodically since [1–21].

The purposes of this review are to update the topic of the nature of ligand labilization, starting with and complementing in some aspects the excellent review by Zinato [18], to review the recent developments in theory, including a new theory of photostereochemistry, to attempt to assess the applicability of the latter theory and finally to attempt an impartial but critical review of our knowledge regarding the nature of the excited states involved in Cr(III) photoreactions.

The topics of luminescence and photochemistry of polypyridyl chromium(III) complexes [22] and a general theoretical approach to the

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problem of prompt reaction by excited states [23] which bears on Cr(III) have recently been reviewed in this Journal and overlap with these will be avoided.

B. LIGAND LABILIZATION STUDIES

The predominant reaction mode observed on photolysis of Cr(III) complexes in the ligand field bands is photosubstitution by solvent. For some molecules isomerizations and racemizations have been observed together with one or two examples of photoanation discussed later. Redox processes are unimportant but for a few exceptions.

The early studies of the quantum yield of ligand loss in complexes with six equivalent Cr-atom bonds (called hereafter O_h complexes, even though this is often not the true symmetry) led to three generalizations [18]:

(1) the quantum yield increases with the ligand field strength of the ligands;

(2) the quantum yields are wavelength independent;

(3) the apparent activation energies of photochemistry, where known, are small (ca. 3 kcal mol^{-1}).

The update of the data, shown in Table 1, where the arrangement is in approximately increasing sequence of ligand field strength, still supports the latter two observations, but it is clear that the first is not generally valid. The overview reveals that other, more important, parameters than ligand field strength are influencing yields in major ways. Low yields appear often with π-bonding chelating ligands. But note that ethylenediamine and ammonia complexes behave very similarly, as do $[Cr(H_2O)_6]^{3+}$ and $[Cr(ox)_3]^{3-}$, showing that the chelation and/or the ligand flexibility appears not to be a major factor in these systems at least. The overview of Table 1 suggests that a search for generalizations of the above type is unlikely to be a very useful approach and that greater understanding is likely to come from detailed studies of particular single systems. Although complexes generally show the same quantum yield for irradiation into either of the quartet bands or the doublet band, it should be noted also that a small wavelength dependence of photochemical and emission yields has recently been observed on irradiation at various wavelengths in the red edge of the lowest energy quartet absorption band. This has been ascribed to variations in intersystem crossing yields as a function of the vibrational energy of the Franck–Condon state and is discussed further in section D of this review.

The extensive studies of ligand labilization in mixed-ligand Cr(III) complexes, the current data on which are summarized in Tables 2–4, essentially originated from the 1967 proposal by Adamson [76] that the predominant reaction mode of such a complex was loss of the strong field ligand on the

TABLE 1

Photosubstitution yields for CrL_6 complexes

Complex	Band irradiated[a]			E_{app} (kcal mol^{-1})	Ref.
	L_2	L_1	D		
$[Cr(urea)_6]^{3+}$	0.10	0.10	0.095	3.0	24
$[Cr(H_2O)_6]^{3+}$	–	0.01–0.03	–	~10	25
$[Cr(Ox)_3]^{3-}$	0.09[b]	0.08[b]	0.07[b]	2.1	26
$[Cr(acac)_3]$	0.01	0.011	0.011	3.7	27
$[Cr(tfa)_3]$	0.002[b]	0.002[b]	–		28
$[Cr(NCS)_6]^{3-}$		0.27	–		24
$[Cr(NH_3)_6]^{3+}$	0.47	0.47	0.47	1.0 [30]	29–34
$[Cren(NH_3)_4]^{3+}$	0.43	0.44	–		33
cis-$[Cr(en)_2(NH_3)_2]^{3+}$	0.44	0.47	–		33
trans-$[Cr(en)_2(NH_3)_2]^{3+}$	0.46	0.47	–		33
$[Cr(en)_3]^{3+}$	0.37	0.37	0.40	<3.0 [35]	33,35–37
$[Cr(phen)_3]^{3+}$	–	0.04[b]	–		38,39
$[Cr(bpy)_3]^{3+}$	–	0.18	–	$\leqslant 2.8$[c]	22,40
$[Cr(CN)_6]^{3+}$	0.11	0.12	–	2.9 [41], 8 [42]	41,42

[a] Quantum yield on irradiation into doublet (D), lowest excited quartet (L_1) or next higher quartet (L_2) regions. [b] Photoracemization or isomerization. [c] Calculated from data of ref. 40.

TABLE 2

Photosubstitution yields for $[Cr(NH_3)_5X]^{n+}$ and $[Cr(en)_2NH_3X]^{n+}$ ions

Complex	Band irradiated, Quantum yield						Config. of product	Ref.
	CT, ϕ_{NH_3}	CT, ϕ_X	L_2, ϕ_{NH_3}	L_2, ϕ_X	L_1, ϕ_{NH_3}	L_1, ϕ_X		
$[Cr(NH_3)_5H_2O]^{3+}$			0.2		0.15			43
$[Cr(NH_3)_5Cl]^{2+}$	0.35	0.23	0.38	0.007	0.36	0.005	*cis*	44,45
$[Cr(NH_3)_5Br]^{2+}$	0.20	0.26	0.37	0.011	0.35	0.009	*cis*	46
$[Cr(NH_3)_5NCS]^{2+}$			0.46	0.030	0.48	0.021 [a]	*cis*	47,48
$[Cr(NH_3)_5CO_2R]^{2+}$					0.25–0.45	>0.1	*cis*	49
$[Cr(NH_3)_5F]^{2+}$			0.43		0.43	0.0042	[b]	50,51
$[Cr(NH_3)_5CN]^{2+}$	0.31	<0.0005	0.33	<0.0005	0.33	<0.0005	2/3 *cis* [b]	52
			L_2, ϕ_{NH_3}	L_2, ϕ_{en}	L_1, ϕ_{NH_3}	L_1, ϕ_{en}		
t-$[Cr(en)_2NH_3Cl]^{2+}$			0.30	0.10	0.34	>0.01	*cis*	53
t-$[Cr(en)_2NH_3NCS]^{2+}$					0.2	0.3		54
t-$[Cr(en)_2NH_3F]^{2+}$			0.28	0.16	0.27	0.14	[b]	50

[a] Doublet irradiation gave $\phi_{NH_3} = 0.15$, $\phi_{NCS^-} = 0.018$. [b] The photostereochemistry of this molecule is discussed in detail in section G.

TABLE 3

Room temperature photosubstitution yields in *trans*-$[CrL_4XY]^{n+}$ ions on L_1 irradiation

Complex	Predominant products	ϕ^a	Remarks	Ref.
$[Cr(NH_3)_4Cl_2]^+$	*cis*-$[Cr(NH_3)_4H_2OCl]^{2+}$	0.44	$\phi_{NH_3}=3\times10^{-3}$	55
$[Cr(NH_3)_4(H_2O)Cl]^{2+}$	*cis*-$[Cr(NH_3)_4H_2OCl]^{2+}$	0.40	$\phi_{Cl^-}<4\times10^{-3}$ $\phi_{NH_3}=0.02$	55
$[Cr(NH_3)_4(H_2O)(NCS)]^{2+}$	*cis*-$[Cr(NH_3)_4(H_2O)NCS]^{2+}$	0.42	$\phi_{NCS}=0.02$ $\phi_{NH_3}=5\times10^{-3}$	55
$[Cr(NH_3)_4(NCS)Cl]^+$	*cis*-$[Cr(NH_3)_4(H_2O)Cl]^{2+}$	0.27	$\phi_{NH_3}=3\times10^{-3}$	55
	cis-$[Cr(NH_3)_4(H_2O)NCS]^{2+}$	0.14		
$[Cr(NH_3)_4(H_2O)_2]^{3+}$	*cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$	0.35	$\phi_{NH_3}<0.02$	55
$[Cr(NH_3)_4F_2]^+$	1,2-F-6-H_2O-$[Cr(NH_3)_3F_2H_2O]^+$	0.24	$\phi_{F^-}=0.008$	56
	1,6-F-2-H_2O-$[Cr(NH_3)_3F_2H_2O]^+$	0.10	$=0.008$	
$[Cr(NH_3)_4(CN)_2]^+$	1,2-CN-6-H_2O-$[Cr(NH_3)_3(CN)_2H_2O]^+$	0.08	$\phi_{CN^-}<0.005$	57
	1,6-CN-2-H_2O-$[Cr(NH_3)_3(CN)_2H_2O]^+$	0.16		
$[Cr(en)_2Br_2]^+$	*cis*-$[Cr(en)_2(H_2O)Br]^{2+}$	0.36	$\geqslant$95% *cis*	58
$[Cr(en)_2Cl_2]^+$	*cis*-$[Cr(en)_2(H_2O)Cl]^{2+}$	0.32	$\geqslant$99% *cis*	58,59
$[Cr(en)_2(NCS)Cl]^+$	*cis*-$[Cr(en)_2(H_2O)Cl]^{2+}$	0.18	$\phi_{H^+}=6\times10^{-3}$	60
	cis-$[Cr(en)_2(H_2O)NCS]^{2+}$	0.04	Temp. dep. ratio	
$[Cr(en)_2(NCS)_2]^+$	*cis*-$[Cr(en)_2(H_2O)NCS]^{2+}$	0.23 (0.18) [62]		61,62
	$[Cren(enH)H_2O(NCS)_2]^{2+}$	0.13 (0.07) [62]		
$[Cr(en)_2NCSF]$		0.27	$\phi_{H^+}=0.07$	63
$[Cr(en)_2FCl]^+$	*cis*-$[Cr(en)_2(H_2O)F]^{2+}$	0.31		64
$[Cr(en_2)F_2]^+$	$[Cren(enH)(H_2O)F_2]^{2+}$	0.35^b	$\phi_{F^-}\leqslant0.08$ Stereochemical change	65–67
$[Cr(en)_2(CN)_2]^+$	$[Cren(enH)(H_2O)(CN)_2]^{2+}$	0.58	$\phi_{CN}\leqslant0.02$ Isomers unknown	68
$[Cr(cyclam)Cl_2]^+$	*trans*-$[Cr(cyclam)(H_2O)Cl]^{2+}$	3.3×10^{-4}	$\phi_{H^+}<5\times10^{-4}$	69,70
$[Cr(tet)Cl_2]^+$	*cis*-$[Cr(tet)(H_2O)Cl]^{2+}$	0.06	$\phi_{H^+}<7\times10^{-3}$	70
$[Cren(H_2O)_2Cl_2]^+$	1-Cl-$[Cren(H_2O)_3Cl]^{2+}$	0.12		71
	2-Cl-$[Cren(H_2O)_3Cl]^{2+}$	0.10		

[a] Quantum yield for dominant reaction modes. [b] Literature values vary from 0.5–0.23. Most recent value of 0.35 adopted [67]. [c] tet=1,4,8,11-tetraazaundecane. [d] cyclam=1,4,8,11-tetraazacyclotetradecane.

