Coordination Chemistry Reviews, 46 (1982) 159–244
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

PHOTOPHYSICS, PHOTOCHEMISTRY AND SOLAR ENERGY CONVERSION WITH TRIS(BIPYRIDYL)RUTHENIUM(II) AND ITS ANALOGUES

K. KALYANASUNDARAM

Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne (Switzerland)

(First received 28 August 1981; in revised form 5 January 1982)

CONTENTS

0010-8545/82/0000–0000/$21.50

ABBREVIATIONS

bpy	bipyridine (2,2′-derivative unless stated otherwise)
phen	phenanthroline (1,10 derivative unless stated otherwise)
terpy	terpyridine (2,2′,2″)
TPTZ	tripyridyl *s*-triazine (2, 4, 6)
en	ethylenediamine
acac	acetylacetone
ox	oxalate
py	pyridine
imid	imidazole
Me	methyl
Et	ethyl
iPr	isopropyl
t-Bu	t-butyl
SCE	saturated calomel electrode
NHE	normal hydrogen electrode
MLCT	metal to ligand charge transfer
LMCT	ligand to metal charge transfer
CTTS	charge transfer to solvent
phos	phosphorescence
fluor	fluorescence
ϕ, ph	phenyl (ϕ also used as a symbol for quantum yield)
EDTA	ethylenediamine tetraacetate (disodium salt)
NTA	nitrilotriacetic acid
TEOA	triethanolamine
TEA	triethylamine
DMA	N,N′-dimethylaniline
PTH	phenothiazine
MPTH	*N*-methylphenothiazine
AQS	anthraquinone-2,6-disulphonate
MV^{2+}	*N*,*N*′-dimethyl-4,4-bipyridinium dication (methyl viologen)
NMPz	*N*-methylpyrazinium
DMF	*N*,*N*′-dimethylformamide
bpz	bipyrazyl

A. INTRODUCTION

The field of inorganic photochemistry is currently experiencing a phenomenal growth. The excited state chemistry of tris-chelated complexes of Ru(II) with ligands 2,2′-bipyridyl and 1,10-phenanthroline, in particular, has attracted intense interest in recent years. As one of the few transition metal complexes that luminesces strongly in solution at room temperature and exhibits powerful photosentitisation capacity for electron- and energy-transfer processes, it has generated some lively debate on the fundamental questions concerning the factors that govern the excited state processes. Further impetus for more investigations has been the intriguing possibility of its capacity to split water into its elements by the utilisation of visible light. The literature on $Ru(bpy)_3^{2+}$ is consequently quite extensive and is growing rapidly. Our aim here is to illustrate some of the wide variety of photochemical studies on the bpy, phen complexes of Ru(II), in the hope of stimulating more in depths studies on this and related complexes of other transition metals. Topics under review here cover areas such as photophysical studies leading to the characterisation of the excited state manifold, photochemical investigations on quenching via redox and energy transfer, photoredox systems for the light induced H_2 and O_2 evolution from water, studies in photoelectrochemical cells including sensitization of semiconductor electrodes, photochemistry with surfactant derivatives as well as studies in multiphase systems of monolayers, micelles, vesicles, polyelectrolytes, zeolites, cellulose etc. The literature coverage is fairly extensive and an attempt has been made to provide a summary of existing data in the form of numerous tables. Several shorter reviews covering various topics under discussion already exist [1–15]. Unless stated otherwise, all studies refer to the tris-chelated complexes of Ru(II) with 2,2′-bipyridyl or 1,10-phenanthroline as ligands.

B. CHARACTERISATION OF THE EXCITED STATES

(i) Photophysical studies

For the characterisation of the excited state, there is hardly any other transition metal complex or organic molecule that has received more careful scrutiny and attention than the complex $Ru(bpy)_3^{2+}$. Table 1 presents a chronological listing of some of these studies [16–55]. Assignments of the orbital, spin labels to the various absorption bands and of luminescence has been very vacillatory. Numerous studies that have been carried out can be broadly classified into four main topics: (a) early studies leading to the assignment of the lowest emitting excited state as due to the MLCT in

TABLE 1

Photophysical studies and evolution of models on the nature of the luminescent and photoactive excited states of $Ru(bpy)_3^{2+}$

Year	Authors	Ref.	Processes studied and assignments
1959	Paris and Brandt	16	Emission; π^*-d CT fluor.
1964	Porter and Schläfer	17	Emission; $(^3T_{1g} \rightarrow {}^1A_{1g})$ $d-d$ (LF) phos.
1965	Crosby, Perkins and Klassen	18	Emission; $(^1T_{1g} \rightarrow {}^1A_{1g})$ $d-d$ (LF) fluor.
1966	Palmer and Piper	19	Polarised crystal spectra; CT
1967	Day and Sanders	21	Crystal field calc.
1967	Klassen and Crosby	20	Absorption, emission in low temp. glasses
1968	Klassen and Crosby	22	Absorption, emission of Ru^{2+} chelate, CT luminescence
1968	Demas and Crosby	23	
1968	Zuloaga and Kasha	24	Q. mech., spectral studies; CT fluor.
1968	Hanazaki and Nagakura	25	M.O. calc. on $Fe(bpy)_3^{3+}$; CT transitions in EPA
1969	Lytle and Hercules	26	Temp. dependence of τ, ϕ (80–285 K); CT phosphorescence
1970	Demas and Crosby	27	ϕ, τ at 77 K in alcohol glass; CT spin forbidden
1971	Demas and Crosby	28	
1973	Fujita and Kobayashi	29	Polarisation of emission in EPA at 77 K; lowest emitting triplet is $^3E \rightarrow {}^1A$
1973	Harrigan and Crosby	30	T vs. (ϕ, τ) in the range 2–70 K; an electronic coupling model involving three states
1973	Harrigan, Hager and Crosby	30a	
1974	Crosby, Hipps and Elfring	31	Emission at 2–10 K and magnetic field effects
1974	Baker and Crosby	31a	Assignment of spin labels to excited states
1975	Hager and Crosby	32	ϕ, τ for substituted bpy complexes; CT luminescence; rapid thermal relaxation among emitting levels
1975	Hager, Watts and Crosby	33	Theoretical correlations of energy level splittings and rate parameters
1975	Hipps and Crosby	34	Electron ion coupling model for $d\pi^*$ excited states
1975	Van Houten and Watts	35	T vs. (ϕ, τ) in H_2O in the range (273–373 K); isotope effects; two sets: a lower set of

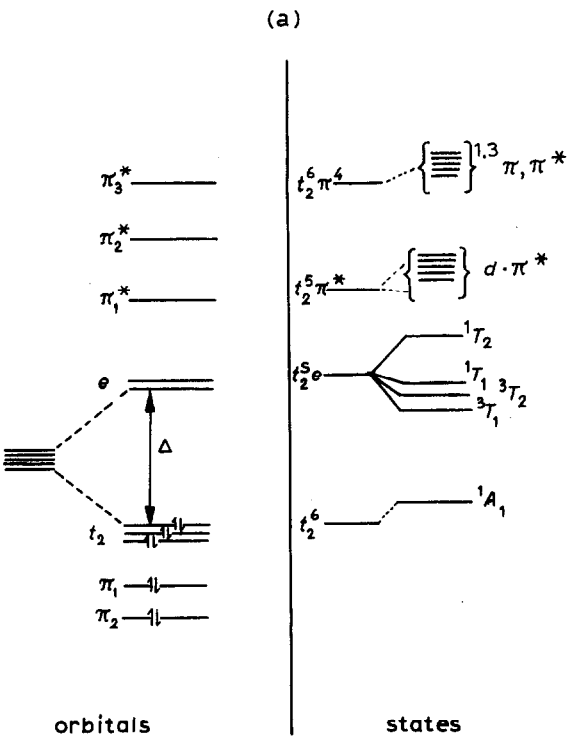
TABLE 1 (continued)

Year	Authors	Ref.	Processes studied and assignments
1976	Van Houten and Watts	36	luminescent CTTL type; upper sets nonluminescent, photo-substitutionally active
1976	Bensasson et al.	56	Transient absorption spectrum for the excited state by laser photolysis
1976	Allsopp et al.	37	T vs. (ϕ, τ) in various solvents; model for upper reactive excited state levels
1978	Allsopp et al.	38	T vs. (ϕ, τ) in various solvents; model for upper reactive excited state levels
1979	Lachish et al.	58	Reinvestigation of the transient absorption spectrum for the excited state by laser photolysis
1979	Creutz et al.	60	
1979	Bensasson et al.	59	
1979	Dallinger and Woodruff	39a	Resonance Raman spectrum for the charge transfer excited state of $Ru(bpy)_3^{2+}$
1979	Felix et al.	40	Polarised single crystal absorption at 8 K
1980	Felix et al.	41	Extent of spin orbit coupling: symmetry less than D_3 suggested for the excited state
1980	DeArmond et al.	43,46	Luminescence photoselection spectra at 77 K
1980	Hipps	42	Luminescence photoselection study: EIP model questioned
1981	Elfring and Crosby	45	Luminescence of mixed ligand complexes
1981	Belser et al.	44	CD spectrum of Δ-$Ru(bpy)_3^{2+}$ and spectral analysis
1981	Motten et al.	50	EPR of $Ru(bpy)_3^{+}$ and $Ru(bpy)_3^{-}$: one electron ring model
1981	Ceulemans et al.	52	Interpretation of photoselection data
1981	Forster and Hester	39	Resonance Raman spectrum for the excited state: detailed analysis

character; (b) low temperature (2–100 K) studies of luminescence quantum yields (ϕ) and of lifetimes (τ), leading to the development of the "closely coupled three-level model"; (c) studies of temperature dependence of ϕ, τ in

fluid solutions (273–373 K) and those in films (77–273 K) leading to the location of the upper photoreactive states and (d) complimentary studies of luminescence polarisation (photoselection), resonance Raman spectral studies and flash photolysis studies which cast doubt on D_3 symmetry descriptions for the excited state.

Before we elaborate the photophysical studies, towards a theoretical description of the excited states manifold, it is useful to digress a little on the localised molecular orbital model of the excited states. Figure 1(a) shows a simplified representation of the electronic situation for a d^6-complex (such as Ru(II)) in an octahedral microsymmetry (D_3). The ground and the low lying excited states can be discussed in terms of the t_{2g} (stabilised) and e_g (destabilised) d orbitals of the metal ion and π-bonding, π^*-antibonding orbitals of the ligand aromatic system. In a strong field configuration, the ground state would be $(t_{2g})^6$, leading to $^1A_1$ ground state label. One electron excitations would then lead to four possible orbital types for the excited states: $d \rightarrow d^*$, $d \rightarrow \pi^*$, $\pi \rightarrow d^*$ and $\pi \rightarrow \pi^*$, both singlets and triplets. Transitions such as promotion of an electron from t_2 to e orbitals are essentially confined to the metal and such $d \rightarrow d$ or metal-centred transitions give rise to weak (Laporte forbidden) absorption bands ($\epsilon =$ ca. 100). Excitation of a



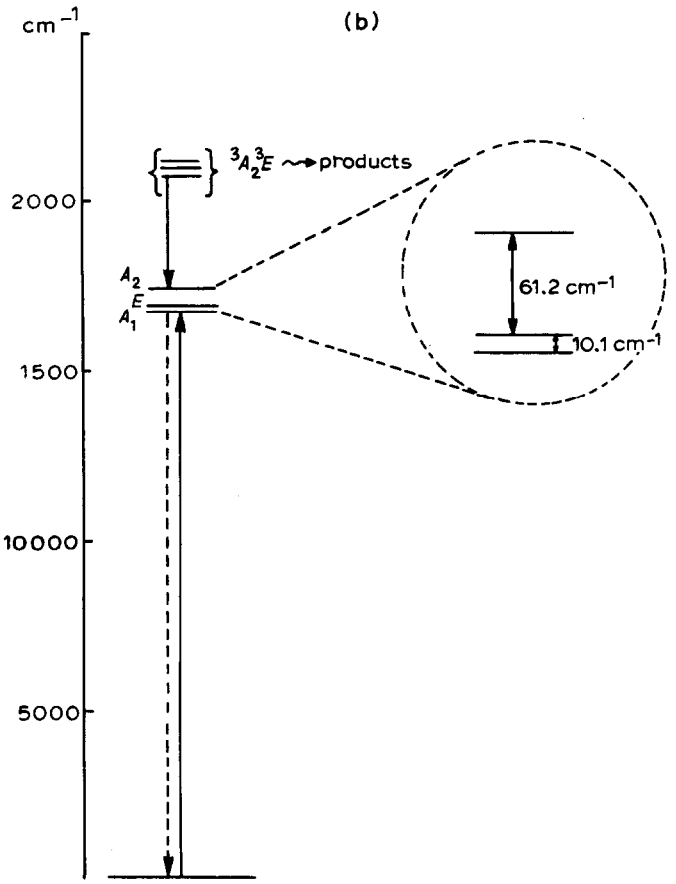


Fig. 1. Electronic state, orbital descriptions for the luminescent photoactive excited states of $Ru(bpy)_3^{2+}$.

metal t_2 electron to π^*-antibonding orbital on the ligand gives rise to $d \rightarrow \pi^*$ states. Such transitions involving transfer of electronic charge from the metal to the ligand (or vice versa) are labelled charge transfer (MLCT or LMCT) transitions. These transitions have significant absorptions in the visible region ($\epsilon =$ ca. 20,000–25,000). Transitions within the ligand π-bonding orbital to the π^*-antibonding orbital, labelled $\pi \rightarrow \pi^*$ or ligand-centred transitions, usually lie at high energies and are substantially ligand in character. In addition, in suitable cases there can be interactions with the solvent molecules leading to charge transfer to solvent (CTTS) transitions as well. These descriptions of transitions as metal-centred, ligand-centred or as charger transfer are somewhat arbitrary and they lose their meaning whenever the states cannot be described adequately with localised orbital configura-

tions. This is what actually caused considerable confusion in the assignment of absorption, emission bands of the $Ru(bpy)_3^{2+}$ over several years.