TABLE 4

Photosubstitution yields in *cis*-$[CrL_4XY]^{n+}$ ions on L_1 irradiation

Complex	ϕ_A	ϕ_X	Remarks	Ref.
$[Cr(NH_3)_4Cl_2]^+$	0.32	0.15 ± 0.05	Products stereoretained?	72
$[Cr(NH_3)_4F_2]^+$	0.46	≤ 0.06	$\frac{1,2\text{-}F_2\text{-}6\text{-}H_2O}{1,6\text{-}F_2\text{-}2\text{-}H_2O} = 2:1$ [b] Some $1,2\text{-}F_2\text{-}3\text{-}H_2O$	56
$[Cr(en)_2ox]^+$	0.16	< 0.002		73
$[Cren(ox)_2]^-$	0.02	< 0.001		73
$[Cr(en)_2NCSCl]^+$	0.14	0.004	$\phi_{NCS} \approx \phi_{Cl^-} = 0.002$	74
$[Cr(en)_2Cl_2]^+$	0.13	0.02		59,72
α-$[Cr(trien)Cl_2]^+$	0.015	0.10	Products stereoretained?	72
$[Cr(en)_2(CN)_2]^+$	0.51	0.09		68
$[Cr(tren)F_2]^+$	[a]	0.21	Product stereoretained	75

[a] Not observed, no upper limit given. [b] The photostereochemistry of this molecule is discussed in section G.

weak field axis. At the time of the proposal this was not required by the evidence presented [77] but demonstrations that the proposal might be useful soon followed from a number of laboratories [55,59,60]. In the course of these studies it was further shown that the "axial labilization" seen in the photochemistry of these molecules was associated with very complete stereochemical change [55,58–60] and this provided an explanation of the puzzling and/or disputed *cis*-stereochemistry of the product in acidopentamine photolyses [78].

The end result of the accumulation of further data has been to complicate this simple picture considerably. This is seen by a careful study of the behaviour patterns summarized in Tables 2–4. At this juncture only the phenomenology will be dealt with. The more recent theoretical developments are discussed in the next section.

The attempts to arrive at generalizations similar to those for O_h complexes has led to the following suggested "rules".

(1) All other things being equal, there is a rather crude relation between total yield and overall ligand field strength.

(2) A number of complexes exhibit predominant loss of the strong field ligand on the weak field axis, but there are many exceptions, particularly with π-bonding ligands, and those which follow this rule usually show details of wavelength (and temperature) dependence which indicate that this is at best a gross description.

(3) Whether labilization is on the weak field axis or, where relevant, in the equatorial plane, stereochemical change generally occurs (this is not gener-

ally established for *cis* diacido complexes, Table 4).

(4) If the ligands constrain the complex to prevent stereochemical change (or formation of a transition state of higher or lower coordination number) then the quantum yield may be abnormally low.

(5) Apparent activation energies, where measured, are usually small (0–10 kcal mol^{-1}).

Note that these generalizations are established, if at all, only for a limited range of ligand types in aqueous solutions at ordinary temperatures and pressures and also studies of *cis* diacido complexes are far fewer than *trans*. Rule (1) appears to have little merit. The range of quantum yields observed is small, reflecting the similarity of the ligands present, but nevertheless there is a sizable number of comparisons opposite to this rule, for example for the acidopentammines alone (Table 2) NCS^-, Br^-, $Cl^- > H_2O$, and NCS^-, $F^- > CN^-$.

Studies of temperature dependence of quantum yield have generally yielded small apparent activation energies [44,46,50,53,56,60,63,74], supporting rule (5), but the data are few and have not been included in the tables.

The data of Table 2 for $[Cr(NH_3)_5X]^{2+}$ and the model *t*-$[Cr(en)_2NH_3X]^{n+}$ compounds are, except for $[Cr(NH_3)_5CN]^{2+}$, all consistent with (2) above, but for the acidopentammines it is unknown whether *cis* or *trans* ammonia is photoaquated. Studies of *trans*-$[Cr(NH_3)_4(^{15}NH_3)Cl]^{2+}$ [79], and the compounds *trans*-$[Cr(en)_2NH_3X]^{2+}$ for $X = NCS^-$, Cl^- and F^- revealed [50,53,54] significant photoaquation of the *trans* ammonia but the latter studies revealed that significant yields of ethylenediamine also occurred in a wavelength and temperature dependent proportion and depending on the nature of X. Also a larger proportion of equatorial ammonia aquation was observed on charge transfer excitation [79]. These results show that rule (2) has some validity but is at best an approximate guide to the behaviour. Also the photoreaction has to proceed via at least two different routes to account for the observed wavelength and temperature dependencies of the equatorial/axial reaction mode ratio [50,53,54]. This aspect is discussed further in sections C–E and G.

The molecule [52] $[Cr(NH_3)_5CN]^{2+}$ is alone amongst the acidopentammines studied to date in containing an acido ligand stronger than ammonia on the unique axis. The observation of ammonia photoaquation is consistent both with rule (2) above and with the more elaborate theories discussed later. Unfortunately there is again no knowledge of the position of the displaced ammonia so that the interpretation of the stereochemical data, the validity of rule (2) and the application of theory is quite uncertain. A study of the molecule *trans*-$[Cr(en)_2NH_3CN]^{2+}$ or *trans*-$[Cr(NH_3)_4(^{15}NH_3)CN]^{2+}$ would be very interesting, though difficult, and would help to eliminate the ambiguities.

The more extensive data (Table 3) on *trans* diacido complexes together with the limited data on *cis* diacido complexes (Table 4) provide further support. Loss of the strong field ligand on the weak field axis occurs frequently and for the *trans* complexes is associated with a high degree of stereochemical change in concurrence with rules (2) and (3). This was true also for *trans*-$[Cr(en)_2NH_3X]$, for $X = F^-$ and Cl^-, Table 2. To a large extent the exceptions apparent or otherwise, to this behaviour have been more illuminating. First there has been some question as to whether complexes which lose the equatorial ligand predominantly, for example *t*-$[Cr(en)_2F_2]^+$ and *t*-$[Cr(en)_2(NCS)_2]^+$, do or do not photoreact by a pathway which involves stereochemical rearrangement. This question, the resolution of which was obscured by the fact that the stereochemical signposting in these compounds was inadequate, has now been resolved both for *t*-$[Cr(en)_2F_2]^+$ [65–67] and by studies of *trans*-$[Cr(NH_3)_4F_2]^+$ [56] and $[Cr(NH_3)_4(CN)_2]^+$ [57]. All of these compounds photoreact in a way that is consistent with, but does not completely require, the same type of stereochemical change found for axial labilization. The discussion of the details of this photostereochemistry are deferred to section G.

Representing a different type of exception, *trans*-$[Cr(en)_2FCl]^+$ loses chloride in disagreement with rule (2). This is explicable in the more rigorous theories to follow, in terms of the π-bonding capability of fluoride.

The study of *trans*-$[Cr(cyclam)Cl_2]^+$ and $[Cr(tet)Cl_2]^+$ (Table 3) was important. It demonstrated that constraining the complex to prevent formation of either a five or seven-coordinate intermediate resulted in a very low quantum yield and established the importance of steric factors in the photochemistry. It also suggests that stereochemical change could be a requirement of the photoreaction mechanism. Unfortunately there have not been many studies of this phenomenon to date.

Recent work by Sheridan and co-workers on *cis* complexes, points out some of the complexities, however. The data for *cis*-$[CrL_4Cl_2]^+$ ions (Table 4) reveal [72] a very irregular behaviour of the minor chloride yield in the series, but the data for *cis*-α-$Cr(trien)Cl_2^+$ show that constraining the ligand in the equatorial plane (weak axes) can cause an enhancement of the aquation of the "non-rule" (chloride) ligand. Sheridan and co-workers find the same phenomenon in difluoro β,β'',β'''-(triaminotriethylamine) chromium(III) [75], where ϕ_{F-} is 0.20. In view of these complexities it was somewhat fortuitous that the first test of rule (2) was based on a study of *cis* and *trans*-$[Cr(en)_2Cl_2]^+$ which are perhaps "better behaved" than some other *cis*/*trans* pairs.

To summarize, steric effects of this type appear in some instances to quench the photochemistry and in others to cause enhancement of the non-rule (2) ligands in a manner that is not currently well understood.

Within the bounds of the restricted set of ligands, solvents and conditions studied to date and the difficulties noted, the behaviour of chromium(III) complexes is reasonably well described by the generalizations (2)–(5) set out above. With experience and judgement predictions of the photochemistry of new molecules is even possible, though perhaps hazardous. The rich variety of d^3 complex photochemistry suggests, however, that detailed studies of particular complexes, their wavelength, temperature, medium and pressure dependencies of emission and product yields, their stereochemistry and the sensitization and quenching of photochemistry and emission are more likely to be rewarding and to provide more insight than the search for overall trends in behaviour, which seem at present likely to show the complex variations described earlier. In the ensuing sections we therefore further pursue these more detailed studies.

For ligand field excitation, Cr(III) complexes do not generally show photoredox decomposition pathways. For some molecules, however, there is definite evidence for the operation of photoredox mechanisms on higher energy irradiation. Typical are the observations on $[Cr(NH_3)_5Br]^{2+}$ [80], $[Cr(NH_3)_5N_3]^{2+}$ [81] and *trans*-tris(1,1-trifluoro-2,4-pentanedionato) chromium(III) [28,82].

C. DEVELOPMENT OF PHOTOCHEMICAL THEORY

Although the proposal of preferential photosubstitution of the strong field ligand on the weak field axis was presented by Adamson [76] as empirical, it was subsequently realized by a number of workers that a possible basis for such behaviour could reside in the localization of quartet state sigma antibonding electron density on the weak field axis. This idea was developed by Zink [83,84] and by Wrighton et al. [85] both of whom emphasized in addition the importance of π-bonding effects in stabilizing π donor and destabilizing π acceptor ligands.

In a series of papers Zink set out the nature of the bonding changes in the various doublet and quartet excited states [83], showed theoretically that the axial electron density in the lowest quartet excited state would lead to loss of the strong field ligand on that weak field axis [83], reviewed the possible reactivity of the doublet state [83,86], considered the role of configuration interaction [86] and carried out model molecular orbital calculations for a number of complexes [87], obtaining generally satisfactory agreement with experiment. In this latter work the principle was applied that the leaving ligand would be the one with the greatest overlap integral with the sigma anti-bonding electron. Zink [87] further emphasized (as had this author [14]) the role of the vacant t_{2g} orbital in the putative reactivity of the lowest excited quartet state and offered this as a rationale of the stereochemical change associated with photoreaction. In these papers, Zink laid a fundamental theoretical basis for future developments of our understanding of d^3 photochemistry, although some of the discussion comparing theory with experiment is open to serious question. The final model arrived at [87] unfortunately required molecular orbital calculations of overlap populations which makes it inconvenient for use by experimentalists. In addition, and more importantly, it emphasized the aspect of bond labilization, rather than overall bond strength in the excited state. There was no adequate explanation of the observed stereochemical change and the historic question of doublet versus quartet reactivity was unresolved, this latter situation persisting partially to the present day.