Figure 2 presents the absorption and the emission spectrum of the $Ru(bpy)_3^{2+}$ complex in aqueous solution at room temperature. Indicated therein are the current assignments for the various absorption bands [3,7]. Absorptions at $\lambda = 185$ nm ($\log \epsilon = 4.95$), 208 sh ($\log \epsilon = 4.67$) and 285 nm ($\log \epsilon = 4.94$) are easily assigned as ligand-centred π–π^* transitions by comparison with the spectrum of the protonated bipyridine ligand [26,60a,60b]. Similarly, the weak shoulders at 323 nm and at 345 nm ($\log \epsilon = 3.81$) as well as the twin peaks at 238 nm ($\log \epsilon = 4.47$) and at 250 nm ($\log \epsilon = 4.40$) are assigned to the metal centred d–d transitions. The intense absorption band in the visible with maximum at 452 nm ($\log \epsilon = 4.16$) is assigned to a CT transition in which an electron is promoted from the metal t_2 orbital to the excited t_1 orbital associated with the ligands (core $^2t_2^6 \rightarrow {}^2t_2^5\pi^*$). The assignment of the long wavelength absorption tail above 500 m (at 546 nm with $\epsilon = 700$) has been the object of long dispute. Crosby et al. [18] originally assigned it to a $d \rightarrow d$ transition due to its low extinction coefficient and later [22] labelled the tail as due to the vibrational component of the charge transfer band. Its recent assignment to a spin-forbidden MLCT

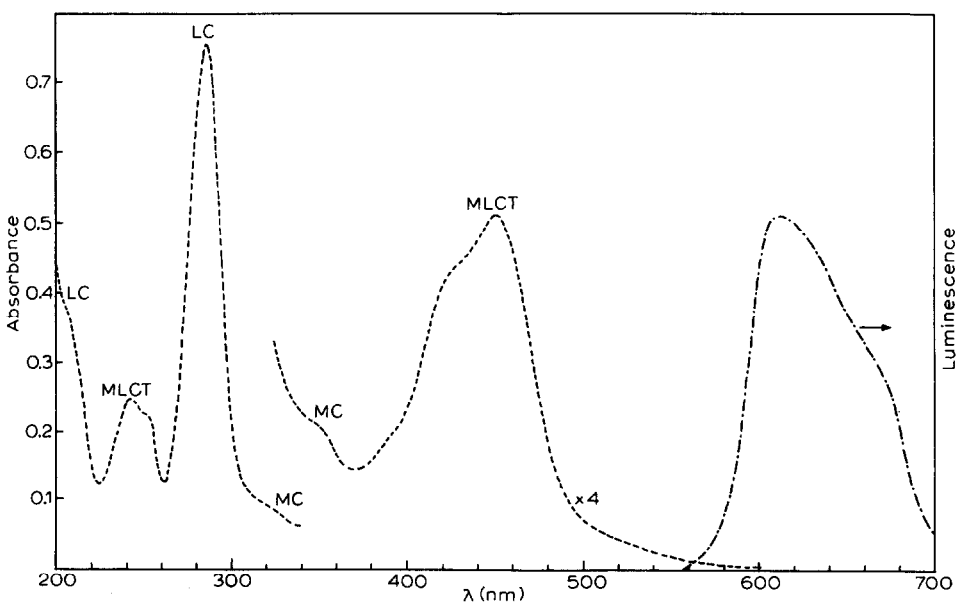


Fig. 2. Absorption and emission spectrum for $Ru(bpy)_3^{2+}$ in aqueous solution at room temperature along with the assignments for the various bands.

transition has been found to be consistent with various experimental results. It is also believed that it is this band which gives rise to the luminescence [24,26].

The orbital nature of the emitting state has long been a centre of controversy. $Ru(bpy)_3^{2+}$ shows a broad, structureless orange-yellow emission in solution at 293 K around 600 nm. In glassy solutions at 77 K however, the spectrum is well resolved. The band origins are at 579.9 nm for the $Ru(bpy)_3^{2+}$ and at 565 nm for the $Ru(phen)_3^{2+}$. At low temperatures both the absorption and the emission show vibrational progression with $\Delta\nu$ = ca. 1300 cm^{-1} for the bpy complex and $\Delta\nu$ = ca. 1700 cm^{-1} for the phen complex.

Paris and Brandt [16] initially assigned the emission as due to the π^*–d CT fluorescence and this was disputed by later authors who assigned it as due to d^*–d ligand field phosphorescence [17], d^*–d ligand field fluorescence [18], charge transfer [19,22] π^*–d charge transfer phosphorescence [26] and finally as π^*–d charge transfer luminescence with no specific multiplicity [22]. The reasons for the shift in assignments are wide. They range from identification of certain absorption bands to impurities, arguments based on similarity/dissimilarity of the absorption, emission bands of other d^6-complexes and long emission lifetimes usually associated with spin-forbidden triplet–singlet transitions. Crosby et al., in an elegant series of studies [3,18,20,22,23,27,28,30–34,45,47] extending over a decade, have attempted to provide a unifying, rational picture for the absorption and luminescence properties of the $Ru(bpy)_3^{2+}$ complex. These include synthesis and characterisation of optical properties of a series of substituted bpy, phen complexes and mixed ligand complexes with concomitant development of appropriate theoretical models. Table 2 summarises data on the absorption, redox and luminescence properties of the $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$ complexes in aqueous solution at 25°C. Table 3 presents similar data for a series of substituted Ru(II) complexes, both of the type RuL_3^{2+} and RuL_2X_2 (where L stands for some substituted bpy, phen ligand and X Cl, CN^-, ox, en, etc.) and also mixed ligand complexes. It is now firmly established that the luminescence from the RuL_3^{2+}-type complexes is essentially of charge transfer type, spin-forbidden in character at least at 77 K [28].

In $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, the unique, intense charge transfer emission occurs at lower energy than does ligand π–π^* phosphorescence in the free ligand. This in conjunction with the intense CT absorption bands implies a substantial metal d-ligand π interaction. If the magnitude of the d-orbital contribution is large, spin–orbit coupling associated with this system will mix singlets and triplets such that, for these systems spin quantum number S is not well defined. Consequently, the emission is better described as occurring from a manifold of spin–orbit states rather than from a spin triplet electronic state. The electronic states would then be delocalised

TABLE 2

Absorption, redox and luminescence properties of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ in aqueous solution at 25°C

Property [a]	$Ru(bpy)_3^{2+}$		$Ru(phen)_3^{2+}$	
Ground state absorption				
λ max (nm)	452, 345,285		447, 422, 262	
ε (mM)	14.6, 6.5, 87.0		19.0, 18.3, 115	
Redox potentials [60–67]	In H_2O (vs. NHE)	In CH_3CN (vs. SCE)	In CH_3CN (vs. SCE)	
E_0 ($Ru^{2+/3+}$), V	1.26	1.29	1.26	
E_0 ($Ru^{2+/+}$), V	−1.28	−1.33	−1.36	
E_0 ($Ru^{2+*/3+}$), V	−0.86	−0.81	−0.87	
E_0 ($Ru^{2+*/+}$), V	0.84	0.77	+0.82	
Excited state absorption [56–60]				
λ (nm)	310, 358, 452			
ε (mM)	27.3, 2.1			
φ	1.00			
Energy	2.12 eV			
Luminescence [28,36,43a,45]	Uncorrected	Corrected	Uncorrected	Corrected
Emission max. (298 K) (nm)	607 nm	613, 627 sh	593	605, 625
Emission max. (77 K) (EPA) (nm)	580, 633, 692		565, 610, 664, 726	
τ and φ (H_2O, 298 K)	0.62 μs, 0.042		0.92 μs	
τ, φ (EtOH, 77 K)	5.2 μs; 0.38		9.8 μs; 0.60	
φ (photoaquation, 75°C, HCl 1 M)	$\sim 10^{-3}$			
Stokes shift	1.1 kK			
Isotope effects [35]	φ (lum.)	τ (μs) (lum.)		
$Ru(bpy)_3^{2+}$ in H_2O, 25°C	0.04	0.62		
$Ru(bpy)_3^{2+}$ in D_2O, 25°C	0.07	1.02		
$Ru(bpy)_3^{2+}$-d_8 in H_2O, 25°C	0.047	0.69		
$Ru(bpy)_3^{2+}$-d_8 in D_2O, 25°C	0.079	1.25		

[a] τ = Lifetime; φ = quantum yield.

through the entire D_3 chelate system i.e., the orbitals are multi-ring orbitals as opposed to single chelate ring orbitals, as formulated for complexes of Rh(III). This would then imply an effective C_{2v} symmetry for the excited state. We elaborate more on this later.

Based on the luminescence quantum yields and decay characteristics in polymethylmethacrylate (PMMA) matrix, Crosby et al. [30,30a] proposed an electron-ion parent coupling (EIP) model and used it to assign the symmetries of the manifold of states inferred from the experimental data. The salient features of the model are as follows: (i) It treats the luminscence complex in terms of a $4d^5$ Ru core and three bpy ligands with one transferred electron in the lowest antibonding π^* orbital of the coupled ligands (belonging to the a_2 representation of point group D_3). (ii) Analysis leads to a set of three emitting levels separated by about 10 and 80 cm^{-1} respectively, whose relative populations are described by a Boltzmann distribution throughout the luminescence process. (iii) The symmetries of the three levels are A_1, E and A_2 in order of increasing energy. A schematic representation of this is shown in Fig. 1(b). Later in 1975, extending this model, Crosby et al. [32,33] predicted a temperature-dependent intensity distribution for the luminescence and also a strong z-polarised luminescence between 6 and 30 K and an unspecified polarisation below 6K. With the recent results on polarised absorption, emission data, the EIP model has been subject to some criticism.

Polarised single crystal absorption data of $Ru(bpy)_3^{2+}$ in $Zn(bpy)_3SO_4 \cdot 7H_2O$, $Zn(bpy)_3Br_2 \cdot 6\ H_2O$ host crystals has been reported by Palmer and Piper [19]. The absorption in the visible perpendicular to the C_3 axis is more than ten times as intense as that parallel to C_3, i.e. the CT absorptions are dominantly x–y polarised (z- is the three fold axis direction). Their results have recently been confirmed by Felix et al. [40,41] who noted the inequivalence of the x,y polarisation in the Br^--host crystal. These authors also associate the differences in the x–y polarised absorption coefficients with low site symmetry in the host. Photoselection data measured by Fujita and Kobayashi [29] and also by DeArmond et al. [43,46] also indicate dominant x,y polarisation in the emission of the $Ru(bpy)_3^{2+}$ complex in EPA host matrix at 77 K. The value for the limiting polarisation ratio $P = (I_{\|} - I_{\perp})/(I_{\|} + I_{\perp})$, however is far in excess of what one would predict for a purely x,y polarized absorption, followed by an x,y polarised emission. Hipps' measured P values of $> 1/7$ [42] cannot be obtained from a D_3 symmetry molecule whose emission is principally x,y polarised, irrespective of the absorption polarisation. The conclusions are that, the $Ru(bpy)_3^{2+}$ ion, in the PMM or EPA matrix is not of D_3 symmetry in its ground state and/or excited state. Such a situation would arise from either of the following two sources: (a) the ground state ion may have less than D_3 symmetry due to

TABLE 3

Absorption and luminescence properties of substituted bpy, phen complexes of Ru(II) [a]

Ru complex	Absorption	Emission	τ (77K)	τ (4K)	ϕ (77K)	Ref.
	λ_{max} (nm) and ϵ (mM)	λ (nm)at 77K	(μs)	(μs)		
(i) *RuL_3^{2+} type*						
$Ru(bpy)_3^{2+}$	456 (14.6), 286 (79.2), 244 (25.6)	584, 630, 680	5.3	129	0.376	28, 43a 45
$Ru(6\text{-}Mebpy)_3^{2+}$	448 (11.1), 293 (71.3), 247 (29.3)	585, 630	4.1		0.097	43a
$Ru(6,6'\text{-}Me_2bpy)_3^{2+}$	446 (7.44), 297 (51.8), 248 (21.5)	589, 636, 701	2.5		0.018	43a
$Ru(4,4'\text{-}Me_2bpy)_3^{2+}$	460 (16.3)		5.2		0.34	32, 33
$Ru(4,4'\text{-}\phi_2bpy)_3^{2+}$	474 (32.7)		4.7	100	0.57	30, 33 30b
$Ru(phen)_3^{2+}$	446 (19.0), 417 (18.1), 263 (113)	568, 614, 666	9.8	242	0.60	28, 43a 45

$Ru(2\text{-Mephen})_3^{2+}$	446 (14.4), 267 (104), 224 (95.3)	576, 615	5.9		0.122	43a
$Ru(2,9\text{-}Me_2phen)_3^{2+}$	501 (258), 270 (81.6), 232 (13.2)	588, 631	2.3		0.048	43a
$Ru(4,7\text{-}\phi_2phen)_3^{2+}$			9.8		0.68	30b, 36
$Ru((2'\text{-pyQn})bpy)_3^{2+}$	483	658				43b
$Ru((2,2'\text{-}Qn_2)bpy)_3^{2+}$	524 (9.0), 625 (1.5)	719, 760				43b
(ii) *$Ru(L_2L')$ type (mixed ligands)*						
$Ru((bpy)_2(4,4'\text{-}Me_2bpy))^{2+}$		586, 637, 694	5.2	116	0.35	45
$Ru((bpy)_2(4,4'\text{-}\phi_2bpy))^{2+}$		594, 645, 694	5.6	144	0.46	45
$Ru(bpy_2, phen)^{2+}$	447 (15.3), 425 (13.5)	575, 624, 676	6.6	166	0.44	45, 36a
$Ru(bpy)_2(5,6\text{-}Me_2phen)^{2+}$		577, 626, 678	6.1	154	0.42	45
$Ru(bpy)_2\cdot(4,7\text{-}Me_2phen)^{2+}$		583, 631, 680	5.6	140	0.38	45
$Ru(bpy)_2\cdot(4,7\text{-}\phi_2phen)^{2+}$	452 (14.8), 428 (13.9)	589, 639, 699	9.4	189	0.54	45
$Ru(phen_2, bpy)^{2+}$		570, 620, 666	9.1	203	0.56	45, 36a

[a] Absorption data are in CH_3OH at room temperature and emission data are in CH_3OH–EtOH glass (1:4, v/v) at 77 K. τ = Lifetime; ϕ = quantum yield.

asymmetric potential field of the surrounding environment and also to the formation of ion-pairs in low dielectric constant matrices, or (b) the ion may distort in the excited state with the excited electron localised in one of the three ligands.

The assignments of Felix et al. [40,41] that, "The two prominent peaks in the visible MLCT spectrum cannot be attributed to the vibrational structures of one single electronic transition but must instead be assigned to two different states." is in disagreement with refs. 34, 44, 52 and 52a. Measurement of the CD spectrum of Δ-$Ru(bpy)_3^{2+}$ in the region of MLCT [44] shows significant CD activity for the most intense visible absorption band.

The question as to whether the electron located on the ligands are delocalised in a MO extending over all the ligands or whether they are located on an orbital of one ligand remains to be solved [45]. The excited state resonance Raman data reported recently [39,39a] (the Raman spectra shows lines corresponding to reduced bpy ($bpy^{-\cdot}$) ligand) for the emitting state is the most direct evidence for the presence of single ring orbitals in the excited state of the complex. Other experimental evidence on this line comes from EPR [50] and flash photolysis [58–60] studies. Transient absorption spectrum for the emitting excited state show significant absorptions in the region corresponding to singly reduced bipyridyl anion ($bpy^{-\cdot}$). Similarly EPR of $Ru(bpy)_3^+$ suggests that the reduced electron is located on a single ligand rather than delocalised over the three. In solution, the electron hops from one ligand to another broadening the ESR line. In triply reduced $Ru(bpy)_3^-$, one electron is on each ligand and there is no hopping. Theoretical studies by Day et al. [21,55] and also of Kràl [53,54] are in accord with such models. Consistent with this line of interpretation are the recently reported absorption spectra of $[Ru(bpy)_3]^z$ species, $z = 2+, 1+, 0$ and -1 [51]. The spectra are shown in the insert in Figure 3. The fully reduced species $[Ru(bpy)_3]^-$ shows a detailed resemblance in band positions and structures to [Na(bpy)] and $[Mo(CO)_4(bpy)]^-$ which both contain chelated bpy^- radical anion. Also stepwise reduction of $[Ru(bpy)_3]^{2+}$ is accompanied by progressive growth of the bands which typify $[Ru(bpy)_3]^-$ and by matching loss of bands characteristic of the parent complex. Interestingly, the lower-valent Ru-complexes show significant absorption in the IR region. As will be shown later in section D, bpy, phen complexes of Ru(II) readily undergo photoredox reactions with a variety of molecules; reactions in which the excited state is either oxidised to give $Ru(bpy)_3^{3+}$ or reduced to yield $Ru(bpy)_3^+$. Such ease of oxidation or reduction of the excited state is often explained in terms of a model where the excited state has complete CT character with an electron deficient d^5 (Ru^{3+}) centre and an excess electron localised on one of the bpy ligands as in ($Ru^{3+}bpy_2.bpy^{-\cdot}$). The significant isotope effects in ϕ and τ observed for the luminescence (for data in H_2O,

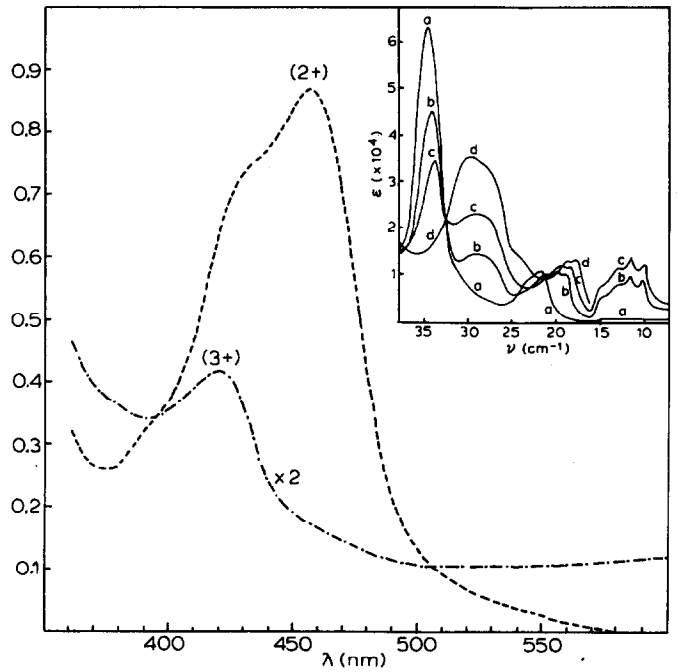


Fig. 3. Absorption spectrum of $Ru(bpy)_3^{3+}$ in 1 N H_2SO_4, prepared from the (2+) complex by oxidation with PbO_2. Shown in the insert are the absorption spectra of various reduced forms of $[Ru(bpy)_3]^z$ complexes with $z = +2$ (spectrum a); $z = +1$ (spectrum b); $z = 0$ (spectrum c); $z = -1$ (spectrum d).

D_2O see Table 2) suggest that the CT excited state also has considerable CTTS character.

Recently there have been some doubts as to the photochemical stability of the $Ru(bpy)_3^{2+}$ complex towards substitutional photochemistry, especially at elevated temperatures. As mentioned earlier, according to the EIP model, there exist three closely coupled levels, A_1, E and A_2 which are responsible for the luminescence at low temperatures 4–77 K. Based on the photoinertness of the complex to substitution and deuterium isotope effects on the emission, it has been proposed that the number of levels responsible for the properties of the complex to be nearly the same as at 77 K. However, extrapolation of Crosby's model to higher temperature leads to significant differences between the measured and calculated ϕ and τ. To reconcile the data, van Houten and Watts [36] have proposed another model which assumes, "A lower set of luminescent levels which undergo weakly coupled radiationless deactivation and a higher set of non-luminescent levels which undergo strongly coupled radiationless deactivation. The lower set of levels

are of CTTL character but modified with CTTS configurations. The lower levels are photoinert whereas the upper levels which are located at ca. 3600 cm^{-1} above the lower set, give rise to ligand substitutional photochemistry." Allsopp et al. [37,38] who also made a temperature dependence study of the luminescence (ϕ, τ) reached similar conclusions. A simplified model of the luminescent, photoactive excited states of the $Ru(bpy)_3^{2+}$, based on the above discussions is presented in Fig. 1b. More discussions on the substitutional photochemistry of $Ru(bpy)_3^{2+}$ can be found in section K.

(ii) Flash photolysis studies

With the availability of pulsed (nanosecond) laser flash photolysis facilities, attempts have been made to record the transient absorption spectrum corresponding to the luminescent excited state of $Ru(bpy)_3^{2+}$ by several authors [56–60]. Figure 4 presents the transient absorption spectrum [58] recorded at the end of a 20 ns 530 nm Nd laser pulse. It corresponds to the luminescent state of $Ru(bpy)_3^{2+}$. It has been verified to be so, by its similarity in lifetime to that of emission as well as its quenching in the presence of additives which effectively decrease luminescence ϕ and τ. Even though the spectrum reported earlier by Bensasson et al. [59] appears similar to this one, the extinction coefficients reported by these authors apparently are in error. An $\epsilon = 27{,}300$ for the peak around 360 nm is in good agreement with the value reported recently by Sutin and co-workers [60]. The extinction

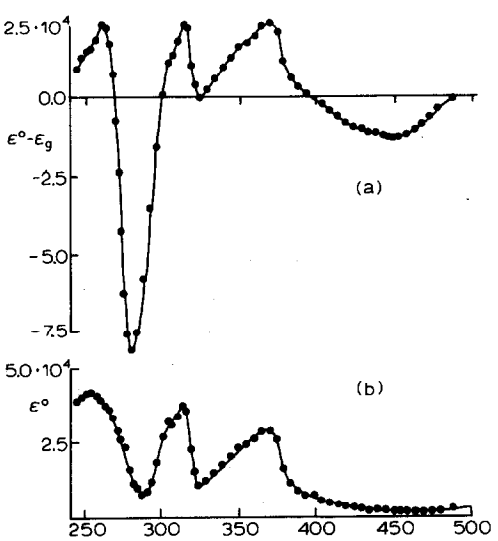


Fig. 4. Transient absorption spectrum for the luminescent excited state of $Ru(bpy)_3^{2+}$ in water at room temperature. (Spectrum recorded at the end of a 20 ns 530 nm Nd laser pulse.)

coefficient at the wavelength corresponding to the ground state absorption maximum, viz. at 452 nm, has been estimated to be 2100. The quantum yield for the formation of the CT excited state has been estimated to be 1.0 [28,59] and the luminescence lifetime in water at room temperature is about 620 ns Meisel et al., [59] have examined the transient absorption changes upon excitation in water with a conventional microsecond flash photolysis set up and have observed efficient formation of e^-_{aq}. by a photo ionisation process

$$Ru(bpy)_3^{2+} * \rightarrow Ru(bpy)_3^{3+} + e^-_{aq} \quad (1)$$

Photoionisation, however, occurs only upon excitation with UV light.

Flash photolysis is a powerful technique for the study of photoredox reactions for it allows a direct monitoring of the decay of the excited state as well as the formation and decay of the redox products. It enables one easily to distinguish quenching by redox process as against static, energy transfer processes and also determination of the rate constants for the forward and reverse electron transfer. As will be evident in section D, the technique has been used quite extensively in recent years in the study of $Ru(bpy)_3^{2+}$ photochemistry. Meyer et al. have developed an interesting variation of the technique (differential flash photolysis) and applied it to $Ru(bpy)_3^{2+}$ photochemistry. By monitoring the growth and decay of the photoredox products in the quenching of a non-luminescent, non absorbing excited state, they have shown that it is possible to estimate lifetimes for excited states not easily detectable. By competitive electron transfer, it is also possible to derive rate constants for electron transfer between various metal complexes.

C. ENERGETICS OF VARIOUS REDOX STATES OF $Ru(bpy)_3^{2+}$

A distinctive feature which makes studies with bpy, phen complexes extremely interesting and worthwhile is the ability to vary significantly the redox properties of the resulting metal complex by appropriate substituents in the ligand. Thus it is possible to fabricate Ru(II) complexes which are good oxidants or reductants in the excited state or in the ground state. Since the early electrochemical studies by Bard and co-workers [61] and of Saji and Aoyagui [62–66] on the $Ru(bpy)_3^{2+}$ complex, numerous bpy, phen complexes with various substituents have been synthesised and their redox properties assessed. Essential for deciphering excited state redox reactivity [67–74] is information on oxidation potentials for various redox states of the $Ru(bpy)_3^{2+}$ complex in the ground state. Cyclic voltammetric studies of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ show several reversible waves corresponding to successive one e^- oxidations and reductions and the following midpoint potentials were

readily evaluated:

Ru-complex and medium	Midpoint potential (V)				
	(3+/2+)	(2+/+)	(1+/0)	(0/−1)	(−1/−2)
$Ru(bpy)_3^{2+}$, H_2O (vs. NHE)	1.26	−1.28			
$Ru(bpy)_3^{2+}$, CH_3CN (vs. SCE)	+1.29	−1.33	−1.52	−1.76	−2.4
$Ru(phen)_3^{2+}$, CH_3CN (vs. SCE)	+1.36	−1.44	−1.54	−1.84	−2.24

Thus, the Ru complexes in the +3 state are good oxidants (capable of oxidising water to O_2 ($E_0(O_2/H_2O) = +1.23$ V)) and in the +1 state good reductants (capable of reducing water to H_2 ($E_0(H^+/H_2) = 0.0$ V)).

The Ru complex in the +3 oxidation state is readily prepared in acid solutions or nonaqueous media either by controlled potential electrolysis or with chemical oxidants such as PbO_2, Cl_2. In aqueous mildly acidic solutions, the $Ru(bpy)_3^{3+}$ is reduced to the +2 state in a thermal reaction with water. Figure 3 presents the absorption spectrum of $Ru(bpy)_3^{3+}$ in 1 N H_2SO_4 where the half life for reduction is several hours. The molar extinction coefficients at the absorption maxima are 3300 at 420 nm and 680 at 680 nm. The absorption in the red region is very broad. $Ru(bpy)_3^+$, however,

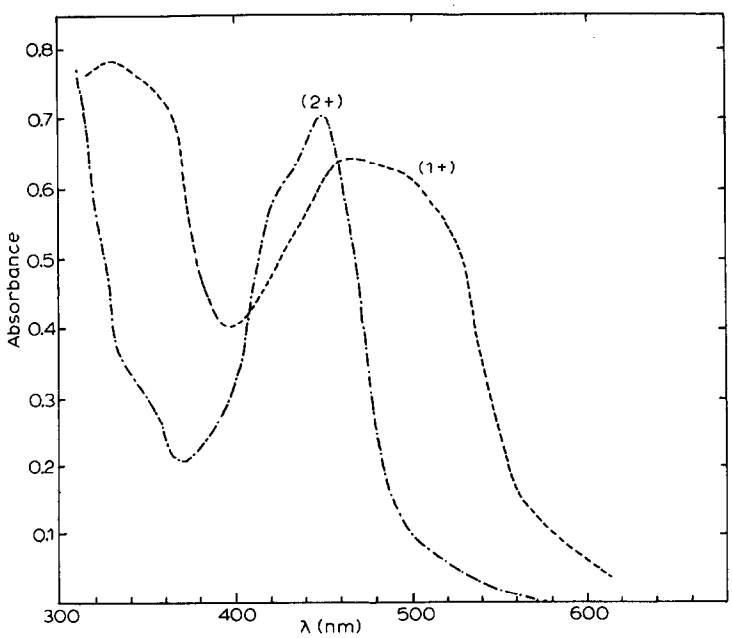


Fig. 5. Absorption spectrum of $Ru(bpy)_3^+$ in CH_3CN prepared by controlled potential electrolysis.

being a strong reductant can be prepared only under anaerobic conditions in nonaqueous solutions. In the presence of water there is a very rapid oxidation reaction to yield mainly the +2 complex. Figure 5 presents the absorption spectra of the bpy complex in the +1 state, recorded by electrochemical methods. The absorption spectrum of $Ru(bpy)_3^+$ after reaction with water has been described by various workers [75–79]. The molar extinction coefficient for the absorption peak of $Ru(bpy)_3^+$ at 495 nm is about 14000 M^{-1} cm^{-1}. As mentioned earlier, recent work [51] describes absorption spectral features of $[Ru(bpy)_3]^z$ species (with $z = +2, +1, 0, -1$) prepared in situ electrochemically (cf. Fig. 3).