More recently Vanquickenborne and Ceulemans [88] (VC) have presented, building on this background, a more readily applicable semi-empirical theory of ligand labilization based on the angular overlap model. They assumed, on the basis of the prevailing experimental evidence, a model of exclusive lowest excited quartet state reactivity and calculated, using the empirical ligand field parameters, the bond strengths of the various M–L bonds in the excited state. The model was successful in rationalizing the existing data where the ligand σ and π parameters were available. They also showed that the strong field ligand/weak field axis rule is equivalent to a consideration of only the M–L bond labilization due to the sigma antibonding electron density in the excited state. In contrast their calculations are of the total M–L excited state bond strengths, and where these two differ, as for example for fluoro complexes, their predictions are correct and the simple rule fails.

A case in point is the behaviour of the fluoroammine complexes $[Cr(NH_3)_5F]^{2+}$, *trans*-$[Cr(en)_2FCl]^+$ and *trans*-$Cr(en)_2FCl$ which behave in a very puzzling manner [50,51] from the viewpoint of the earlier models. The behaviour is, however, completely explicable in terms of the VC model [89,90], which assigns the negligible fluoride yields to the strength, even in the excited state, of the Cr–F bond.

In a very recent paper Vanquickenborne and Ceulemans [91] have extended their model to complexes with D_{2h} micro symmetry such as those listed in Table 4.

This theory has now been tested further and extended to include the possible reactivity of the higher lying quartet states. Where two different reaction modes are found, the complexes often exhibit a wavelength and temperature dependence of their quantum yield ratios. For several such complexes the direction of these changes corresponds to reaction by both the lowest and the next lying excited quartet states [50,53,56,58,60,63]. Extension of the theory to predict the reactivity of this additional reactive state gives a satisfactory explanation of the temperature and wavelength dependence observed and is discussed further later in this review. At this point we note only that this theory may usefully be extended to consider the potential reaction patterns of higher lying quartet excited states, even though it was not initially presented this way.

In a subsequent paper Vanquickenborne and Ceulemans [92] extended their application of the angular overlap model to calculation of the energetics for various reaction pathways and hence developed the first theory of the photostereochemistry of d^3 (and d^6) complexes.

The model assumes that the lowest quartet state is the reactive state and that the first step in reaction is dissociation of the labilized ligand to leave a square pyramidal (sp) five-coordinate intermediate. There are then shown to be symmetry restrictions on the collapse of this sp intermediate to yield a trigonal bipyramidal (tbp) intermediate which will be produced either in its ground or excited state, depending on the relative sigma and pi parameters of the remaining ligands. Further symmetry restrictions then pertain to the attack by solvent on the tbp intermediate to yield product in its ground state. The rigorous derivation of the symmetry restrictions for any complex should be based on the full state correlation diagrams and the appropriate conserved symmetries, for details of which the reader is referred to the original [92] paper.

The predictions of the complete theory are, however, in simple cases, the same as those shown by Vanquickenborne and Ceulemans to be derived from the simple pictorial considerations of Fig. 1 for the archetypal complex, $[Cr(NH_3)_5Cl]^{2+}$. Loss of the weak field (z) axis ammonia, the predicted mode for the ^4E lowest lying excited state [93], yields the sp intermediate with an occupied $d_{z^2-x^2}$ (or $d_{z^2-y^2}$) orbital which takes on more of the character of d_{z^2}. The allowed ligand rearrangement in this species is downward rotation of the ammonia molecules on the x axis to yield in its ground state (since $\Sigma\sigma_{Cl^-} < \Sigma\sigma_{NH_3}$) the tbp ($C_{2v}$) species with the chloride equatorial. Entry of water in the trigonal plane *trans* to the chloride is disfavored (since it forces the equatorial ammonia molecules back up against the occupied $d_{z^2-x^2}$ orbital, thereby correlating with the excited state of *trans*-$[Cr(NH_3)_4H_2OCl]^{2+}$). In contrast, water entry *cis* to the chloride is allowed as it leads naturally to the ground state of the product, *cis*-$[Cr(NH_3)_4H_2OCl]^{2+}$.

By such means the stereochemical change revealed in the data for axial labilization in Tables 2–4 is readily and fairly satisfactorily accounted for. This simple pictorial model is easy to understand, usually correct and therefore very useful for qualitatively predicting the photostereochemistry for more difficult complexes. This has also been used in at least one case, to successfully predict the photostereochemistry of a higher lying quartet excited state [90].

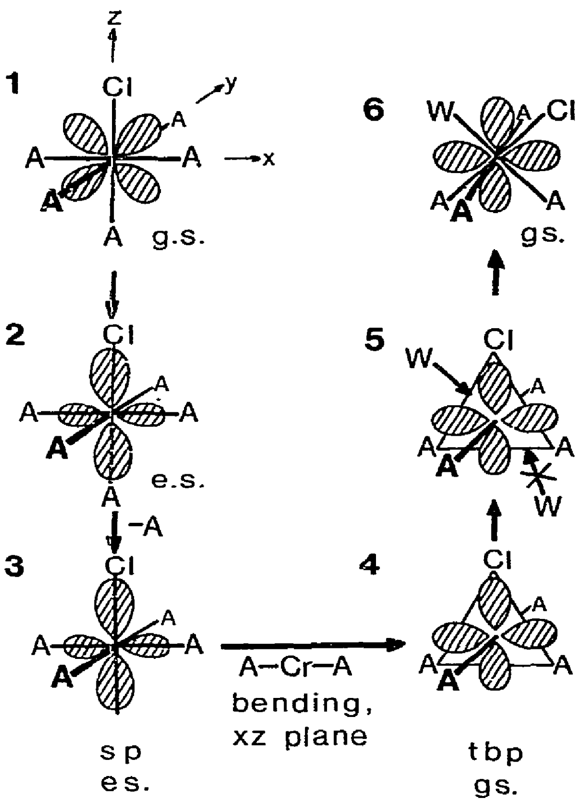

Fig. 1. Pictorial representation of the photostereochemistry of a Cr(III) complex according to the Vanquickenborne/Ceuleman's theory. (1) The ground state ($^4B_1$) of $[Cr(NH_3)_5Cl]^{2+}$ ($A=NH_3$) with its occupied d_{xz} orbital shown. (2) Excitation to the lowest ^4E excited state corresponds to promotion of a d_{xz} or d_{yz} electron to a sigma antibonding orbital of mixed d_{z^2} and $d_{x^2-y^2}$ character, ($d_{z^2-x^2}$ or $d_{z^2-y^2}$ respectively, for the situation where all six ligands are equivalent). The figure shows the situation for that ^4E component corresponding to vacation of d_{xz} and occupancy of a ($d_{z^2-x^2}$)-like orbital with >75% d_{z^2} character (due to the smaller overall ligand sigma donor strength on the z axis in $[Cr(NH_3)_5Cl]^{2+}$ {$\epsilon_\sigma(NH_3)=0.718\ \mu m^{-1}$, $\epsilon_\sigma(Cl)=0.558\ \mu m^{-1}$}.) This excitation labilizes the axial (z axis) Cl and NH_3 ligands and to a lesser extent the x axis NH_3 ligands. (3) The preferential loss of the z axis ammonia ligand leads to a square pyramidal (sp) five coordinate intermediate (chloride apical) in its electronically excited state. This intermediate can lower its energy significantly by an allowed x axis NH_3–Cr–NH_3 bending downwards in the xz plane to yield (4). (4) The electronic ground state of a trigonal bipyramidal intermediate (tbp) with the chloride ligand in the equatorial plane. (5) Entry of a solvent molecule (W) in the equatorial plane of this ground state tbp intermediate *trans* to the chloride ligand is forbidden since it correlates with the excited state of *trans*-$[Cr(NH_3)_4(H_2O)Cl]^{2+}$. In contrast, W entry *cis* to the equatorial chloride is allowed, as shown, as it correlates with (6), the ground state of the product *cis*-$[Cr(NH_3)_4(H_2O)Cl]^{2+}$. Note that the excited state of this tbp intermediate has the d_{xz} orbital occupied and should show the opposite selection rule, therefore leading in theory to *trans*-$[Cr(NH_3)H_2OCl]^{2+}$ product.

There are, however, situations involving lower symmetry complexes or equatorial labilization where the simple pictorial procedure corresponding to the one-electron orbital energy model is misleading and inapplicable. In such circumstances it is usually obvious that the pictorial approach is inappropriate and recourse to the full treatment must be made. Such a situation occurs both for $[Cr(NH_3)_5F]^{2+}$ [89,90] and *cis*-$[Cr(NH_3)_4F_2]^+$ [56]. The analysis and comparison with experiment for these molecules reveals a further feature. The postulated tbp intermediates are produced in electronically excited states, and must be presumed to aquate at least in part from these excited states [56,89,90] in order to explain the observed products by means of the VC theory. This is discussed in detail in section G.

The theory presented thus far covers only the gross aspects of the photoreactions, assumed to involve predominantly the lowest quartet excited state. Many chromium(III) complexes show wavelength and temperature dependence of their reaction mode ratios, including stereochemistry, clearly implicating more than one state in reaction. These further aspects are discussed after the next section dealing with the question of excited state participation.

Also we defer discussion of the evidence bearing on a choice between the VC theory of photostereochemistry and the alternative edge-displacement model [14]. It is an important question to decide whether any symmetry restriction is actually operating.

With the growth of evidence that some at least of the photochemistry of Cr(III) complexes is extremely rapid and may compete with vibrational relaxation (section D), Hollebone [94] has recognized the desirability of a theoretical approach applicable to such "prompt" reactions. In his recent paper the model leads to selection rules for the vibronic states potentially involved in such very rapid reactions. He also shows that spectroscopic evidence for two d^3 systems supports the prediction that a t_{1u} buckle mode participates in excitation to the $^4T_{2g}$ state. This he concludes would favour associative mechanisms for photoreaction of this state. More detail and the implications for Cr(III) photochemistry are presented in a recent review [23]. We note only that the prediction differs significantly from that of the conventional group theoretical approach [95] and it would be desirable to have some resolution between the alternatives based on further data analyses.

A further alternative mechanism for photoracemization was suggested by the angular overlap calculations of Burdett [96] which imply that a trigonal prismatic intermediate could be favoured in a d^3 photochemical reaction.

D. SPECTROSCOPIC AND PHOTOPHYSICAL STUDIES

Essential to the interpretation of the photochemical behaviour of Cr(III) complexes has been the understanding of excited state properties obtained by spectroscopic and photophysical experiments. These have concerned emission quantum yield (or intensity) and emission lifetime and their wavelength, temperature, medium and environmental dependencies plus quenching and sensitization experiments. The topics of environmental effects [20] and quenching and sensitization [15] have been recently reviewed.