The excited state redox potentials are obtainable from the redox potentials of the corresponding ground state and the spectroscopic excited state energy with the assumption that the excited state energy is all available as free energy for the excited state redox processes. Such assumptions are justified provided the "Stokes shifts" are quite small (i.e. the excited state has approximately the same size, shape and solvation and thus the enthalpy content, as the ground state). For $Ru(bpy)_3^{2+}$ complexes, the experimental results amply confirm this assumption. Spectroscopically, the excited state energy has been computed to be 2.12 eV (O–O bands at ca. 575 nm). With the ground state redox potentials available by cyclic voltammetry, it is possible to compute the potentials for the excited state in a redox quenching reaction with another molecule

$$Ru(bpy)_3^{2+}* + Q \rightarrow Ru(bpy)_3^{3+} + Q^- \text{ (oxidative)} \tag{2}$$

$$Ru(bpy)_3^{2+}* + Q \rightarrow Ru(bpy)_3^{+} + Q^+ \text{ (reductive)} \tag{3}$$

$$E_0\left[Ru(bpy)_3^{2+*/3+}\right] = E_0\left[Ru(bpy)_3^{2+/2+*}\right] - E_0\left[Ru(bpy)_3^{2+/3+}\right]$$
$$= -2.12 + 1.26 = -0.86 \text{ V}$$

Similarly

$$E_0\left[Ru(bpy)_3^{2+*/+}\right] = E_0\left[Ru(bpy)_3^{2+/+}\right] - E_0\left[Ru(bpy)_3^{2+/2+*}\right]$$
$$= -1.28 - (2.12) = +0.84 \text{ V}$$

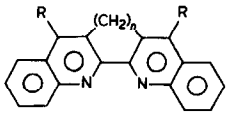
Comparing the redox potentials for the ground and excited states, it follows, that, for the $Ru(bpy)_3^{2+}$ complex, the excited state is a better reductant and also a better oxidant. Experimental verification for the above estimates on the excited state redox potentials comes from studies of luminescence quenching. By comparison of the quenching efficiency for a series of quenchers covering a range of redox potentials, it is possible to estimate the redox potentials for the excited state with the aid of Marcus and Rehm–Weller theories [80–83] and these are discussed in the next section. Alternatively, for a given quencher, it is possible to vary the redox potential of the

TABLE 4

Spectral and redox properties of a series of substituted bpy, phen complexes of Ru(II) (RuL_3^{2+} type) in aqueous solutions

Ligand L	Absorption		Emission (298 K)		Excited state energy (eV)	Ground state redox potentials (V) (vs. NHE)		Excited state redox potentials (V) (vs. NHE)		Ref.
	λ_{max} (nm)	ϵ(mM)	λ_{max} (nm)	τ (μs)		E (M/M^+)	E (M/M^-)	E^*(M/M^+)	E^*(M/M^-)	
bpy	452	14.6	613, 627	0.62	2.12	+1.26	−1.28	−0.86	+0.84	67
4,4′-Me_2bpy	460	14.3	628	0.33	2.04	+1.10	−1.44	−0.94	+0.69	67
6-Mebpy	448	11.1	585, 630							73
6,6′-Me_2bpy	446	7.44	589, 636							73
4,4′-$\phi_2$bpy	474	32.7	638	0.67	2.02	+1.17		−0.85		30b
4-NO_2bpy	462	17.0				+1.43	−1.06			71
4,4′-Cl_2bpy	480	20.4				+1.55	−0.55			71
4,4′-t-Bu_2bpy	456	16.8				+1.11				71
phen	447	19.0	605, 625	0.92	2.18	+1.26	−1.36	−0.87	+0.82	67
5-Mephen	450	19.4	605, 625	1.33	2.15	+1.23	−1.31	−0.92	+1.00	67
5-Clphen	447	18.4	605, 625	0.94	2.15	+1.36	−1.15	−0.77		67
5-NO_2phen	449	20.0	606	0.005	2.15	+1.46		−0.67		67
5-Brphen	448	18.8	605, 625	1.04	2.15	+1.37		−0.76		67

2-Mephen	446	14.4	576, 615							73
2,9-Me_2phen	501	25.8	588, 631							73
4,7-Me_2phen	445	25.3	613, 627	1.74	2.12	+1.09	−1.47	−0.94	+0.67	67
5,6-Me_2phen	453	20.4	608, 625	1.81	2.14	+1.20	−1.34	−0.93	+0.80	67
3,4,7,8-Me_4phen	438	24.5	605, 625	1.39	2.15	+1.02		−1.11		67
3,5,6,8-Me_4phen	440	19.8	605, 625	2.22	2.15	+1.09		−1.04		67
4,7-$\phi_2$phen	462	32.8	605, 625			+1.22	−1.31			67



(L)

L(I), R=Ph, $n=2$	540	17.1				+1.42	−0.90			71
L(II), R=Me, $n=2$	540	10.6				+1.26	−0.90			71
L(III), R=H, $n=2$	544	9.63				+1.43	−0.76			71
$Ru(bpz)_3^{2+}$	443	15.0	603	1.04			−0.80		+1.30	72a
RuL_2^{2+} type										
$Ru(terpy)_2^{2+}$	473	16.2	628	0.005		+1.25	−1.36			67
$Ru(TPTZ)_2^{2+}$	501	19.2	505	0.005		+1.49	−0.77			67

TABLE 5

Absorption and redox properties of a series of mixed ligand, bisbipyridyl complexes or Ru(II) with substitution in ligands [28,71,74]

Ru complex	Absorption		Redox potentials [b]		
	Medium	λ_{max} (nm) and ϵ(mM)	Medium	$E(M/M^+)$	$E(M/M^-)$
Mixed ligands					
$Ru(bpy_2 \cdot (4,4'Cl_2bpy))^{2+}$	CH_3CN	448 (12.6), 396 (6.75)	CH_3CN	+1.30	−1.14
$Ru(bpy_2 \cdot (4\text{-}NO_2bpy))^{2+}$	CH_3CN	493 (14.5), 429 (11.2)	CH_3CN	+1.37	−0.57
$Ru(bpy_2 \cdot (4,4'\text{-}t\text{-}Bu_2bpy))^{2+}$	CH_3CN	450 (14.5), 429 (13.0)	CH_3CN	+1.28	−1.35
$Ru(bpy_2 \cdot phen)^{2+}$	CH_3CN	447 (13.3), 425 (13.5)	CH_3CN	+1.26	−1.36
$Ru(bpy_2 \cdot (4,7\text{-}\phi_2phen))^{2+}$	CH_3CN	452 (14.8), 428 (13.9)	CH_3CN	+1.25	−1.32
$Ru(bpy)_2 \cdot (2,9\text{-}Me_2phen))^{2+}$	CH_3CN	450 (13.7), 427 (11.3)	CH_3CN	+1.27	−1.34
$Ru(bpy_2 \cdot (L(I)))^{2+}$ [a]	CH_3CN	532 (10.9), 496 (6.4)	CH_3CN	+1.30	−0.91
$Ru(bpy_2 \cdot (L(II)))^{2+}$ [a]	CH_3CN	528 (9.4), 448 (8.3)	CH_3CN	+1.26	−1.00
$Ru(bpy_2 \cdot (L(III)))^{2+}$ [a]	CH_3CN	528 (9.24), 440 (8.4)	CH_3CN	+1.31	−0.91

Bisbipyridyl complexes					
$Ru(bpy_2 \cdot Cl_2)$	CH_2Cl_2	556 (9.4), 380 (9.4)	CH_3CN	+0.31	
$Ru(bpy)_2 \cdot Br_2)$	CH_2Cl_2	548 (9.3), 378 (9.5)	CH_3CN	+0.37	
$Ru(bpy_2 \cdot (NCS)_2)$	CH_2Cl_2	520 (8.3), 366 (9.1)	CH_3CN	+0.67	
$Ru(bpy_2 \cdot (CN)_2)$	DMF	513 (10.5), 347 (9.0)	DMF	+1.09	−1.30
$Ru(bpy_2 \cdot (NCS)(Cl))$	CH_2Cl_2	535 (8.2), 372 (9.0)	CH_3CN	+0.50	
$Ru(bpy_2 \cdot py \cdot (NCS))^+$	CH_2Cl_2	488 (8.7)	CH_3CN	+0.85	
$Ru(bpy_2 \cdot py \cdot (Cl))^+$	CH_2Cl_2	505 (8.2), 358 (10.0)	CH_3CN	+0.76	
$Ru(bpy_2 \cdot py \cdot (NO_3))^+$	CH_2Cl_2	488 (8.1), 346 (10.5)	CH_3CN	+0.91	
$Ru(bpy_2 \cdot py \cdot (NO_2))^+$	CH_2Cl_2	461 (7.9), 340 (11.0)	CH_3CN	+1.06	
$Ru(bpy_2 \cdot py \cdot (CH_3COO))^+$	CH_2Cl_2	499 (9.2), 348 (11.6)	CH_3CN	+0.89	
$Ru(bpy_2 \cdot (py)_2)^{2+}$	CH_2Cl_2	460 (9.2)	CH_3CN	+1.29	
$Ru(bpy_2 \cdot (t\text{-Bupy}))^{2+}$	CH_2Cl_2	464 (8.5), 338 (13.0)	CH_3CN	+1.23	
$Ru(bpy_2 \cdot (CH_3CN)_2)^{2+}$	CH_2Cl_2	426 (8.7)	CH_3CN	+1.23	

[a] For a description of ligands L(I), L(II), L(III) see Table 4.

[b] All potentials quoted are vs. SCE.

RuL_3^{2+}* excited state by suitable substitution at the bpy, phen ligand with electron donating or withdrawing groups. In Tables 4 and 5 we have collected data on the absorption, redox and luminescence properties of a series of substituted bpy, phen complexes of Ru(II). These include tris-chelates RuL_3^{2+} made up of the same ligand L as well as mixed ligand complexes where one of the bpy or phen ligands is replaced by the other or by ligands such as oxalate, Cl^-, CN^-, en, etc. The data clearly demonstrate the extent of "fine tuning" possible in the redox properties by simple substitution.

D. PHOTOREDOX REACTIONS

(i) Quenching mechanisms and their discrimination

The most striking aspect of the $Ru(bpy)_3^{2+}$ photochemistry is its rich photoredox chemistry. The excited state redox potentials estimated from corresponding ground state values and the excited state energy indicate that the luminescent excited state is a strong reductant as well as a good oxidant. As elaborated in an earlier section, this is due to the presence of an electron deficient d^5 metal centre and an excess electron located in the ligand network in the excited state. In addition, studies have shown that $Ru(bpy)_3^{2+}$ sensitises formation of triplet excited states in inorganic, organic molecules by the process of energy transfer.

Thus, whenever the excited state is rapidly deactivated in bimolecular reactions with external additives (often called "quenchers"), one can visualise three principal means:

(a) excited state acts as an energy donor

$$Ru(bpy)_3^{2+}* + Q \rightarrow Ru(bpy)_3^{2+} + Q* \tag{4}$$

(b) excited state acts as a reductant (oxidative quenching)

$$Ru(bpy)_3^{2+}* + Q \rightarrow Ru(bpy)_3^{3+} + Q^- \tag{5}$$

(c) excited state acts as an oxidant (reductive quenching)

$$Ru(bpy)_3^{2+}* + Q \rightarrow Ru(bpy)_3^{+} + Q^+ \tag{6}$$

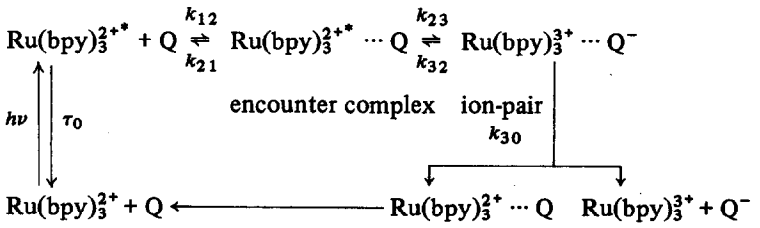
The actual quenching mechanism will be determined by both thermodynamic and kinetic factors and most often establishment of the actual mechanism is by no means a trivial exercise. The ability to undergo energy transfer is related to the O–O spectroscopic energy levels (spectral overlap) of the donor–acceptor pair and that of electron-transfer to the redox potentials. The kinetic factors are associated with the activation energy needed to reorganise the inner and outer shells before electron/energy

transfer takes place. More than one mechanism may be operative simultaneously.

Quenching by electron transfer (or charge transfer) is expected to imply some relationship between the quenching rate constant and the redox properties of the quenchers. As will be shown in the next section, this is verified experimentally by a comparison of the quenching rate as a function of redox potential for a series of structurally similar quencher molecules. Of considerable assistance in assignment is direct evidence for the formation of oxidised/reduced forms of the quencher and/or of the Ru complex in flash photolysis experiments for reversible redox systems and by continuous irradiation on irreversible systems. Similarly, growth of transient absorption or luminescence corresponding to the acceptor excited states on time scales concurrent with the decay of the Ru-complex excited state (a few hundred nanoseconds) is adequate evidence for the energy transfer process. In cases where the quencher excited states are non-absorbing or non-luminescent, assignments to energy transfer mechanisms rest either on the observation of sensitised photoaquation from the appropriate acceptor excited states or on the ruling out of electron transfer from thermodynamic data. The fact that the redox potentials of the Ru-complexes can be "tuned" by appropriate substitution has been exploited by Lin and Sutin [84] to distinguish electron transfer processes as against energy transfer. For the quenching of $Ru(bpy)_3^{2+}$ excited state either by electron energy transfer by various molecules (organic and inorganic) elaborated in this section and the next, one or more of the above guidelines have been utilised for establishment of the mechanism. As was mentioned earlier, for non-absorbing, non-luminescent Ru-complexes, Meyer and co-workers [79,85] have profitably used the technique of differential flash photolysis. It should be pointed out that, in addition to the above dynamical quenching processes, if there is extensive ground state association (complexing or ion-pairing) between the Ru-complex and the quencher, there can be additional quenching modes via static quenching.

(ii) Theoretical correlations of quenching rates

The kinetics of electron transfer quenching of excited states can be analysed in terms of the following reaction scheme, originally proposed by Rehm and Weller [80,81]



(7)

k_{12} and k_{21} are forward and reverse rate constants for the formation of an association complex between the excited state and Q prior to electron transfer. k_{23} and k_{32} are rate constants for electron-transfer within the encounter complex and corresponding back transfer to return to the excited state respectively. k_{30} is a combined rate constant for processes following the quenching step which lead to net quenching. This includes back e^- transfer to give the ground state and a competitive step to yield separated products. Using the Stern–Volmer relationship and steady state approximations, it is possible to obtain the following equation for the observed bimolecular quenching rate constant k_q^{obs}

$$k_q^{obs} = \frac{k_{12}}{1 + \frac{k_{12}}{\Delta v \cdot k_{30}}\left[\exp\left(\frac{\Delta G_{23}^*}{RT}\right) + \exp\left(\frac{\Delta G_{23}}{RT}\right)\right]} \tag{8}$$

where ΔG_{23} and ΔG_{23}^* are the free energy difference and free energy of activation between the encounter complex and the ion-pair, respectively. $\Delta v = (k_{12}/k_{21})$ represents the encounter volume. Equation (8) reduces to eqn. (9) when ΔG_{23} becomes large and negative and to eqn. (10) when Δk_{23} becomes large but positive.

$$k_q = \frac{k_{12} \cdot \Delta v \cdot k_{30}}{\Delta v \cdot k_{30} + k_{12} \exp\left(\frac{\Delta G_{23}^*}{RT}\right)} \tag{9}$$

$$k_q = \frac{\Delta v \cdot k_{30}}{2} \exp - \left(\frac{\Delta k_{23}}{RT}\right) \tag{10}$$

ΔG_{23} can be written in terms of redox potentials of the Ru-complex and the quencher as in eqn. (11)

$$\Delta G_{23} = E_{1/2}\left[\mathrm{Ru(bpy)_3^{2+}/Ru(bpy)_3^{2+*}}\right] - \mathrm{E_{1/2}[Q/Q^-]} + \mathrm{W_p} - \mathrm{W_r} \tag{11}$$

where W_p and W_r represent the work required to bring the product ions ($Ru(bpy)_3^{3+}$ and Q^-) and reactants ($Ru(bpy)_3^{2+}$* and Q) together to form the ion pair and encounter complex respectively. For uncharged species W_r is always negligible. W_p can be estimated from Debye–Hückel theory and is ≤ 0.05 eV in most unfavourable cases. From eqns. (9)–(11) it follows that a plot of log k_q^{obs} versus $E_{1/2}$ [Q/Q^-] is expected: (a) to be linear at low $E_{1/2}(Q/Q^-)$ values with slope $= -(1/2.3RT)$; and (b) approach a plateau at higher $E_{1/2}$ (Q/Q^-). For reductive quenching, an analogous situation exists and a similar plot will approach a plateau at low $E_{1/2}$ (Q/Q^+) values.

The above predictions based on simple extension of Rehm–Weller treatment have been amply verified for a wide variety of redox quenchers, both for oxidative and for reductive quenching. Rate data for a series of nitro

TABLE 6

Quenching rate constants for the oxidative quenching of $Ru(bpy)_3^{2+*}$ [a] by various organic molecules

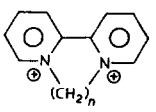
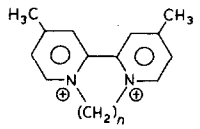
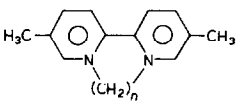
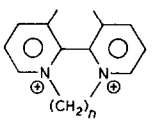
Quencher	Medium	$E_{1/2}$ (V) [a] (vs. SCE)	k_q (M^{-1} s^{-1})
A. Nitroaromatics [68,136]			
Nitrobenzene	CH_3CN	−1.15	2.0×10^5
4-Me nitrobenzene	CH_3CN	−1.20	3.0×10^5
4-F nitrobenzene	CH_3CN	−1.13	8.3×10^5
4-Cl nitrobenzene	CH_3CN	−1.06	8.0×10^6
3-Me nitrobenzene	CH_3CN	−1.04	1.66×10^7
3-NO_2 benzaldehyde	CH_3CN	−1.02	4.9×10^7
4,4′-Dinitrobiphenyl	CH_3CN	−1.0	1.2×10^8
4,4′-Dinitrostilbene (*cis*)	CH_3CN	−1.0	1.8×10^8
4-Me nitrobenzoate	CH_3CN	−0.95	6.6×10^8
m-Dinitrobenzene	CH_3CN	−0.90	1.56×10^9
p-Nitrobenzaldehyde	CH_3CN	−0.86	2.0×10^9
o-Dinitrobenzene	CH_3CN	−0.81	3.1×10^9
p-Dinitrobenzene	CH_3CN	−0.69	6.6×10^9
p-Nitronitrosobenzene	CH_3CN	−0.52	9.2×10^9
B. Viologens (bipyridinium salts) [137–143,68]			
2,7-Me_2 diazaphenanthrene	CH_3CN	−0.42	2.9×10^9
4,4′-$(Me\text{–}NC_5H_4\text{–}C_5H_4N\text{–}Me)^{2+}$	CH_3CN	−0.46	2.4×10^9
4,4′-$(Me\text{–}NC_5H_4\text{–}CH{=}CH\text{–}C_5H_4\text{–}Me)^{2+}$ (*trans*)	CH_3CN	−0.50	2.4×10^9
2,2′-$(Me\text{–}NC_5H_4\text{–}CH{=}CH\text{–}C_5H_4\text{–}Me)$	CH_3CN	−0.52	1.6×10^9
3,3′-$(Me\text{–}NC_5H_4\text{–}CH{=}CH\text{–}C_5H_4\text{–}Me)$	CH_3CN	−0.60	5.6×10^8
3,4′-$(Me\text{–}NC_5H_4\text{–}CH{=}CH\text{–}C_5H_4\text{–}Me)$	CH_3CN	−0.63	7.7×10^8
2,2′-$(MeN\text{–}C_5H_4\text{–}C_5H_4\text{–}Me)^{2+}$	CH_3CN	−0.73	9.1×10^7
3,3′-$(MeN\text{–}C_5H_4\text{–}C_5H_4\text{–}Me)$	CH_3CN	−0.84	1.0×10^6
4,4′-$(R\cdot NC_5H_4\cdot NC_5H_4\cdot R)^{2+}$, R=$CH_3$	H_2O	(−0.44)	1.03×10^9
4,4′-$(R\cdot NC_5H_4\cdot NC_5H_4R)^{2+}$, R=$-CH_2CH_2OH$	H_2O	(−0.40)	1.09×10^9
4,4′-$(R\cdot NC_5H_4\cdot NC\ H_4R)^{2+}$, R=$-CH_2C_5H_5$	H_2O	(−0.33)	1.37×10^9
2,2′-$(R\cdot NC\ H_4\cdot NC_5H_4R)^{2+}$, R=$-CH_3$	H_2O	(−0.72)	1.8×110^9
$n=2$ 	H_2O	(−0.37)	1.44×10^9
$n=3$	H_2O	(−0.55)	5.74×10^9
$n=4$	H_2O	(−0.65)	3.24×10^9

TABLE 6 (continued)

Quencher	Medium	$E_{1/2}$ (V) [a] (vs. SCE)	k_q (M^{-1} s^{-1})
$n=2$ 	H_2O	(−0.49)	9.94×10^9
$n=3$	H_2O	(−0.70)	4.0×10^9
$n=4$	H_2O	(−0.78)	0.96×10^8
$n=2$ 	H_2O	(−0.48)	9.5×10^9
$n=2$ 	H_2O	(−0.59)	6.0×10^9
C. Quinones [144]			
Benzoquinone	H_2O	(0.29)	3.7×10^9
1,3,5-Trimethylbenzoquinone	H_2O	(0.11)	2.4×10^9
Anthraquinone 2,6-disulphonate	H_2O	(−0.22)	6.0×10^9

[a] $E_{1/2}$ values quoted in parentheses are vs. NHE.

aromatics, viologens, amines and methoxy benzenes where this has been verified are collected in Tables 6 and 7. In cases where the nature of the redox products are identified by flash photolysis techniques, for a series of structurally similar quenchers, plots of log k_q vs. $E_{1/2}$ (Q/Q^-) or $E_{1/2}$ (Q/Q^+) can be used in a complementary manner to estimate the redox potentials of the metal complex excited state.

Analogous treatments of electron-transfer mechanisms by Marcus [82] and Hush [83] however, predict that plots of log k_q vs. $E_{1/2}$ should be parabolic, with log k_q decreasing as ΔG becomes more negative ("inverted Marcus region"). There have been several attempts to locate cases where one observes this inverted Marcus behaviour. While quenching of $Ru(bpy)_3^{2+}$* by various tris-bipyridyl metal complexes shows some positive results, similar quenching of $Ru[bpy_2(CN)_2]$* by *N*-ethyl pyridium ions show no fall off even when ΔE approaches 2.0 eV. Evidences cited in support have often been subject to criticism.

For electron transfer reactions involving metal complexes (mostly by an outer sphere mechanism) it is also possible to calculate rate constants for

TABLE 7

Rate parameters for reductive quenching of $Ru(bpy)_3^{2+}$ by various organic molecules [68,78,144,146]

Quencher	Medium	$E_{1/2}$ (D/D^+) (V) (vs. SCE) [a]	k_q ($M^{-1}\,s^{-1}$)	k_2 ($M^{-1}\,s^{-1}$)
TMPD	CH_3CN	0.15	1.0×10^{10}	5.2×10^9
N,N'-dimethylaniline	CH_3CN	0.85	7.1×10^7	4.1×10^9
N,N'-diethylaniline	CH_3CN	0.76	1.5×10^8	
p-($Me_2\cdot N\cdot C_6H_4-C_6H_4\cdot NMe_2$)	CH_3CN	0.43	4.3×10^9	
p-$Me_2N\cdot C_6H_4-OMe$	CH_3CN	0.55	5.0×10^9	
p-$Me_2N\cdot C_6H_4-Me$	CH_3CN	0.71	1.5×10^9	
p-$Me_2N\cdot C_6H_4-Cl$	CH_3CN	0.89	7.4×10^8	
Triphenylamine (NPh_3)	CH_3CN	1.06	9.5×10^5	Irrev.
α-Naphthylamine	CH_3CN	0.63	1.2×10^8	
p-Anisidine	CH_3CN	0.71	6.4×10^8	
Tetramethylbenzidine	CH_3OH	(0.69)	7.4×10^9	
Diphenylamine ($NHPh_2$)	CH_3OH	(0.80)	2.5×10^7	
Phenothiazine (PTH)	CH_3OH	(0.73)	5.6×10^9	1.1×10^5
Phenothiazine	CH_3CN		4.1×10^9	
N-methylphenothiazine	CH_3OH		1.3×10^9	
10-Me phenothiazine	CH_3CN		1.6×10^9	
Dimethyldithiofulvalene	CH_3OH	(0.78)	4.0×10^9	
4-Aminodiphenylamine	CH_3CN	0.27	6.7×10^9	
N,N-diphenyl *p*-phenylene-diamine	CH_3CN	0.35	5.8×10^9	
Benzidine	CH_3CN	0.46	4.5×10^9	
N,N'-dimethyl-*p*-toluidine	CH_3CN	0.65	1.1×10^9	
Diethyldithiocarbamate	CH_3CN	0.05	4.0×10^9	
Ethylxanthate	CH_3CN	0.21	3.6×10^9	
p-Methoxydithiobenzoate	CH_3CN	0.19	9.0×10^9	
O,O'-diethyldithiophosphate	CH_3CN	0.71	7.1×10^9	
Benzhydroquinone	H_2O	0.29	5.0×10^7	
Trimethylbenzhydroquinone	H_2O	0.11	5.0×10^7	

[a] Potentials quoted in parentheses are vs. NHE.

electron transfer from Marcus theory. Consider for example the equation

$$*Ru(bpy)_3^{2+} + Ru(NH_3)_6^{3+} \rightleftharpoons Ru(NH_3)_6^{2+} + Ru(bpy)_3^{3+} \quad (12)$$

According to the treatment of Marcus, Sutin, Balzani, et al. the rate constant for electron transfer

$$k_{12} = (k_{11}\cdot k_{22}\cdot K_{12}\cdot f_{12})^{1/2} \quad (13)$$

$$\log f_{12} = (\log K_{12})^2/4\log(k_{11}k_{22}/Z^2) \quad (14)$$

where k_{11}, k_{22} are the self-exchange rates for the reductant and oxidant couples; K_{12}, the equilibrium constant for the reaction and Z, the collision frequency (normally taken as 10^{11} M^{-1} s^{-1}) when f_{12} in the above equation is ca. 1 (that is when $(\log K_{12})^2$ and/or $k_{12}k_{22}$ are sufficiently small), the equation reduces to

$$k_{12} \sim (k_{11}k_{22}K_{12})^{1/2} \tag{15}$$

Thus if a series of related relations with f_{12} = ca. 1 is studied as a function of the driving force, a plot of $\log k_{12}$ vs. $\log K_{12}$ should be linear with slope 0.5 and intercept 0.5 $\log k_{11}k_{22}$.

(iii) Quenching by inorganic ions and molecules

The quenching of the excited state of $Ru(bpy)_3^{2+}$ by a variety of inorganic ions and molecules has been investigated by many workers. Available data on the quenching rate constant k_q, assignment to the quenching as redox or energy transfer and redox quantum yields for the products are summarised in Table 8. Ions such as Fe^{3+}, Cu^{2+}, Eu^{3+}, Tl^{3+}, Ag^+, Hg^{2+} and $S_2O_8^{2-}$ quench $Ru(bpy)_3^{2+}$* oxidatively to yield $Ru(bpy)_3^{3+}$ as the product. With Eu^{2+}, SO_3^{2-} and ascorbate, the excited state is photoreduced. Quenching by Cr^{3+} and Ti^{3+} presumably occurs via energy transfer.