The early work established that either or both phosphorescence and fluorescence may occur, and identified phosphorescence as a relatively long-lived, structured, narrow band emission with small Stokes shift, consistent with the t_{2g}^3 configuration of the doublet excited state. In contrast the fluorescence was broad, structureless and significantly Stokes shifted to the red consistent with the $t_{2g}^2e_g^1$ excited state configuration. In addition the type of emission observed was closely related to the spacing of the quartet and doublet states, which in turn was determined by the overall ligand field strength [97,98].

These facts and the independence of the emission spectra on excitation wavelength led to the kinetic scheme for the d^3 system shown in Fig. 2 (solid lines) and on which consideration of both the emission and photochemistry has traditionally been based.

More recent studies have further characterized the doublet state. Thus the species can be produced in sensitization experiments and can be quenched either by energy or in some cases electron transfer [99,100]. The energy transfer efficiencies have been found to correlate with factors such size [101] and charge and the nephelauxetic parameters [102,103] of the ligands in the complex.

Where the lifetime of the excited state of an acceptor molecule is longer than or comparable to that of the donor, energy transfer can be reversible, and a general treatment of the transient and steady state kinetics of this situation has been presented [104]. An experimental study of this effect has been published [105] and confirms that quenching constants derived from Stern Volmer kinetics neglecting back energy transfer will be in error only by a small amount. (The paper claims much larger errors but this is supported neither by the observations nor the kinetic analysis presented.)

Both energy transfer [106–108] and electron transfer techniques [109] have been used to estimate values for the intersystem crossing yields. For chromium(III) complexes the yields are often large and values approaching unity have been observed [106,108] revealing that intersystem crossing can be a very facile process.

Forster and co-workers have studied both intersystem crossing yields and their dependence on temperature and environment. For $[Cr(CN)_6]^{3-}$ and $[Cr(en)_3]^{3+}$ in solid state lattices $\eta_{isc} = 1$ and appears to be temperature independent [108,110]. Furthermore the intersystem crossing yields for $[Cr(CN)_6]^{3-}$ [111], $[Cr(NCS)_6]^{3-}$ and *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ [112] have

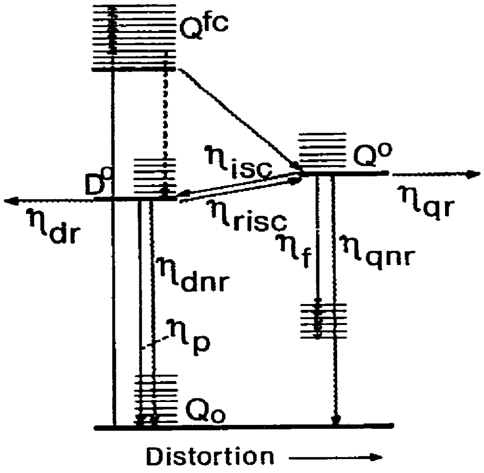

Fig. 2. Conventional potential energy diagram and kinetic scheme for a d^3 system. The diagram shows on the left the ground quartet state of the configuration, labelled Q_0, and the absorption of this state over a broad range of energies to reach the Franck–Condon quartet excited state Q^{FC} which retains ground state geometry and solvation. This may then relax with considerable distortion from the ground state geometry, together with possibly large solvation changes, to give the vibrationally relaxed electronically excited quartet state Q^0. This state may then react with efficiency η_{qr}, decay radiationlessly to ground state, η_{qnr}, fluorescence (in rare cases), η_f, or undergo intersystem crossing, η_{isc}, to excited doublet state D^0. As shown, the doublet state, since it arises from the t_{2g}^3 configuration, has geometry very similar to Q_0 and Q^{FC}. The doublet may in turn react, η_{dr}, decay radiationlessly, η_{dnr}, phosphorescence, η_p, or undergo reverse intersystem crossing back to quartet, η_{risc}. Recent evidence now suggests the importance of the process $Q^{FC} \rightarrow D^0$ (broken line) prompt intersystem crossing, with an efficiency η_{pisc} that may approach 1. There is also recent evidence for the involvement of intermediate states not shown here; see text for details.

been found to be unaffected by different solution media. Several workers have studied doublet absorption spectra by flash techniques [113–118]. In sum, the doublet state is a well characterized species with its own particular chemistry and this background knowledge is of vital importance in studies of the photochemistry.

In contrast little information about the quartet state has been obtainable. In particular the energy of the thermally relaxed quartet state is not known with certainty for any compound under the photochemically relevant conditions of room temperature solution.

Unlike the doublet state with its t_{2g}^3 configuration showing little distortion in the excited state, the quartet state, $t_{2g}^2e_g^1$, can be expected to relax considerably from the initial geometry during the process of vibrational relaxation and solvent reorientation. It is to be expected therefore that the extent of this relaxation and therefore the energy of the relaxed but electronically excited quartet state should be sensitive to environmental influences. This has been found to be the case.

For $[Cr(urea)_6]^{3+}$ in various salts at low temperature Laver and Smith [119] found, for example, that the fluorescence wavelength maximum was significantly influenced by changes in crystal lattice due to differing counter ions, and a variation over 1600 cm^{-1} was observed. Also the concomitant fluorescence intensity changes correlated with the apparent energy spacing between doublet and quartet consistent with a mechanism of delayed (E-type) fluorescence. At the same time only small and uncorrelated changes in the energy of the quartet absorption band occurred, and the phosphorescence wavelength remained essentially unchanged. It appears likely from these and similar results that the energy decrease on relaxation in solution might be even larger, and could be expected to vary for different solution media. This is suggested by an early study of solvent dependence of phosphorescence intensity [120].

It has been suggested [13] that the energy corresponding to the wavelength at the red end of the absorption spectrum at which the absorptivity is 5% of the band maximum is a reliable predictor of the energy of the relaxed excited quartet level. The equation $E(^4T_2^0) = 0.0111\bar{\nu}_{0.05} - 0.0088 \mu m^{-1}$ was suggested to give a satisfactory estimate. This procedure was based on an examination of solid state (or glass) emission data. It works extremely well for solid $[Cr(en)_3](ClO_4)_3$ (0.198, calc. [13]; 0.199, expt. [95]), one of the few complexes for which the vibronic structure on the quartet absorption spectrum enables an assignment of the electronic origin. It is somewhat less successful for aqueous $[Cr(H_2O)_6]^{3+}$ (0.152, calc. [13], 0.162 expt. [94]), and more generally this procedure is of unknown validity for the solution state.

Also it is important to recognize that the quartet origin obtained from Franck–Condon analysis (or the $\bar{\nu}_{0.05}$ rule) applied to the absorption spectrum leads to the minimum for the excited state potential well extrapolated from absorption data at ground state geometry, solvation, etc. Although it has been claimed that this is the appropriate procedure [95], this is not known to be so. The process of excited state relaxation in solution may involve different distortions and solvation changes than those required by the vibronic absorption selection rules. Therefore the absorption spectral analyses may be somewhat irrelevant to the determination of the energy of the vibrationally relaxed excited quartet state in solution. This is indeed suggested by the data of Laver and Smith [119] for the analogous situation in crystalline media. Shifts in the fluorescence maxima [119], which likely reflect changes in excited state relaxation and therefore in the energy of $^4T_2^0$, do not (and would not be expected to) show in the absorption spectrum.

Attempts to directly measure quartet excited state absorption [115] or emission spectra in solution have failed generally, although one case of a broad emission band which appears to be delayed fluorescence has been reported [121] and is being further investigated.

The failure to observe quartet excited state absorption, even in picosecond experiments is slightly puzzling but is perhaps explicable in terms of the very short solution lifetime of the initially produced quartet state. This has been found to lie in the range 5–20 ps where it has been possible to measure it [115,122] indirectly from the rise time of the phosphorescence. Note that this measurement, being indirect and of a process preceding the relaxed quartet state, does not require such a short lifetime for the relaxed quartet excited state [123] which remains a completely uncharacterized species.

Although the conventional wisdom represented by Fig. 2 has been very useful and has assisted in the proper analysis of the kinetics of photochemistry and emission, recent studies have begun to reveal that it can be misleading in its simplicity for some complexes, perhaps even a majority.

Thus a study of *d*-$[Cr(en)_3]^{3+}$ photoracemization and emission showed that the doublet emission yield and the percentage photoreaction occurring via the doublet (the quenchable reaction) both decreased for excitation wavelengths in the tail of the lowest quartet absorption band. This was consistent with a higher intersystem crossing yield from the vibrationally excited quartet state [124]. On the basis that the apparent activation energies for $[Cr(en)_3]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ phosphorescence of 10.4 kcal mol^{-1} were the same independent of excitation wavelength it was further concluded [125] that these observations could not be due to "solvent-restricted quartet relaxation" [11] as this would imply different activation energies for 400 and 514 nm excitation. The observations were therefore suggested to arise from intersystem crossing in competition with vibrational relaxation. Similar emission behaviour was reported [124] for $[Cr(NH_3)_6]^{3+}$. Wavelength dependence of photochemical yields via the doublet state has since been reported for $[Cr(phen)_3]^{3+}$ racemization [126] and $[Cr(bpy)_3]^{3+}$ ligand substitution [127]. These and similar conclusions are substantiated by the measurements of phosphorescence rise time [115,116] which demonstrate that intersystem crossing is sufficiently fast to be potentially competitive with vibrational equilibration.

The question of solvent restricted relaxation in these systems has been raised again by recent work on the wavelength dependence of $[Cr(en)_3]^{3+}$ phosphorescence intensity in 80% glycerol/water versus water. Conti et al. [128] find that the decrease in emission intensity on excitation to the red edge of the absorption band is less pronounced in the viscous solvent, possibly revealing an important role of solvent in the intersystem crossing process.

Earlier work from the same laboratory [129] identified a further complication. For $[Cr(CN)_6]^{3-}$ the phosphorescence spectrum observed in water was dependent on excitation wavelength in the red edge of the first quartet absorption band as was the doublet lifetime both in water and 80% glycerol/water. These phenomena were attributed to the photoselection of different solvates which clearly must interconnect on a time scale slower than the lifetime of the doublet in these media (ca. 10^{-7}–10^{-6} sec). The occurrence of such photo-selection processes could be highly relevant to this question of wavelength dependence of emission yield, lifetime, and photochemical yield on excitation at different wavelengths in an absorption band, particularly where even shorter lived excited states are involved.

Cumulatively these studies demand an important change in the conventional picture of intersystem crossing. A scheme such as Fig. 2 must allow for intersystem crossing both from the vibrationally excited and the relaxed electronically excited quartet state. For the remainder of this review intersystem crossing will be considered to be able to compete with vibrational relaxation and may therefore be prompt, slow or both. Indeed in the discussion of the photochemistry some further evidence for prompt intersystem crossing will be presented. This change is reflected in Fig. 2 by the inclusion of the dotted line for prompt intersystem crossing with efficiency η_{pisc}.