Oxidative quenching by Fe^{3+} has been extensively investigated, as it is one of the few cases where the reverse e^- transfer occurs very inefficiently [84–90]

$$Ru(bpy)_3^{2+}* + Fe^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(bpy)_3^{3+} + Fe^{2+} \tag{16}$$

In 0.5 M H_2SO_4, the rate constants for forward and back electron transfer are 2.7×10^9 and 5.2×10^6 M^{-1} s^{-1} respectively. Under steady state conditions, this would imply a conversion of >25% of the Ru-complex into the 3+ state and hence the reaction has also been examined as a candidate for a photogalvanic cell system (cf. Section H). The quenching reaction (16) yields over 80% redox products. The nature of the acid medium influences rate constants considerably (forward and reverse) and also the steady state conversion yields. This is due to the change in the chemical nature of the quenching species themselves. Fe^{3+} exists as $Fe(H_2O)_6^{3+}$ only in $HClO_4$, and in media such as HCl and H_2SO_4, it is present as $FeCl_4$, $Fe(SO_4)_2^-$ etc. The rate data can be satisfactorily explained in terms of Marcus theory for outer sphere e^- transfer reactions.

Quenching by ions such as Tl^{3+} (in $HClO_4$ or H_2SO_4) and $S_2O_8^{2-}$ leads to irreversible formation of $Ru(bpy)_3^{3+}$ with a quantum yield of 2.0

TABLE 8

Rate parameters and redox quantum yields in the quenching of $Ru(bpy)_3^{2+}$* by inorganic ions and molecules

Quencher	Medium	k_q (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})	Mechanism	ϕ_{redox}	Ref.
Fe^{3+}	H_2SO_4 (0.5 M)	2.7×10^9	5.2×10^6	Oxid.	0.83 (Ru^{3+})	84–90
Fe^{2+}	$HClO_4$ (0.5 M)	1.6×10^7				86, 88
Cu^{2+}	H_2SO_4 (0.5 M)	6.2×10^7	9.7×10^8	Oxid.	0.56 (Ru^{3+})	91–93
Eu^{2+}	H_2O, $\mu=0.5$	2.8×10^7	4.5×10^7	Reduc.	1.0 (Ru^{+})	88
Eu^{3+}	H_2O, $\mu=0.5$	$\leq0.8\times10^5$	3.0×10^9	Oxid.	>0	76, 77
Cr^{3+}	H_2O, $\mu=0.5$	1.2×10^7		Energy transfer		67
Tl^{3+}	$HClO_4$ (0.5 M)	1.1×10^8	Irrev.	Oxid.	2.0 (Ru^{3+})	86, 94
Tl^{3+}	HCl (1.0 M)	3.3×10^9				94
Tl^{+}	$HClO_4$ (0.5 M)	$<10^6$				86
Ti^{3+}	HCl (1.0 M)	6.0×10^6		Energy transfer	<0.2	95–97
Ag^{+}	H_2O	3.5×10^6	1.2×10^{10}	Oxid.		98, 99
Ag^{+}	CH_3CN	1.1×10^5	5.5×10^9	Oxid.		98
$S_2O_8^{2-}$	H_2SO_4 (0.5 M)	5.6×10^8	Irrev.	Oxid.	2.0 (Ru^{3+})	100, 101
$S_2O_4^{2-}$	Acetate buffer (0.02 M)	2.4×10^9				88
O_2	H_2O, $\mu=0.5$	3.3×10^9		Energy/oxid.		67, 102–107
SO_3^{2-}	H_2O, $\mu=0.5$	3.0×10^5	$<10^6$	Reduc.		108
Ascorbate	H_2O, $\mu=0.5$	2.0×10^7	1.0×10^9	Reduc.	0.5 (Ru^{+})	109
Hg^{2+}	$HClO_4$ (0.1 M)	1.5×10^8	2.0×10^9	Oxid.	>0.6 (Ru^{3+})	110
$HgCl_2$	$HClO_4$ (0.1 M)	3.8×10^8			<0.01	110
Sb^{3+}	H_2SO_4	$<10^6$				107

[86,94,100,101].

$$Ru(bpy)_3^{2+}* + Tl^{3+} \rightarrow Ru(bpy)_3^{3+} + Tl^{2+} \quad (17)$$

$$Ru(bpy)_3^{2+} + Tl^{2+} \rightarrow Ru(bpy)_3^{3+} + Tl^{+} \quad (18)$$

$$\text{Overall: } 2\,Ru(bpy)_3^{2+} + Tl^{3+} \underset{\phi=2.0}{\overset{h\nu}{\rightarrow}} 2Ru(bpy)_3^{3+} + Tl^{+} \quad (19)$$

The higher quantum yield arises due to a dark oxidation of a second molecule of $Ru(bpy)_3^{2+}$ by the photoreduced quencher molecule, as shown in eqn. (18).

In photoredox systems involving Ag^+ or Hg^{2+} as quenchers, the reduced quencher molecules can dimerise (or aggregate) [98,99,110] in reactions such as

$$Ru(bpy)_3^{2+}* + Ag^+/Hg^{2+} \rightarrow Ru(bpy)_3^{3+} + Ag^0/Hg^+ \quad (20)$$

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (21)$$

or

$$Hg^+ + Hg^+ \rightarrow Hg_2^{2+} \quad (22)$$

and subsequently back react with $Ru(bpy)_3^{3+}$ in a slow step. Under such conditions, $Ru(bpy)_3^{3+}$ lives long enough to be scavenged by other reductants such as TEOA and the system shows significant photopotentials.

With Tl^{3+} and Hg^{2+}, change in the nature of the acid medium influences drastically the quenching rates and yield of the redox products. Quenching studies in HCl medium show that even though quenching rates are higher (for Tl^{3+}, k_q (HCl) $= 3.3 \times 10^9$ M^{-1} s^{-1} as compared to 1.1×10^8 M^{-1} s^{-1} in H_2SO_4), $\phi(Ru^{3+}) < 10^{-2}$. Here the negatively charged quencher molecules such as $TlCl_4^-$, $HgCl_4^{2-}$ interact efficiently with the doubly charged Ru-complex but the radical ion pairs do not escape the primary cage.

Oxygen is one of the few molecules which effectively quenches $Ru(bpy)_3^{2+}*$ [102–107] ($k_q = 3.3 \times 10^9$ M^{-1} s^{-1}). Singlet oxygen formation by energy transfer has been suggested with singlet oxygen traps. However, in acid media, the quenching mechanisms appear to be complicated. Sutin and co-workers [15] suggest an electron transfer mechanism to yield initially $Ru(bpy)_3^{3+}$

$$Ru(bpy)_3^{2+}* + O_2 \rightarrow \left(Ru(bpy)_3^{3+} \cdots O_2^-\right) \rightarrow Ru(bpy)_3^{3+} + O_2^- \quad (23)$$

$$Ru(bpy)_3^{3+} + O_2^- \rightarrow Ru(bpy)_3^{2+} + O_2(^1\Delta_2) \quad (24)$$

and O_2^- which react back to give $Ru(bpy)_3^{2+}$ and singlet oxygen ($^1\Delta_2$). $Ru(bpy)_3^{3+}$ indeed has been observed in laser flash photolysis experiments in oxygenated solutions of $Ru(bpy)_3^{2+}$. Recently, Kunimura and Onimura [107] have observed efficient formation of Sb(IV) upon photolysis of oxygenated

$Ru(bpy)_3^{2+}$–Sb(III) solutions. Since Sb^{3+} itself does not quench the $Ru(bpy)_3^{2+}$* effectively at concentrations employed, an alternative mechanism involving reaction of $Ru(bpy)_3^{3+}$ (photogenerated via reaction 23) with Sb^{3+} has been proposed.

(iv) Quenching by inorganic metal complexes

Wide interest in $Ru(bpy)_3^{2+}$ photochemistry started almost a decade ago with reports by Gafney and Adamson [111] and by Fujita and Kobayashi [112–114] that $Ru(bpy)_3^{2+}$ sensitises redox decomposition of metal complexes such as $Co(NH_3)_5Cl^{2+}$ and $PtCl_4^{2-}$ and energy transfer in various Cr(III) complexes. Since then quenching by a wide variety of inorganic complexes has been examined and these include oxalates [136], bipyridyls [121], phenanthrolines [60,88], ammines [88,111], cyanides [123,127], acac [93], EDTA [129,130] complexes and binuclear μ-oxo bridged Co complexes. Available data on the quenching rate constants and details on quenching assignment and redox product quantum yields are summarised in Table 9.

Sensitised redox decomposition of Co(III) complexes has been investigated in detail and mechanisms of reaction have been the subject of controversy. Co(III) complexes such as $[Co(NH_3)_5X]^{2+}$ upon photoreduction to the Co(II) state, readily decompose yielding the aquo complex ($X = Cl^-$, Br^- or I^-)

$$Ru(bpy)_3^{2+}* + [Co^{III}(NH_3)_5X]^{2+} \rightarrow Ru(bpy)_3^{3+} + [Co^{II}(NH_3)_5X]^{+} \quad (25)$$

$$[Co^{II}(NH_3)_5X]^{+} \xrightarrow{H_2O} Co_{aq}^{2+} + 5NH_3 + X^- \quad (26)$$

Natarajan and Endicott, in a series of papers [116,117,129,130] reporting their photolysis, scavenging studies on EDTA and ammine complexes of Co(II), argued that the mechanism involved is triplet–triplet energy transfer followed by intramolecular oxidation of one of the ligands of the Co(III) substrates.

$$Ru(bpy)_3^{2+}* + [Co(NH_3)_5Br]^{2+} \rightarrow Ru(bpy)_3^{2+} + [Co(NH_3)_5Br]^{2+*} \quad (27)$$

$$[Co(NH_3)_5Br]^{2+}* \rightarrow Co_{aq}^{2+} + 5NH_3 + Br^{\cdot} \quad (28)$$

$$Br^{\cdot} + Br^- \rightarrow Br_2^- \quad (29)$$

$$Br_2^- + Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + 2\,Br^- \quad (30)$$

Contesting this interpretation, Navon and Sutin [115] argue that the sensitised decompositions occur via direct electron transfer, as outlined in eqns. (25) and (26). Since $Ru(bpy)_3^{3+}$ is produced [115] in yields close to 100% for all halides, Endicott mechanism implies that the oxidising radicals ($X\cdot$ and

TABLE 9

Rate parameters and redox quantum yields for the quenching of $Ru(bpy)_3^{2+}$* by metal complexes

Quencher	Medium	k_q	ϕ_{redox}	Mechanisms and other data	Ref.
A. Amine complexes					
$Co(NH_3)_6^{3+}$	H_2SO_4 (0.5 M)	10^7			111, 115
$Co(NH_3)_5Cl^{2+}$	H_2SO_4 (0.5 M)	9.3×10^8	1.0 (Ru^{3+})	Oxid, irrev.	111, 115
$Co(NH_3)_5(H_2O)^{3+}$	H_2SO_4 (0.5 M)	0.15×10^9	1.0 (Ru^{3+})	Oxid., irrev.	115
$Co(NH_3)_5Br^{2+}$	H_2SO_4 (0.5 M)	2.5×10^9	1.0 (Ru^{3+})	Oxid., irrev.	111, 115–117
$Ru(NH_3)_6^{3+}$	H_2SO_4 (0.5 M)	2.4×10^9			87, 88, 115
$Ru(NH_3)_5Cl^{2+}$	H_2SO_4 (0.5 M)	2.7×10^9			115
B. Oxalato complexes					
$Fe(C_2O_4)_3^{3-}$	H_2SO_4 (0.5 M)	3.6×10^9	$<10^{-3}$		111, 118
$Cr(C_2O_4)_3^{3-}$	H_2SO_4 (0.5 M)	8.5×10^9	0.03 (racemisation)	Energy transfer	118
$Co(C_2O_4)_3^{3-}$	H_2SO_4 (0.5 M)	6.7×10^9	0.85	Oxid.	118
C. bpy, phen complexes					
$Rh(bpy)_3^{3+}$	H_2SO_4 (0.5 M)	6.2×10^8	0.15 (Ru^{3+})	Oxid., $k_2 = 3.0 \times 10^9$	119, 121
$Rh(bpy)_2(H_2O)_2^{3+}$	H_2SO_4 (0.5 M)	4.4×10^8		Oxid.	121
$Cr(bpy)_3^{3+}$	H_2SO_4 (0.5 M)	3.3×10^9		Oxid., $k_2 = 2.6 \times 10^9$	111, 122
$Os(bpy)_3^{2+}$	H_2O, $\mu = 0.1$	1.5×10^9		Reduc., energy transfer	60
$Fe(bpy)_3^{3+}$	H_2O, $\mu = 0.5$	1.0×10^9		Energy transfer	60
$Fe(phen)_3^{3+}$	H_2O, $\mu = 0.1$	1.1×10^9		Oxid., energy transfer	60
$Rh(phen)_3^{3+}$	H_2SO_4 (0.5 M)	6.8×10^8		Oxid.	60
$Ru(terpy)_2^{2+}$	H_2O, $\mu = 0.1$	1.5×10^9		Energy transfer	60
$Ru(TPTZ)_2^{2+}$	H_2O, $\mu = 0.5$	1.2×10^9		Oxid., energy transfer	60

$Co(phen)_3^{3+}$	H_2O, $\mu=0.5$	3.0×10^9			88
$Co(phen)_3^{2+}$	H_2O, $\mu=0.5$	8.9×10^8			88
D. Cyanide complexes					
$Fe(CN)_4^{3-}$	H_2O, $\mu=0.5$	6.5×10^9		Oxid.	123a, 127, 128
$Fe(CN)_6^{4-}$	H_2O, $\mu=0.5$	3.3×10^9		Reduc.	123a, 127, 128
$Co(CN)_6^{3-}$	H_2O, $\mu=0.5$	10^6		Oxid.	123a, 127
$Ni(CN)_4^{2-}$	H_2O, $\mu=0.5$	5.6×10^9		Energy transfer	123a, 127
$Cr(CN)_6^{3-}$	H_2O, $\mu=0.5$	9.5×10^8		Energy transfer	123a–127
$Mo(CN)_8^{4-}$	H_2O, $\mu=0.5$	3.4×10^8		Reduc., stat.	123a, 127, 128
$Ru(CN)_6^{3-}$	H_2O, $\mu=0.5$	10^7		Reduc.	123a, 127
$Os(CN)_6^{4-}$	H_2O, $\mu=0.5$	1.2×10^9		Reduc.	123a, 127
$Pd(CN)_4^{2-}$	H_2O, $\mu=0.5$	10^6			123a, 127
$Pt(CN)_4^{2-}$	H_2O, $\mu=0.5$	10^6			123a, 127
E. Acetylacetonate complexes					
$Ni(acac)_2$	H_2O, $\mu=0.5$	2.7×10^7			93
$Co(acac)_3$	H_2O, $\mu=0.5$	5.6×10^8			93
$Co(acac)_2$	H_2O, $\mu=0.5$	5.8×10^7			93
$Cr(acac)_3$	H_2O, $\mu=0.5$	3.0×10^8			93
$Cu(acac)_2$	H_2O, $\mu=0.5$	1.1×10^9			93
F. EDTA complexes					
Co(HEDTA) NO_2	H_2O, pH 3.0	1.3×10^9	0.71 (Co^{2+})	Oxid., irrev.	129, 130
Co(HEDTA) Br	H_2O, pH 3.0	3.0×10^9	0.80 (Co^{2+})	Oxid., irrev.	129, 130
Co(HEDTA) Cl	H_2O, pH 3.0	0.8×10^9	0.24 (Co^{2+})	Oxid., irrev.	129, 130
Co(EDTA) H	H_2O, pH 3.0	0.3×10^9	0.10 (Co^{2+})	Oxid., irrev.	129, 130
G. $(Co(NH_3)_5L^{n+}$ complexes					
L = *p*-nitrobenzoate	pH 5.8 buffer	2.4×10^9	0.11 (Co^{2+})		131, 132
= *o*-nitrobenzoate	pH 5.8 buffer	1.3×10^9	0.05 (Co^{2+})		131, 132
= benzoate	pH 5.8 buffer	1.5×10^8	0.45 (Co^{2+})		131, 132
= acetate	pH 5.8 buffer	2.1×10^8			131, 132
= pyridine	pH 5.8 buffer	2.1×10^8	0.80 (Co^{2+})		131, 132
= *N*-Mebpy	pH 5.8 buffer	1.1×10^9	0.92 (Co^{2+})		131, 132
= 4,4′-bpy	pH 5.8 buffer	5.7×10^8			131, 132

TABLE 9 (continued)

Quencher	Medium	k_q	ϕ_{redox}	Mechanisms and other data	Ref.
H. Dimeric Co-ammine complexes					
$((NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5)^{5+}$		1.9×10^9	0.8	Oxid.	133–135
$((NH_3)_5Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4)^{4+}$		4.0×10^9	0.8	Oxid.	133–135
		4.0×10^9	0.8	Oxid.	133–135
$((en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2)^{4+}$		3.2×10^9	0.8	Oxid.	133–135
$((bpy)_2Co(\mu\text{-}NH_2,O_2)Co(bpy)_2)^{4+}$		3.0×10^9	0.8	Oxid.	133–135
$((phen)_2Co(\mu\text{-}NH_2, O_2)Co(phen)_2)^{4+}$		8.1×10^9	0.8	Oxid.	133–135
I. $Fe(CN)_5L$ (cyanoferrate) complexes					
$Fe(CN)_5CO^{3-}$	H_2O, $\mu=0.5$	6.0×10^6			128
$Fe(CN)_5(imid)^{3-}$	H_2O, $\mu=0.5$	3.8×10^9			128
$Fe(CN)_5(py)^{3-}$	H_2O, $\mu=0.5$	4.2×10^9			128
$Fe(CN)_5(NO)^{2-}$	H_2O, $\mu=0.5$	6.0×10^9			128
$Fe(CN)_5(DMSO)$	H_2O, $\mu=0.5$	5.6×10^7			128
$Fe(CN)_5(NMPz)$	H_2O, $\mu=0.5$	5.3×10^9			128

X_2^-) be produced from excited states of the Co with close to unit efficiency and these radicals react quantitatively with $Ru(bpy)_3^{2+}$. It is difficult to conceive both of these conditions being satisfied by the Co complexes. Furthermore, none of the Co(III) complexes investigated had any low-lying reactive excited states to act as energy acceptors. Data on the variation in the yield of $Ru(bpy)_3^{3+}$ and Co^{2+} in mixed solvent systems (such as 50% 2-propanol) similarly, can be interpreted without invoking competitive radical reactions.

Among the tris(oxalato) complexes of Co(III), Cr(III) and Fe(III), only the Co(III) complex quenches $Ru(bpy)^{2+}*$ by electron transfer efficiently ($\phi_{redox} = 0.85$). Depending on the nature of the halide (X^-) ion, oxidative quenching by Co(HEDTA)X complexes produce Co_{aq}^{2+} with quantum yields 0.1–0.80. Efficient oxidative quenching ($\phi_{Co} =$ ca. 0.8) has been demonstrated recently for Co(μ-oxo) dimeric complexes as well.

Quenching by cyanide complexes has received some attention [123–128]. $Ni(CN)_4^{2-}$ and $Cr(CN)_6^{3-}$ have been shown to quench by energy transfer and $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, $Ru(CN)_6^{3-}$ reductively. With Pd, Pt and Co cyanides quenching is very inefficient and $Fe(CN)_6^{3-}$ quenches $Ru(bpy)_3^{2+}*$ fairly efficiently by the oxidative process.

With most of the anionic metal complexes, there is evidence for extensive ion-pairing with $Ru(bpy)_3^{2+}$ resulting in some static quenching of the excited states. Where there is additional quenching by static means, the $Ru(bpy)^{2+}*$ emission intensity is quenched faster than the lifetime. (With static quenching the excited ion pair very rapidly deactivates so that the emission yields decrease without appreciable changes in τ.)

$$Ru(bpy)_3^{2+} + 2\,X^- \overset{K}{\rightleftharpoons} \left[Ru(bpy)_3^{2+}(X^-)_2\right] \tag{31}$$

From the observed deviation in the Stern–Volmer plot and Debye–Hückel theory, it is possible to calculate even the ion-pairing constant for the association of the type shown in eqn. (31). Table 10 summarises data on ion pairing constants determined by quenching of $Ru(bpy)_3^{2+}$ by inorganic complex systems.

(v) Oxidative quenching by organic molecules

Formation of $Ru(bpy)_3^{3+}$ as a redox product in the oxidative quenching of $Ru(bpy)_3^{2+}*$ has been demonstrated for various organic molecules by flash photolysis studies. Compounds investigated include nitroaromatics, quinones and bipyridinium ions (also called "viologens"). Quenching by viologen salts has been of wide interest, [68,137–143] due to the role they play as a relay in light induced H_2 evolution from water experiments. The simple bipyridinium salt, methyl viologen, (abbreviated often as MV^{2+}), for example quenches

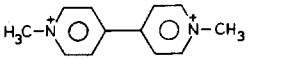
TABLE 10

Ion-pairing constants for $Ru(bpy)_3^{2+}$ –quencher complexes derived from static quenching of the excited state of $Ru(bpy)_3^{2+}$*

Quencher	Medium	k_q (M^{-1} s^{-1})	Ion-pairing const. [a]	Ref.
$Mo(CN)_8^{4-}$	H_2O	3.4×10^8	300 [128a]	93, 105, 123a, 127, 128a
$IrCl_6^{3-}$	H_2O	1.2×10^{10}	<50 [128a]	93, 128a
$PtCl_4^{2-}$	DMF	1.0×10^{10}	1000 [128a] 250 [93]	93, 105, 118, 128a, 136
$Cr(C_2O_4)_3^{3-}$	H_2O	8.5×10^9	7820 [114]	114, 118
$Co(C_2O_4)_3^{3-}$	H_2O	6.7×10^9	4600 [118] 1900 [93]	93, 118
$Cr(mal)_3^{3-}$	H_2O		3260	114
$Cr(CN)_6^{3-}$	H_2O	9.5×10^8	9480 [114] 400 [93]	93, 114, 123a, 127
$Fe(CN)_6^{4-}$	H_2O	3.3×10^9	3600	93, 123a, 127
$Fe(CN)_6^{3-}$	H_2O	6.5×10^9	2000	93, 123a, 127
$Ni(CN)_4^{2-}$	H_2O	5.6×10^9	1600	93, 123a, 127

[a] For more than one reference and/or values shown, ref. no. after the ion-pairing constants refers to work from which taken.

$Ru(bpy)_3^{2+}$* oxidatively to yield the one-electron reduced radical $MV^{\cdot+}$ and $Ru(bpy)_3^{3+}$.



$$Ru(bpy)_3^{2+}* + MV^{2+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + MV^{+} \quad (32)$$

$$Ru(bpy)_3^{3+} + MV^{+} \xrightarrow{k_2} Ru(bpy)_3^{2+} + MV^{2+} \quad (33)$$

In CH_3CN, k_q and k_2 are 2.4×10^9 M^{-1} s^{-1} and 8.3×10^9 M^{-1} s^{-1} and in H_2O, the corresponding values are 5.6×10^9 M^{-1} s^{-1} and 2.4×10^9 M^{-1} s^{-1} respectively. Rehm–Weller type plots of log k_q vs. $E_{1/2}$ have been presented [141] for a series of viologen salts in support of the electron transfer quenching. However, quantitative studies by flash photolysis have shown that only 30% of the redox products escape cage recombination to undergo diffusion-controlled back electron transfer of the type shown in eqn. (32). As the reaction involves two positively charged ions, it is subject to strong coulombic effects [139]. In systems for H_2 evolution, one uses reductants such as EDTA to scavenge $Ru(bpy)_3^{3+}$ in competition with back transfer. Photoproduced MV^{+} ions subsequently reduce H^+ to H_2 over a redox catalyst such as Pt

$$2\,MV^{+} + 2\,H^{+} \xrightarrow{Pt} 2\,MV^{2+} + H_2 \quad (34)$$

A summary of redox potentials, quenching rate constants, redox yields for various viologens, nitroaromatics and quinone systems can be found in Table 6.

Quinones are also known to quench $Ru(bpy)_3^{2+}$* at diffusion controlled rates by the oxidative mechanism [144].

(vi) Reductive quenching by organic molecules

The luminescent excited state of $Ru(bpy)_3^{2+}$ is also efficiently quenched reductively by numerous organic molecules, aromatic amines [68,78] and dithioanions [146] in particular

$$Ru(bpy)_3^{2+}* + D \rightleftharpoons Ru(bpy)_3^{+} + D^{+} \quad (35)$$

$Ru(bpy)_3^{+}$ being a strong reductant, reacts with various substances including water and so these reactions are preferably carried out in nonaqueous media such as CH_3CN or CH_3OH. In solvents like CH_3CN, the redox reactions are reversible. In CH_3OH or H_2O, most oxidised amines deprotonate and then dismutate, so that the quenching reactions are only partially reversible. Dimerisation/oligomerisation of amine cations such as that of DMA^+ are also known to occur. In such cases it is possible to accumulate one or the other of the redox products.

Quenching parameters for organic molecules where the quenching process has been shown to be reductive are collected in Table 7 along with their redox potentials. For most cases even though the absorption spectra of $Ru(bpy)_3^{+}$ and of the oxidised donors are known, efficiencies for electron transfer (ϕ_{redox}) have not been determined. Only with phenothiazine ϕ_{redox} has been estimated to be 0.60 [78].

Using irreversible reductants such as dithioanions, Deronzier and Meyer [146] have attempted to build up $Ru(bpy)_3^{+}$ as a stable species during continuous photolysis with no success. The slow back reaction between the disulphides and the reduced Ru(II) complex returns the system to its initial state. However, they have shown that in multicomponent systems containing $Ru(bpy)_3^{2+}$, dithiocarbonate (dtc^-) and weak electron acceptors, it is possible to build sufficient quantities of radical anions of these acceptors for spectroscopic analysis.

E. ENERGY TRANSFER STUDIES OF TRIPLET EXCITED STATES

The early interest in $Ru(bpy)_3^{2+}$ photochemistry concerned its potential use as an energy sensitiser of triplet excited states for various organic and inorganic molecules

$$Ru(bpy)_3^{2+}* + A \rightarrow Ru(bpy)_3^{2+} + A* \quad (36)$$

As mentioned in the last section (section D(i)), assignments of quenching processes to "energy transfer" on firm grounds require either direct observation of the acceptor phosphorescence or at least photoreactions arising from the excitation into the acceptor excited states. The number of authenticated cases of energy transfer from $Ru(bpy)_3^{2+}*$ has been few. Various quencher systems where the "energy transfer" mechanism has been invoked are collected in Table 11 along with the acceptor energy levels accessible and the quenching rate constants.

In the very early studies Demas and Adamson [118] demonstrated sensitised photoaquation of $PtCl_4^{2-}$ to occur by an energy transfer process. With most inorganic complexes, in the absence of direct observation of emission from acceptor excited states, sensitised photodecomposition/photoaquation is often taken as adequate evidence for the occurrence of the energy transfer. Thus, in earlier studies, sensitised redox decomposition of a series of Co(III) ammine, oxalato complexes were assigned to energy transfer [116,117]. This assignment has been subject to long debate, as was elaborated in section D(iv); these redox decompositions are now believed to occur by direct electron transfer followed by intramolecular redox decomposition. To avoid ambiguities, knowledge of the exact location of acceptor energy levels and also of the excited states from which photoreactions occur is essential.