There has been concern with not only the question of prompt intersystem crossing and solvent restricted relaxation but also with the importance of reverse intersystem crossing under photochemical conditions. Evidence which bears on this becomes of considerable importance in the context of the debate on doublet versus quartet reactivity. Because much of the emission work was carried out at low temperature in solids or glasses a need was apparent for more data under photochemically relevant conditions. A relevant study [130] of the variation of emission lifetime and its activation energy in various solvents for a variety of chromium complexes led to the proposal of a set of "emission rules":

(1) For complexes with six equivalent Cr–L bonds, the emission lifetime in room temperature fluid solution decreases with decreasing ligand field strength.

(2) If two different kinds of ligand are coordinated the emission lifetime will be relatively short if that ligand which is preferentially substituted in the thermal reaction lies on the weak field axis of the complex.

A rationale offered for these rules suggested that doublet chemical reaction controlled the doublet solution lifetime in complexes where the thermally substituted ligand lay on the weak field axis.

A separate investigation [121] of the emission spectra, absolute quantum yield of emission and lifetime of a number of Cr(III) complexes in room temperature aqueous solution showed a more complex dependence of quantum yield and lifetime on the ligands and geometry. Thus *cis* acido complexes generally emitted with 1/10th the yield of the corresponding *trans* compound independent of the nature of the ligands on the weak field axis. Similarly substitution of ethylenediamine for two ammonias had no effect on yield in hexammine type complexes, but in complexes containing an acido ligand caused a tenfold reduction.

While some complexes did exhibit the behaviour predicted by the above rules there was a sufficiently large number for which reliable data are available which do not fit the pattern that one must doubt their generality or fundamental nature.

Of considerable importance, the work led to the discovery of at least one compound (possibly three), *trans*-$[Cr(en)_2F_2]^+$ which shows in room temperature aqueous solution an efficient (ϕ = ca. 2×10^{-4}) emission with large Stokes shift, broad spectral band width and μsec lifetime, the characteristics expected for delayed (E-type) fluorescence. This establishes intersystem crossing followed by reverse intersystem crossing under conditions where the molecule photolyses with a quantum yield [65–67] of 0.35. We return to this in the section on photochemistry.

While there is debate about the causes, all workers agree that the solution emission lifetimes and activation energies, and intensities show significant solvent effects either for different solvents or on changing from solid state to solution [116–118,129–132]. The Arrhenius plots are linear (the temperature ranges involved are often, but not always, small) leading to the suggestion that the lifetime is controlled by a single process, suggested now by several groups [112,130–132] to be doublet reaction. These arguments are very insecure. The single process (if it is a single process) could well be reverse intersystem crossing, not reaction, and the solvent variation could well arise from varying degrees of relaxation from the Franck–Condon state in different media and lattices as discussed earlier. Contrary to what is occasionally claimed this would not be expected to be revealed by absorption spectral changes. Some of the evidence supports this interpretation, for instance the higher activation energies for the phosphorescence lifetime observed in rigid media [131,132]. The observations of Forster and co-workers in mixed solvents are also consistent. Also note that, for the best documented and analysed case of doublet reactivity $[Cr(bpy)_3]^{3+}$, the "linear Arrhenius plot" is required to be a double exponential [40], undercutting the single activation energy position often used to argue against reverse intersystem crossing. The writer concludes that the importance of reverse intersystem crossing versus doublet reaction remains "not proven" on the basis of emission evidence.

In summary the emission studies support a photodynamical scheme in which excitation occurs to a Franck–Condon state which may then (1) lead to photoreaction, (2) undergo prompt intersystem crossing, and (3) vibrationally equilibrate to the thermally equilibrated electronically excited quartet state. The fates of this latter may be reaction, fluorescence, non-radiative decay and intersystem crossing. For the doublet they are reaction, phosphorescence, non-radiative decay and quenching, and reverse intersystem crossing. The Franck–Condon state initially produced may be looked on as a mixed state of doublet plus quartet character, and in this description there may be no kinetically distinguishable process such as prompt intersystem crossing. The photoselection evidence described earlier also suggests that predispositions for particular solvent environments and particular distortions of the complex may play a role in observations such as the wavelength dependence of intersystem crossing efficiencies, etc. In other words this may be explicable in terms of photoselection of Franck–Condon states having different admixtures of quartet and doublet character and therefore corresponding to a different "prompt intersystem crossing yield". The scheme is summarized in Fig. 2 where the dotted line corresponding to prompt intersystem crossing may represent some very complex and interesting behaviour which should not be overlooked or underemphasized.

E. THE REACTIONS OF EXCITED STATES

The concern of this section will be the origin of the main reaction modes observed for Cr(III) complexes, namely photosubstitution, and in some cases isomerization and racemization. Redox processes will not be discussed.

The discussion of theoretical models for d^3 photochemistry of section C begged the important question of which excited states actually participate in reaction. The purpose of this section is to review as impartially as possible the experimental evidence bearing on this point.

The earliest model of d^3 photochemistry was of doublet photoreaction, apparently based on analogy with the organic triplet, the longer lifetime of the doublet, and the mistaken belief that the lowest doublet state possessed a vacant t_{2g} orbital [134] which would enable bonding of an entering solvent molecule. Doublet irradiation experiments eventually failed, however, to reveal any increase in quantum yield, causing this model to fall into disfavor [18].

An analysis of the temperature dependence of emission and photochemistry between -195 and 25°C of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ (reineckate) led to the suggestion that quartet reactivity occurred [76]. This was first proved directly, however, by the observations of Chen and Porter [135,136] that a 50% unquenchable yield of photoreaction remained on quenching the phosphorescence of reineckate with $[Cr(CN)_6]^{3-}$ in CH_3OH/H_2O/ethylene glycol solvent at -65°C.

Similar quenching experiments on other complexes [18,62] have since demonstrated the frequent occurrence of quartet reaction. The experiments have left open, however, the question of the mechanism of the quenchable fraction of the reaction. It may be from the doublet itself or via reverse intersystem crossing and further quartet reaction, Fig. 2. A general kinetic analysis indicates that this can involve multiple passes [17,62,137] through the doublet and quartet states where forward and reverse intersystem crossings are fast. Some of the evidence bearing on the rates of these processes has been referred to in the previous section. In light of the importance of this question, and the likelihood that any generalizations will be false, the evidence available for specific O_h and non-O_h complexes will now be considered.

(i) $[Cr(CN)_6]^{3-}$

This molecule has been unambiguously demonstrated to undergo photosubstitution of cyanide in DMF by quartet reaction only. Wasgestian showed that the emission behaviour was very solvent dependent while the photochemistry changed little [42] and that quenching of the doublet emission in DMF/water solutions left the photochemical yield unchanged. The quantum yield in this medium is 0.11 and must therefore occur prior to the thermally equilibrated doublet. The obvious precursor to reaction is the quartet state, prior to intersystem crossing, but alternatives such as a distorted, vibrationally excited intermediate mixed state are possible in principle [62,137].

The observation that no reaction occurs from the vibrationally equilibrated doublet state is important. In DMF the doublet lifetime is very long, 6.5 ms [138]. Consequently the rate constant for doublet reaction must be very small compared with the value for the quartet state of $\geqslant 10^9$ s^{-1} that may be implied from failure to observe a phosphorescence rise time and also inferred by analogy with other systems. In water the reaction quantum yield drops only slightly, to 0.08, but the doublet lifetime is very much shorter, ca. 150 ns. This shows that the doublet quenching of $[Cr(CN)_6]^{3-}$ by water is an efficient, but non-reactive process. Also note that the activation energy of the non-radiative decay processes depopulating the doublet in competition with phosphorescence is moderately large ca. 8 kcal mol^{-1} and in addition shows some solvent and environmental dependence. The long doublet lifetime in DMF is consistent with the expectation of a large relaxed quartet/doublet spacing which therefore inhibits reverse intersystem crossing. The data on $[Cr(CN)_6]^{3-}$ are unequivocal and therefore serve as a very useful archetype for the less clearcut situations discussed next.

Note also that $[Cr(CN)_6]^{3-}$ is an important exception to the first of the emission rules mentioned earlier. For $[Cr(CN)_6]^{3-}$ the ligand field strength is large, yet the lifetime of ca. 150 ns in water [128] is quite short, and much shorter than in other solvents. Cyanide is readily thermally substituted in acidic aqueous solutions but as pointed out, the doublet quenching in water is non-reactive. The short lifetime cannot therefore be attributed to doublet reaction, as suggested to account for short doublet lifetimes [130–132] in other molecules.

(ii) t-$[Cr(NH_3)_2(NCS)_4]^-$

At −65°C in $H_2O/CH_3OH/C_2H_4(OH)_2$, 50% of the photoreaction occurs directly from the quartet [135,136] and the remainder was postulated to occur by reverse intersystem crossing and quartet reaction. In room temperature aqueous solutions the quantum yield of 0.31 is three times greater, but the doublet lifetime is now too short to permit quenching studies. Therefore the proportion of prompt quartet reaction under these conditions is not known.

A study [117] has been made of the emission lifetimes and their apparent activation energies ($E^{\ddagger}_{\mathrm{app}}$) in a series of solvents. These ranged from 6 to 200 ns and 9.7 to 14 kcal mol^{-1} respectively and showed a Barclay Butler type correlation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Gutierrez and Adamson [117] therefore concluded that a single process must be controlling the doublet lifetime in all these solvents and proposed that it was doublet chemical reaction rather than reverse intersystem crossing. Similar conclusions were reached in an independent study [112].

The arguments presented in favor of the choice of doublet chemical reaction as the mechanism were rather insecure. They were that: (1) the observed variation with solvent of $E^{\ddagger}_{\mathrm{app}}$ for phosphorescence was not reflected in changes in the ground state absorption spectrum, suggesting no variation in relaxed excited quartet state energy ($^4L^0_1$); (2) the doublet excited state absorption spectrum appeared the same in acetonitrile, and a low temperature glass, reflecting no solvent effect on $^4L^0_1/^2D^0_1$ energy spacing; and (3) the rate constant for the apparent chemical reaction of the doublet varied in parallel with the ground state thermal substitution rate constant.

With regard to (1) the writer has already presented the argument and some evidence that changes in the $^4L^0_1$ energy with solvent would not necessarily be accompanied by wavelength shifts in the ground state absorption spectral maximum. With regard to (2) it is to be expected that the solvent dependence of $E(^4L^0_1) - E(^2D^0_1)$ would reflect mainly the changes in $E(^4L^0_1)$ which are likely to be noticeable rather than in $E(^2D^0_1)$ for which there is excellent emission evidence for the solvent independence. The reference to the solvent independence of the doublet ESA spectrum is completely irrelevant to the question of the energy of $^4L^0_1$; no observations of the highly relevant $^4L_1^0$ absorption spectrum have yet been reported. Finally the parallel variation of ground state and apparent doublet reactivity rate constants does not establish any casual relationships.

These and some other arguments and conclusions of Gutierrez and Adamson [117] have been analysed in detail by Shipley and Linck [139] who present the case that they equally well support the reverse intersystem crossing/quartet reaction mechanism. Further the latter authors emphasize the absence of any increase in photosubstitution quantum yield on doublet irradiation of $[Cr(NH_3)_2(NCS)_4]^-$. This observation is one of the more direct bases for the mechanistic choice, but in reply it has been correctly pointed out [140] that there is in this system uncertainty as to the extent to which "doublet irradiation" actually populates the doublet alone since the doublet absorption feature is overlaid by the tail of the quartet band. It has also been pointed out [141] that values for the reaction efficiencies and intersystem crossing yield can be chosen such that no increase would be expected.

Apart from the crucial question of the extent to which "doublet irradiation" populates only the doublet, the facts by and large are undisputed. Since, however, both protagonists can satisfactorily marshall the basic $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ correlation and values to support either side of the case, it must be concluded that the original authors have failed to prove their case for doublet reaction, and that the mechanism of the quenchable reaction in this molecule remains an open question.

(iii) $[Cr(bpy)_3]^{3+}/[Cr(phen)_3]^{3+}$

The emission, photophysics and photochemistry of these polypyridyl complexes and their substituted analogues has been the subject of a very recent review in this journal [22], and therefore little will be added here. An extensive series of studies has shown that the intersystem crossing yields in these complexes approach 1 and except for rather small unquenchable yields, about 10^{-3}, the photochemistry of these molecules occurs via the doublet state. The pH dependence of the photoreaction parallels that of the ground state thermal reaction, and the reaction has been argued to occur directly from the doublet state.

We note that the argument in favor of direct doublet reaction rather than reverse intersystem crossing and quartet reaction rests on two points: (1) the intersystem crossing yield is $\geqslant 0.97$, therefore the maximum value for the efficiency of quartet reaction is 0.03; (2) the estimated spacing $E(^4L_1^0) - E(^2D_1^0)$ of $\geqslant 20$ kcal mol^{-1} based on the spectral assignment for $[Cr(bpy)_3]^{3+}$ is too large for reverse intersystem crossing to be important. These being correct the arguments are secure. Now that prompt intersystem crossing has been established to occur in other systems the observation that $\phi^2E \geqslant 0.97$ no longer implies inefficient $^4L_1^0$ reaction; it leaves this efficiency completely unknown. This change enables one to model the system differently than set out initially, including a quartet reactivity model. Any mechanism involving reverse intersystem crossing and quartet reaction nevertheless requires $E(^4L_1^0)-E(^2D_1^0)$ to be of the order of 8–9 kcal mol^{-1}, the measured emission apparent activation energy, and therefore less than one half of the spectroscopic estimate. Whether this is possible depends on one's beliefs about the possible energy changes arising from the quartet relaxation in solution and one's confidence in the spectroscopic assignments. Despite these comments this is the best established class of molecules supporting direct doublet reaction.

(iv) $[Cr(en)_3]^{3+}/[Cr(NH_3)_6]^{3+}$

$[\mathrm{Cr(en)_3}]^{3+}$ undergoes photoaquation with $\phi = 0.37$ and 60% of the reaction was shown to be quenchable by metal ions [142]. The quartet therefore reacts directly. A laser flash photolysis study [143] using optical detection techniques showed that some reaction occurred during the 15 ns flash and some thereafter with the doublet lifetime. The ratio of this prompt to slow photochemistry(R) was about 2.5 to 1, a result which has recently been confirmed by a laser flash experiment using conductivity as the detection technique [144]. The optical and conductivity methods therefore show that 70% of the reaction proceeds via the doublet, in agreement with the chemical quenching results.

From a study of the wavelength dependence of R in the study mentioned, it was concluded that the doublet reacted directly, a conclusion which has since been challenged [137,145]. A re-evaluation [137] of the data of Fukuda et al. [143] which allowed for systematic errors, and more importantly elaborated the kinetic scheme to allow for multiple passes through the quartet state, better supports the opposite conclusion, that of reverse intersystem crossing and quartet reaction, although the uncertainties are large and the conclusion therefore insecure.

Note also that for this complex the doublet reactivity model requires more than a doubling of the quantum yield on irradiation directly into the doublet absorption band. In this molecule the doublet is very sharp and well-defined and has been assigned on the basis of the circular dichroism and circularly polarized emission [146]. The latter data suggest that the ^2E and $^2T_{1g}$ absorptions, which are clearly to be seen in this work are not overlaid by the tail of the quartet to any overwhelming extent (for broad band irradiation at wavelengths longer than 625 nm a generous estimate of the quartet contribution would be 50% of the total absorption). The measurements of the quantum yield of photochemistry on doublet irradiation reported to date [36,142] do not reveal any increase within experimental error. In the latest study, Cimolino and Linck [145] find also that the product distribution, including stereochemistry (they show that both *cis*- and *trans*-$[Cr(en)_2(enH)H_2O]^{4+}$ are products, the former exhibiting some retention of optical activity after photolysis of Λ-$Cr(en)_3^{3+}$) is the same on quartet or doublet irradiation. This result is further evidence against the doublet reactivity model, but is weakened by the fact that only 30% of the reaction goes promptly via the quartet under any circumstances, requiring small experimental error in the isomer analysis to be sure of a significant result. Cimolino and Linck also find significantly different product molar absorptivity values from those used by Fukuda et al., casting further doubt on their proof of a doublet reactivity model.

A recent study [147] of Δ- and Λ-$[Cr(en)_3]^{3+}$ photoracemization has, incidentally, suggested that this process occurs ($\phi = 0.015$) by a separate mechanism from the more dominant photosubstitution, and the authors propose a twist mechanism via the trigonal prismatic intermediate implied by the calculations of Burdett [96].

$[Cr(NH_3)_6]^{3+}$ seems to behave very similarly; 70% of the photochemistry is quenchable [31,148] and the lifetime of the doublet state is essentially the same as for $[Cr(en)_3]^{3+}$ under photochemical conditions. There was again no increase in ϕ_{chem} on irradiation in the doublet region [24]. A recent comparison of photoaquation and anation showed [32] the two processes to be competitive, with the total quantum yield (0.45) independent of anion concentration up to 8 M (Cl^-). An extension of this work [148] shows that photoanation and aquation remain competitive under conditions where doublet is quenched completely or not at all. The total quantum yield for all modes was 0.45 under unquenched conditions and 0.14 under quenched conditions and the competition between Br^-, Cl^- and H_2O was the same under both circumstances. Also with an assumed intersystem crossing yield of 0.7 it was found that the reaction efficiencies via doublet and quartet were the same, 0.45. These results were taken to indicate a common reactive species for the two reaction routes, and this was proposed to be a Jahn–Teller distorted configuration of the molecule lying close to the ground state potential surface and accessible either from the Franck–Condon excited quartet state or from the doublet.

For these two molecules then, in the conventional description, quartet reaction occurs promptly, followed by a slow photochemistry via the doublet state, most probably via reverse intersystem crossing and further quartet reaction, the kinetics requiring multiple passes through the doublet state but not requiring an equilibrium between quartet and doublet [137].

(v) t-$[Cr(en)_2(NCS)_2]^+$

Many studies of photochemistry of mixed ligand complexes showing two or more reaction modes have revealed wavelength and temperature dependencies of the reaction mode ratio and therefore require participation of more than one excited state. Also for some systems sensitization experiments, the interpretations of which were unfortunately blurred due to lack of spin restrictions on the energy transfer, have revealed different product ratios for the direct and sensitized reactions. The approach of using quenchers to explore in such systems the rôle of doublet versus quartet was clearly promising. The difficulty, however, was to find suitable systems meeting the requirements, namely two significant reaction modes and a doublet state of sufficiently long lifetime to be quenched and which also ideally would emit under photochemical conditions.

One such molecule is t-$[Cr(en)_2(NCS)_2]^+$ and this was the subject of a very elegant study [62] in which the sensitized emission and photochemistry, the wavelength dependence of emission yield and product quantum yields and the quenching by $[Cr(CN)_6]^{3-}$ were all studied to give a very clear picture of the behaviour of the molecule.

First, from the emission sensitization studies it was concluded that the total intersystem crossing efficiency was 0.8 except in the tail (long wavelengths) of the first quartet absorption when it dropped to about 0.6 (it also fell for irradiation into the charge transfer bands). This result parallels the observations for O_h complexes discussed earlier. Second the total quantum yield of reaction and the ratio ϕ_{NCS^-}/ϕ_{en} were constant at 0.25 and 2.6 for ligand field band irradiation although the thiocyanate yield dropped by 30% for charge transfer irradiation. Finally, complete quenching of the emission by $[Cr(CN)_6]^{3-}$ left 20% of the reaction unquenched, and most important the ratio ϕ_{NCS^-}/ϕ_{en} was the same for the quenched and unquenched reaction. Thus the reaction mode ratio was shown to be the same for the reaction from the quartet and via the doublet, providing strong support for the reverse intersystem crossing/quartet pathway for the latter. We note parenthetically that one uncertainty to which such quenching experiments are vulnerable is reactive quenching. Indeed this has been demonstrated to occur in the hydroxide ion quenching of this complex [149], where it introduces a new pathway for thiocyanate aquation. With $[Cr(CN)_6]^{3-}$, however, the quenching seems "innocent" and similar quenching results are obtained with the very different species $Ni(gly)_2$ and $[Co(NH_3)_5Cl]^{2+}$. Furthermore $[Co(CN)_6]^{3-}$ does not quench [149].

Returning to the interpretation of these results, they seem strongly to require a mechanism of quartet reaction only, unless fortuitously the quartet and doublet should give the same ϕ_{NCS^-}/ϕ_{en}, and this was the interpretation of the original authors. They recognized that spin orbit coupling mixes the quartet and doublet states leading to an upper state with a double minimum, one of doublet, X, and one of quartet character, Y. Low energy excitation would produce Y preferentially; excitation at energies above the crossing point of the two potential surfaces would lead to branching to both X and Y. The model parallels the mixed state description of the absorption process mentioned earlier, as that of Krause and Wasgestian [148] just described, and also is equivalent to a description involving prompt intersystem crossing in competition with vibrational equilibration. These are all equivalent to the basic kinetic scheme shown in Fig. 2. Sandrini et al. [62] analysed their results in such terms (actually in somewhat more detail) and were able with few assumptions to fit their data with the following parameter values: $\eta_{\mathrm{pisc}} = 0.5$; $\eta_{\mathrm{isc}} = 0.6$; $\eta_{\mathrm{risc}} =$ ca. 1.0; $\eta_{\mathrm{qr}} = 0.1$.

The data for this molecule therefore provide a good case for reaction from quartet alone, and identifies the process controlling the doublet lifetime as reverse intersystem crossing. This process has been shown [130] to have an apparent activation energy of 7.6 kcal mol^{-1}; 6.1 ± 0.3 kcal mol^{-1} was earlier reported [120,150], and an *A* factor of about 10^{11}, on this model placing $E(^4L_1^0)$ at this energy or less above the relaxed doublet level.

(vi) *t*-$[Cr(en)_2NCSF]^+$

This molecule also shows two reaction modes with $\phi_{\mathrm{tot}} = 0.38$ and $\phi_{\mathrm{NCS}}/\phi_{\mathrm{en}}$ about 2.5 and wavelength independent and temperature independent for wavelengths $\leqslant 436$ nm. For irradiation at 546 or 578 nm $\phi_{\mathrm{NCS}}/\phi_{\mathrm{en}}$ increases and becomes temperature dependent; the apparent activation energies at 546 nm were ca. 2 kcal mol^{-1} for thiocyanate and 6 kcal mol^{-1} for ethylenediamine [63]. Similar behaviour has been reported for some other systems [50,53]. These results were explained in terms very similar to those outlined above for $[\mathrm{Cr(en)_2(NCS)_2}]^+$. Excitation below the crossing point gives rise to temperature dependent yield ratios, above gives temperature independent branching to the participating states. In this model, however, the participating states considered were the equilibrated split quartet states $^4B_2^0$ (predicted to lose ethylenediamine by theory) and $^4E^0$ (predicted to lose thiocyanate and also ethylenediamine by theory).

A quenching study has provided further evidence [152]. *Trans*-$[\mathrm{Cr(en)_2NCSF}]^+$ phosphoresces in aqueous solution with $\phi = 1.1 \times 10^{-4}$, lifetime about 300 ns and is quenchable by $[\mathrm{Cr(CN)_6}]^{3-}$. Complete emission quenching leaves all of the thiocyanate and most (85%) of the ethylenediamine quenched when irradiated at 546 nm. For irradiation at 436 nm again all of the thiocyanate mode is quenched but only 62% of the ethylenediamine. For the quenchable part of the photochemistry, which occurs via the doublet, $\phi_{NCS^-}/\phi_{en} \approx 4$ for both irradiation wavelengths, but the doublet yield increases with irradiation energy as does the unquenchable ethylenediamine mode. Obviously this does not fit the conventional picture that assigns an increase in reaction quantum yield with decreasing wavelength to an increase in doublet yield since the mode which increases the most, ethylenediamine, is that which is unquenchable. The results fit well with a model of quenchable thiocyanate and ethylenediamine aquation from the lowest quartet/lowest doublet, facilely intercommunicating as in $[Cr(en)_2(NCS)_2]^+$, and unquenchable reaction in parallel. This might be prompt but it seems significant that it is specifically ethylenediamine aquation. It was therefore postulated to occur from the $^4B_2^0$ state with a high efficiency (η = ca. 1.0). It was also suggested that the mechanism of the quenchable reaction might be reverse intersystem crossing to $^4E^0$ for the thiocyanate mode, and to $^4B_2^0$ for the ethylenediamine mode in a 4:1 ratio. This would be consistent with the larger apparent activation energy observed for the ethylenediamine mode.

(vii) *trans*-$[Cr(en)_2F_2]^+$/*trans*-$[Cr(en)_2NH_3F]^{2+}$

As mentioned earlier the first of these molecules in aqueous room temperature solution emits a weak ($\phi = 1.7 \times 10^{-4}$) broad ($\Delta\nu_{1/2} = 0.147\ \mu m^{-1}$) emission [121] of 1.9 μs lifetime [153] which therefore has the characteristics of delayed fluorescence, establishing the importance of reverse intersystem crossing. Also the emission decay is a single exponential with no evidence of any fast fluorescence showing that prompt intersystem crossing is efficient and that essentially all population of the emitting quartet state occurs via the doublet.

Under these same conditions the molecule photolyses with $\phi = 0.35$ [67] and approximately 70–80% of the photoreaction is quenchable [153]. In product absorption monitoring experiments, similar to those for $[Cr(en)_3]^{3+}$, both fast and slow photoproduct production (with 1.9 μs lifetime) are seen and the slow fraction is quenchable by $[Cr(CN)_6]^{3-}$ in parallel with the emission [153]. Similar results have been obtained with *trans*-$[Cr(en)_2NH_3F]^{2+}$, but for this molecule the emission is not at present so firmly assignable as fluorescence.

Two important conclusions can be drawn from these observations:

(1) the fast photochemistry occurs prior to the thermally equilibrated quartet excited state;

(2) that prompt intersystem crossing is efficient, $\eta_{pisc} \rightarrow 0.9$ and is the only significant route for doublet population, consistent with (1). The kinetic analysis of these data leaves room either for direct doublet reaction or for reverse intersystem crossing/quartet reaction, but the circumstantial evi-

dence in favour of the latter is strong. Finally note the strong similarity in overall behaviour between this system and $[Cr(en)_3]^{3+}$; they differ only in the type of emission.

To summarize this section on quartet versus doublet reactivity: one complex reacts only via the quartet, several via quartet and doublet, and several essentially only via the doublet. For those reacting via the doublet, several show strong evidence for reverse intersystem crossing and quartet reaction, with difficulties in the way of a doublet reaction mechanism, although it can not usually be entirely excluded. The polypyridyl complexes show strong evidence for doublet reaction in alkaline solutions, with difficulties in the way of a quartet mechanism although that also may not be entirely excluded.

F. MEDIUM AND OTHER EFFECTS ON PHOTOCHEMISTRY

There have been relatively few studies of the effect of medium, including different solvents, on the reaction modes, quantum yields and stereochemistry of chromium(III) complexes.

The photolysis of the chloropentakis(alkylamino)- compounds was essentially the same [154] in water or in acetone although the chloride quantum yields were smaller in the latter.

A subsequent study [155] of *trans*-$[Cr(en)_2NCSF]^+$ and *trans*-$[Cr(NH_3)_2(NCS)_4]^+$ in various solvents showed that for the anion the yield was sensitive to solvent and mole fraction of water, but for the cation it varied only slightly. This was attributed to the very specific role of the coordinated water, and it was postulated that for the cation the coordination sphere water would be correctly oriented for substitution, but for the anion rotation would be necessary during which time excited state radiationless decay could occur. This type of model has been supported by some of the luminescence work. A further study [156] showed that the cation photochemical reaction yield, here, *t*-$[Cr(en)_2(NCS)_2]^+$, was linear in the Guttman donor number of the solvent, supporting an associative model for photosubstitution at Cr(III). In this study the yield for the anion correlated with the solvent fluidity, consistent again with the importance of solvent reorientation for successful reaction.

Further evidence for the associative nature of Cr(III) photochemistry was obtained from a study [157] of the photoanation of $[Cr(dmso)_6]^{3+}$ in dmso where the limiting azide photoanation yield was approximately three times larger than for thiocyanate, inconsistent with a dissociative mechanism involving scavenging of a five coordinate intermediate.

The studies [32,148] of chloride photoanation of $[Cr(NH_3)_6]^{3-}$ for which photoanation was directly competitive with aquation have been mentioned.

The evidence suggested the photoanation mode derived only from chloride$^-$ containing ion pairs and a (dissociative) interchange mechanism, proceeding through a trigonal prismatic transition state was proposed. Such a trigonal prismatic species, in a different context, has been proposed elsewhere [96,147].

For $[Cr(bpy)_3]^{3+}$, photolysis in DMF has been found [158,159] to lead to an autocatalytic chain reaction involving a Cr(II)–bipyridine complex as the chain carrier. The Cr(II) arises from oxidation of the solvent DMF; this is also thermodynamically feasible in water but does not occur in that solvent. While $[Cr(bpy)_3]^{3+}$ is perhaps not typical, the work does emphasize the possibility of a complete change of mechanism on changing solvent. Also note the recent review [21] of solvent and environmental effects on the spectrum, luminescence and photosubstitution quantum yield of $[Cr(bpy)_3]^{3+}$.

A similar strong dependence of the quantum yield of redox reaction with solvent has been reported [28] for *trans*-tris(1,1,1-trifluoro-2,4-pentanedionato)-chromium(III) where ϕ_{redox} ranged over an order of magnitude between benzene, cyclohexane and alcoholic solvents.

The extensive stereochemical change observed for Cr(III) photochemistry led to the suggestion [14] that the reactions were associative, an argument since rendered impotent by the VC theory of photostereochemistry. Some of the additional evidence from solvent and photoanation studies has just been mentioned. A third approach to the question of the dissociative/associative nature of the photoreactions is the study of the pressure effect on the quantum yield. Angermann et al. have recently shown [34] that apparent volumes of activation ($\Delta V_R^{\ddagger}$) for the excited state rate constants for loss of X and NH_3 in $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5X]^{2+}$ for $X = Cl^-$, Br^-, NCS^- are negative (-10.8, -10.2 and -8.6 ml mol^{-1} for X respectively and 13–9 ml mol^{-1} for NH_3). This supports an associate mechanism for both X and NH_3 photoaquation.

A possible uncertainty in the interpretation of this experiment arises from uncertainty as to the effect of pressure on excited state lifetime (remember that for example, in $[Cr(NH_3)_6]^{3+}$ 70% reaction occurs via the doublet). It has recently been found [160] that the doublet lifetime for $[Cr(en)_3]^{3+}$ decreases by only about 15% in raising the pressure to 2.3 k bar, corresponding to an apparent volume of activation for the doublet decay rate constant of about 2 ml mol^{-1}. If a main process depleting the doublet state were reaction with a large negative apparent activation volume then this should have been reflected in the doublet lifetime pressure variation. It is therefore more consistent with reverse intersystem crossing to the quartet (anticipated to involve minimum $\Delta V^{\ddagger}$) with reaction from the quartet being rate controlling and giving rise to the observed $\Delta V^{\ddagger}$.

In this same work [160], less than 10% change in lifetime with pressure was observed for $[Cr(bpy)_3]^{3+}$ with $\Delta V^{\ddagger} = -0.9 \pm 0.2$. This result seems inconsistent with the established doublet reaction mechanism (which predicts 3 ml mol^{-1}). However, the pressure dependence of lifetime is not as good a criterion as that of reaction and so this pressure dependence is currently being investigated [161] to clarify this point.

It will be evident that the work on solvent dependence and on pressure dependence has been limited in extent up to this point. These approaches, particularly the latter, have considerable potential to further clarify our understanding of Cr(III) photochemistry and should be pursued further.

G. PHOTOSTEREOCHEMISTRY: FURTHER ASPECTS

The data of Tables 2 and 3 have shown that the "axial" labilization of a chromium(III) complex to give a solvent substituted product occurs with stereochemical change. Some effort has been expended to demonstrate that the degree of this stereochemical change is high [50,53,55,58–60,63,162]. That stereochemical change is a strong requirement and almost universal for axial ligand loss has been demonstrated fairly clearly and is one of the few undisputed findings in Cr(III) photochemistry.

The situation for equatorial labilization has not been so clear [65–67]. This is in some measure owing to the restricted number of complexes which show an equatorial photoreaction mode with adequate yield, mostly those that contain fluoride or cyanide ligands on axis. It is also owing, however, to the fact that for equatorial ligand loss, D_{4h} or C_{2v} complexes of the type $[CrA_4XY]$ are inadequately stereochemically signposted to establish unambiguously whether the retained product arises by a retentive or non-retentive pathway, so there is a built-in uncertainty in the experiment.

The first studied compound, *trans*-$[Cr(en)_2F_2]^+$, has now been shown to give products consistent with stereochemical change, but with a large uncertainty as to the extent since the "retained" product is reported to predominate [65–67].

A comparison of the photochemistry of *trans*-$[Cr(en)_2NH_3F]^{2+}$ (A) and $[Cr(NH_3)_5F]^{2+}$ (B), the first of which exhibits a minor ethylenediamine mode, was more illuminating although the interpretation of the results [90] strains the patience and credulity of the reader. The two molecules A and B show very similar wavelength and temperature dependences of their total quantum yields and the axial ammonia loss from A (a constant 65% of the reaction at shorter wavelengths) occurs with stereochemical change. Allowing for the better leaving group ability of ethylenediamine over ammonia [33] this implies a 19% equatorial ammonia loss in B under the same conditions. Assuming that axial ammonia loss in B is subject to complete stereochemical change (supported by the observations on A and other molecules, Tables 2 and 3) then the 15% *trans*-$[Cr(NH_3)_4FH_2O]^{2+}$ found in photolysis of B must arise from equatorial ammonia loss. This establishes a product mix of 80/20 *trans*/*cis*-$[Cr(NH_3)_4H_2OF]^{2+}$ from equatorial ammonia loss in B, demonstrating that extensive stereochemical change occurs. Very definitive results have now been obtained to show that *trans*-$[Cr(NH_3)_4F_2]^+$ [56] and $[Cr(NH_3)_4(CN)_2]^+$ [57] also aquate equatorial ammonia with stereochemical change.

It seems well established therefore that this phenomenon occurs in Cr(III) photochemistry with only few exceptions, and indeed some work has suggested it may even be a requirement of the mechanism of photosubstitution [69,70].

A possible explanation for the stereochemical change involves the excited state forming a seven coordinate transition state with entry of solvent *trans* to the leaving ligand [14]. This constitutes in effect an edge displacement model. Such a mechanism is supported by the idea that the vacant t_{2g} orbital plays an important role in facilitating attack by the entering solvent. Co(III) (d^6) excited states by comparison do not have this path available although they have equivalent sigma antibonding labilization, and the quantum yields of labilization are low and the stereochemical change does not occur. Indeed the photosubstitution pathways and yields for Cr(III) complexes constrained by the ligands to prevent the associative mechanism via the vacant t_{2g} orbital are strongly reminiscent of the behaviour of Co(III).

The simple edge displacement model accounts very well for the stereochemistry observed in axial and equatorial labilization of Cr(III). It may be fine-tuned by allowing for preferential migration of negatively charged ligands to avoid the entering ligand and this works very well in explaining product ratios for most systems. The model begs the important question of why the ligand always enters *trans* but this is not a major defect of the idea. As stated earlier the success of this model was the basis of the initial suggestion that Cr(III) photoreactions were associative [14].

With the advent of the VC theory of photostereochemistry [92] this is somewhat changed. The details of the model and its application to straightforward systems have been discussed in section C. In the remainder of this section the following questions will be considered:

(1) Does the VC theory adequately rationalize the existing data?

(2) Is there any evidence upon which a choice may be made between the VC theory and the edge displacement model? That is, do the molecules know about the VC symmetry restrictions!

(3) How good is the predictive capability of the model?

(4) Does the model reflect reality?

The VC theory [92] proceeds from the assumption that the path to products is predisposed by the formation (or incipient formation) of a "five coordinate intermediate", without the requirement necessarily for complete ligand dissociation. This intermediate is square pyramidal, sp, and as discussed earlier in section C undergoes an allowed rearrangement to a trigonal bipyramidal, tbp, intermediate which adds solvent in a symmetry restricted fashion to give the ground state of the product. This process was shown pictorially in Fig. 2 for the situation of axial labilization from the lowest quartet excited state of $[Cr(NH_3)_5Cl]^{2+}$.

This model adequately explains the gross photostereochemical behaviour of the majority of axially labilized complexes such as are listed in Tables 2 and 3. Vanquickenborne and Ceulemans limited their considerations to the situation, where, however, the predictions are always the same as from the edge displacement model. *Trans*-$[Cr(en)_2FCl]^+$ is one exception as it was reported [64] to give some *trans*-$[Cr(en)_2FH_2O]^{2+}$ product and Vanquickenborne and Ceulemans rationalized [92] this in terms of some rearrangement of the tbp intermediate (due to the σ/π donor properties of F^-) prior to solvent entry. Both the experimental observation [50] and this explanation have been questioned [90].

The work on $[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ photostereochemistry demanded an extension of the model to cover the situation of loss of the equatorial ligand and this was presented in terms of the one electron model by the writer [90] followed by a full analysis by Vanquickenborne and Ceulemans [163]. These analyses showed that in this theory in order to obtain any *trans* product, equatorial amine loss must lead to the excited state of the tbp intermediate (for which the selection rules for water entry are reversed) [92] derived by rearrangement of the sp intermediate produced by loss of equatorial amine from the ^4E state of the complex. Since this electronically excited tbp intermediate can in principle react in the excited state or deactivate to its ground state (yielding *cis* product) branching to produce both *trans* and *cis* product can be expected. Since mainly *trans* product is experimentally observed this implies that the tbp excited state reaction pathway has to predominate.

There remains a problem for the theory in that *trans*-$[Cr(en)_2NH_3F]^{2+}$ shows a temperature dependence of ϕ_{en}/ϕ_{NH_3} at 546 nm but not at shorter wavelengths, implying that these modes do not both completely arise from the same state as is required by the above explanation. The origin of this effect could be, however, elsewhere such as in other excited state participation or photoselection effects, e.g. population of $^4E^0$ species with different predispositions for reaction. Quenching experiments analogous to those for $[Cr(en)_2(NCS)_2]^+$ and $[Cr(en)_2NCSF]^+$ might illuminate this problem.

A very recent study [52] of $[Cr(NH_3)_5CN]^{2+}$ reveals that this molecule photosolvates to a 2:1 mixture of *cis*- and *trans*-$[Cr(NH_3)_4H_2OCN]^{2+}$. The authors concluded by analogy that the *trans* isomer most likely arose from equatorial amine loss but did not analyze the system in terms of the VC model, preferring to defer this to a study of *trans*-$[Cr(NH_3)_4(CN)_2]^+$ where the original position of the labilized ammonia is not in doubt.

On the basis of these data, rather inadequate in terms of the number and variety of equatorial labilizations, the VC theory gives a good account of the behaviour if it is assumed that the quartet state is reactive and that the tbp intermediates may be produced and react in their excited states. It will be noted, in the context of question (3) above, that by extension to excited state tbp reactions, with branching and reaction via ground state, the VC model introduces a new parameter, the branching ratio, and thereby the model loses much of its predictive power. To be fair this seems to be required by the complexity of nature.

The comparative photoaquation of *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$ has recently been used to attempt [56] to choose between the VC model and the edge-displacement model on the basis of the observed and predicted photostereochemistries. The molecules photoaquate ammonia efficiently ($\phi = 0.35$ and 0.45 respectively for irradiation in the lowest quartet state) with very minor loss of fluoride.

Trans-$[Cr(NH_3)_4F_2]^+$ gives 1,6-difluoro-2-aquotriammine chromium(III) (*mer* FWF) and 1,2-difluoro-6-aquotriammine chromium(III) (*mer* WFF) in a 1:2.5 ratio, while *cis* yielded these, plus 1,2,3-difluoro-aquo-triammine (*fac* WFF) additionally in a wavelength dependent manner (1:1.3:0.2 at 546 nm, 1:1.4:0.5 at 365 nm).

For *trans* these results are consistent with either the edge displacement model (which predicts statistically 1:1 *mer* FWF/*mer* WFF with preferential fluoride migration increasing *mer* WFF) or with the VC theory (equatorial NH_3 loss from the lowest ^4E_g state gives an excited state tbp which yields *mer* WFF, and deactivation of this to the ground state produces *mer* FWF). Neither model predicts *fac* WFF and only a negligible amount is found.

For *cis*, the edge displacement model predicts statistically for equatorial ammonia loss 1:1:2 proportions of *mer* FWF:*mer* WFF:*fac* WFF where preferential fluoride migration increases *mer* FWF. For axial ammonia loss it predicts 1:1 proportions of *mer* WFF:*fac* WFF. Therefore either axial or equatorial ammonia loss from *cis*-$[Cr(NH_3)_4F_2]^+$ should lead predominantly to *fac* WFF but experimentally this is the minor product. The edge displacement model fails miserably!

The application of the VC model to this molecule is complicated by the low symmetries encountered. A detailed analysis [56] shows that the lowest tbp intermediate derived from the lowest quartet excited state gives from its electronically excited state, *mer* and from its ground state, *mer* FWF. Thus the VC theory satisfactorily accounts for the low yields of *fac* WFF and provides a strong indication that the reaction pathway is indeed subject to a symmetry restriction.

The further analysis shows that the theory can also account for the directions of the observed wavelength dependencies of the product ratios (although these were not truly significant in light of the analytical uncertainties) if it is assumed that both ^4E and $^4B_2$ states react in a wavelength dependent proportion. It also accounts for the small amounts of *fac* WFF produced and its greater wavelength dependence.

There are some problems though. The most important is that the same excited state tbp is the main precursor of the photoreaction for both *cis* and *trans* and yet must for some reason branch to give quite different excited state/ground state reaction ratios in order to account for the differing *mer* product ratios for the two compounds. This perhaps suggests again that these processes cannot truly occur via the idealized tbp intermediates proposed but that these must have at least some memory of their past. It is unfortunate that an equivalent associative model, which might be able to circumvent this problem, appears to be too difficult to formulate. This suggests, however, that despite the impressive successes of this new theory, the reality is a bit more complex, and our answer to question (4) must be, "no, though it works quite well". Since the theory is now required to allow a different branching ratio for the same excited state intermediate produced from two different sources, the model has lost even more of its predictive power.

A similar study of *t*-$[Cr(NH_3)_4(CN)_2]^+$ has just appeared [57]. The molecule behaves very similarly to the difluoro analogue except that the product ratio is found to be opposite, namely 2:1 *mer* CN W CN:*mer* W CN CN. In this molecule the lowest excited quartet state is now $^4B_{2g}$ which will lose ammonia to give, in the VC theory, *mer* CN W CN only (this concurs with the major product in this example). To explain the *mer* W CN CN requires reaction also via the ^4E_g state which can give rise to the two *mer* isomers. The behaviour therefore is not disimilar to that for the *trans* difluoro and the reversal of the *mer* isomer proportion between the two systems is explicable. For the cyano complex, more than the fluoro, the VC theory demands participation in reaction of two quartet states. Whether this should be taken as evidence for reaction from other than the lowest excited quartet state is debatable, but it is worth mentioning.

The theory of photostereochemistry and its testing is in a fairly youthful stage and continued rapid development can be expected. It certainly seems that the VC theory is much superior to the edge displacement model. The main requirement, to the writer, of any new theory is the recognition of the associative character of Cr(III) photoreactions suggested by much of the evidence discussed elsewhere in the review.

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