$Cr(CN)_6^{3-}$ quenching of $Ru(bpy)_3^{2+}*$ is a clear-cut example of direct energy transfer, as has been demonstrated by the observation of sensitised phosphorescence from the chromium complex [123–127]. Sensitisation by the Ru-complex or erythrosin leads to populating of the lowest doublet state (^2E_g). Sensitisation of $Cr(CN)_6^{3-}$ phosphorescence by organic molecules such as naphthalene, acridine or xanthone however leads to photoaquation. These photoreactions presumably arise from populating the lowest quartet state ($^4T_{2g}$). Quenching of $Ru(bpy)_3^{2+}*$ by energy transfer by various Cr(III) complexes has also been studied in various rigid solutions, host crystals and in double salts by Fujita and Kobayashi [112–114]. Most of the anionic Cr complexes form ion-pairs with the Ru-complexes and hence the energy transfer processes are believed to be intermolecular in the ion-pair.

Sensitisation of triplet excited states of organic molecules [147,148] anthracene, stilbene etc., or of aromatic ketones such as benzophenones are easily shown to occur by a direct energy transfer process. Wrighton et al. [149] have investigated the quenching of $Ru(bpy)_3^{2+}*$ by various metallocenes. With ferrocene and its substituted derivatives, the quenching is very efficient and the mechanism operative is believed to be one of energy transfer. As mentioned in section D(v), the efficient quenching of the Ru-excited state by molecular oxygen is often attributed to an energy transfer process resulting in the production of singlet oxygen. In alcoholic solvents this seems to be the case as evidenced by the high uptake of oxygen in the presence of scavengers such as 2:3 dimethyl butene.

TABLE 11

Rate parameters for the energy transfer quenching of $Ru(bpy)_3^{2+}$ excited state by various molecules

Quencher	E_T (acceptor) (kcal mol^{-1})	Medium	k_q (M^{-1} s^{-1})	Ref.
Inorganic				
$Cr(CN)_6^{3-}$	35.45	H_2O, $\mu=0.5$	9.5×10^8	123–127
		EPA	2.3×10^9	93, 123
$Ni(CN)_4^{2-}$	48.9	H_2O, $\mu=0.5$	5.6×10^9	93, 118, 136
$Pt(Cl)_4^{2-}$			1.0×10^{10}	93, 118, 136
$Cr(C_2O_4)_3^{3-}$	41 (^2E_g) 45 ($^4T_{2g}$)	EPA	1.9×10^9	117
$Cr(mal)_3^{3-}$	40–45	EPA	0.8×10^9	114
$Cr(NCS)_3^{3-}$	40–45	EPA		114
$Fe(bpy)_3^{3+}$		Na_2SO_4 (0.5 M)	1.0×10^9	60
$Os(bpy)_3^{2+}$	41.00	NaCl (0.1 M)	1.5×10^9	60
$Ru(terpy)_2^{2+}$	49.0	Na_2SO_4	1.5×10^9	60
$Ru(TPTZ)_2^{2+}$	49.0	NaCl	1.2×10^9	60

TABLE 11 (continued)

Quencher	E_T (acceptor) (kcal mol^{-1})	Medium	k_q (M^{-1} s^{-1})	Ref.
Ti^{3+}_{aq}	49.80	HCl (1.5 M)	6.0×10^6	95
Cr^{3+}_{aq}	42.9	H_2SO_4 (0.5 M)	1.2×10^7	67
Organics				
Anthracene	42.0	EtOH: C_6H_6	2.2×10^9	147
2-Styrylpyridine(*trans*)	50.0	EtOH: C_6H_6	4.5×10^6	147
4-Styrylpyridine(*trans*)	50.0	EtOH: C_6H_6	4.3×10^6	147
Stilbene (*trans*)	49.0	EtOH: C_6H_6	2.1×10^6	147
Benzophenone		CH_3COOH	2.0×10^9	148
4,4'-Cl_2-benzophenone		CH_3COOH	2.5×10^9	148
4-Phenylbenzophenone		CH_3COOH	2.5×10^9	148
3-Benzoylbenzophenone		CH_3COOH	2.3×10^9	148
Organometallics				
Ferrocene		EtOH	5.9×10^9	149
Acetylferrocene		EtOH	3.4×10^9	149
Benzoylferrocene		EtOH	7.4×10^9	149
Ruthenocene		EtOH	$<10^7$	149
1,1-Diacetylruthenocene		EtOH	$<10^7$	149
Acetylosmocene		EtOH	$<10^7$	149
Cobaltacenium perchlorate		EtOH–H_2O	1.5×10^8	149

F. CHEMILUMINESCENT REACTIONS OF $Ru(bpy)_3^{2+}$

Thermal (dark) electron-transfer reactions of transition metal complexes such as $Ru(bpy)_3^{2+}$ in different oxidation states, often result in the production of the MLCT excited state and subsequent light emission from the solution. The phenomenon is known as chemiluminescence and if the light emission occurs from the reactions of ions generated at an electrode surface, as "electrogenerated chemiluminescence" (ECL). Chemiluminescence has been shown to occur both in the oxidation of $Ru(bpy)_3^{+}$ and also upon reduction of $Ru(bpy)_3^{3+}$ [150–162].

Luminescence corresponding to the emission from the $Ru(bpy)_3^{2+}*$ was first observed by Hercules and Lytle in 1966 [150], upon neutralising an acidic solution of $Ru(bpy)_3^{3+}$ with concentrated alkali (OH^-)

$$Ru(bpy)_3^{3+} + OH^- \rightarrow Ru(bpy)_3^{2+}* + OH^{\cdot} \tag{37}$$

Subsequently similar observations have been made for the thermal reduction of $Ru(bpy)_3^{3+}$ with reductants such as N_2H_4, $NaBH_4$, EDTA [150,151] organic acid salts such as oxalate, pyruvate [161,162] etc. The luminescence is also observed upon reduction of the (3 +) complex with solvated electrons in pulse radiolysis experiments

$$Ru(bpy)_3^{3+} + e_{aq}^- \rightarrow Ru(bpy)_3^{2+}* \tag{38}$$

Similarly reactions of $Ru(bpy)_3^{+}$ with oxidising agents such as 10-methyl phenothiazine radical cation results in $Ru(bpy)_3^{2+}*$

$$Ru(bpy)_3^{+} + MPTH^{\ddagger} \rightarrow Ru(bpy)_3^{2+}* + MPTH \tag{39}$$

In all cases, the emission has been unambiguously assigned to that arising from the direct photoexcitation of the $Ru(bpy)_3^{2+}$ complex.

In distinct contrast to the chemiluminescence involving organic systems [149a, b] ($\phi < 0.5$, often in the range of 1%), the efficiencies of these homogeneous electron transfer reactions of Ru-complex are quite high. In pulse radiolysis experiments in aqueous solution, for example, 38% of the e_{aq}^- consumed produce the $Ru(bpy)_3^{2+}$ MLCT excited state and another 55% produce some high energy products which may occur through a $Ru(bpy)_3^{2+}$ intermediate excited state.

Electrogenerated chemiluminescence resulting from mutual annihilation reactions

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \rightarrow Ru(bpy)_3^{2+}* + Ru(bpy)_3^{2+} \tag{40}$$

has been investigated by Bard and co-workers [157,159], Itoh and Honda [158] and Glass and Faulkner [160]. In these studies, $Ru(bpy)_3^{3+}$, $Ru(bpy)_3^{+}$ species are produced alternately near the electrode by pulse methods and

their mutual reactions followed spectrophotometrically. ECL quantum yields, ϕ_{ECL}, in the range 3.5–6% have been reported for reaction (40) shown above. Compared to the luminescence quantum yield, ϕ_{lm}, of 0.042 for $Ru(bpy)_3^{2+}$* measured in water at 25°C, by direct photoexcitation methods, the reported ϕ_{ECL} values imply that the efficiencies for the formation of the CT excited state in the ion-annihilation reactions are near 100%. Thus, the $Ru(bpy)_3^{2+}$ redox system is the only case known conforming to the predictions based upon the Marcus theory of electron transfer, viz. the highest energetically accessible product state will be the one most efficiently populated in an ECL reaction. This assumption implies that in cases where the emitting state is directly populated (as opposed to energy transfer or T–T annihilation), ECL efficiency in principle should be limited only by the luminescence quantum yield. The fact that with the Ru-complex, ECL efficiencies are close to 100% has also been verified by the measurement of temperature dependence of ECL emission yield, ϕ_{ECL} and its direct correlation with the luminescence quantum yield.

Data on the luminescence intensity versus time (I vs. t) in ECL reactions of the type shown above provide more information about the details of the mechanism. For most ECL systems studied, experimental data on I–t curves deviate significantly from theoretical predictions for ideal energy-sufficient "S-route" systems. (S-route systems are those where emitting species are produced directly in the electron transfer reaction. Energy-deficient systems of T-route are those where the electron transfer is energetically insufficient to leave a product in the observed emitting state.) Recently, Bard, Faulkner and co-workers, have shown independently, by the potential sequential step techniques for the study of I–t behaviour that the $Ru(bpy)_3^{2+}$ system is the first case to follow the ideal S-route behaviour.

G. $Ru(bpy)_3^{2+}$ AS A PHOTOSENSITISER IN SOLAR ENERGY CONVERSION

(i) Photodecomposition of water with metal complexes

Among the various methods that are being explored for the photochemical conversion and storage of solar energy, a challenging problem is the photodissociation of water with visible light. The extensive redox chemistry exhibited by the $Ru(bpy)_3^{2+}$* has prompted several investigations on the possible utility of this complex as a photosensitiser for the above process. The photodecomposition of water can be considered in terms of two half-cell reactions

$$e^- + H_2O \rightarrow OH^- + \tfrac{1}{2} H_2 \quad (41)$$

$$H_2O \rightarrow 2 H^+ + \tfrac{1}{2} O_2 + 2 e^- \quad (42)$$

Generation of a molecule of hydrogen or oxygen involves multielectron transfers (2 e^- for H_2 and 4 e^- for O_2) with the redox potentials for the above processes 0.0 V and 1.23 V (vs. NHE) respectively at pH 0.

Discussions on redox potentials for the various oxidation states for the $Ru(bpy)_3^{2+}$ complex in the ground and excited states (section C) (E_0 Ru(2+ */3+) = −0.81 V; E_0 Ru(3+/2+) = 1.23 V; E_0 Ru(2+ */+) = 0.81 V; and E_0 Ru(+/2+) = −1.26 V) reveal that it is possible to envisage several redox schemes involving some of these states to achieve one or more of the above processes. (Even though the CT excited state has the required redox potential to reduce water directly, there has been no report of its actual occurrence.)

(a) Photoreduction of water either with $Ru(bpy)_3^+$ or with a suitable acceptor relay reduced in an oxidative quenching step.

$$2\,A^- + 2\,H_2O \xrightarrow{\text{cat.}} 2\,A + 2\,OH^- + H_2 \tag{43}$$

$A^- = Ru(bpy)_3^+$ or other reduced acceptors such as Eu^{2+} or MV^+.

(b) Photooxidation of water either with $Ru(bpy)_3^{3+}$ or with some suitable oxidised donor produced in a reductive quenching step.

$$4\,D^+ + 2\,H_2O \xrightarrow{\text{cat.}} 4\,D + 4\,H^+ + O_2 \tag{44}$$

In recent years there have been several successful reports on efficient photogeneration of these strong oxidants and reductants as well as coupling of these to water oxidation or reduction reactions respectively. In this section we review some of these studies. The success of these experiments are due as much as to the development of suitable redox cycles as to the development of redox catalysts for efficient occurrence of reactions (43) and (44).

In schemes where either water oxidation or reduction is carried out, for charge equivalence, it is inevitable that one of the components be oxidised or reduced irreversibly. In general, systems for the light induced H_2 evolution from water have a sensitiser such as $Ru(bpy)_3^{2+}$, an electron acceptor relay (capable of carrying out reaction (43)), an electron donor to regenerate the sensitiser from its oxidised state and a redox catalyst. Similarly, systems for light induced O_2 evolution from water invariably utilise an acceptor which decomposes/disproportionates upon photoreduction and a redox catalyst to facilitate $Ru(bpy)_3^{3+}$ oxidation of water. Multi-electron processes such as shown in eqns. (43) and (44) are grossly inefficient in the absence of redox catalysts. Redox catalysts that have been employed have been both of the homogeneous and heterogeneous type. We also briefly mention studies which utilise $Cr(bpy)_3^{3+}$, $Rh(bpy)_3^{3+}$ as sensitisers for water reduction and $Fe(bpy)_3^{3+}$ for the water oxidation in the dark.

(ii) Photoproduction of hydrogen from water

The photoredox system $Ru(bpy)_3^{2+}$–methyl viologen $(MV)^{2+}$ with EDTA or triethanolamine (TEOA) as the electron donor and a Pt catalyst, has been thoroughly studied as a system leading to light-induced H_2 evolution from water [138,163–189]. Upon visible light excitation, $Ru(bpy)_3^{2+}$ reduces MV^{2+} to its radical, MV^{+}

$$Ru(bpy)_3^{2+} + MV^{2+} \overset{h\nu}{\rightleftarrows} Ru(bpy)_3^{3+} + MV^{+} \tag{45}$$

Kinetic analysis of the oxidative quenching process at different MV^{2+} concentrations by laser flash photolysis yields the rate constants for the forward and reverse electron transfers as 5.5×10^8 M^{-1} s^{-1} and 2.4×10^9 M^{-1} s^{-1} respectively. The reaction is subject to strong ionic strength effects [139]. The cage escape yield for the redox products is about 30%. The back reaction in eqn. (45) can be prevented by the addition of a third component, an electron donor, such as TEOA, which is capable of reducing $Ru(bpy)_3^{3+}$ to the 2+ state

$$Ru(bpy)_3^{3+} + R_2NCH_2CH_2OH \rightarrow Ru(bpy)_3^{2+} + R_2^{+}NCH_2CH_2OH \tag{46}$$

With increasing amounts of TEOA, reaction (46) removes $Ru(bpy)_3^{3+}$ in competition with reverse electron transfer of eqn. (45), leaving part of the MV^{+} formed as a stable product.

The MV^{+} radical yields are pH dependent, decreasing in the acid pH reactions due to reactions such as

$$MV^{+} + R_2^{+}NCH_2CH_2OOH \rightarrow R_2NCH_2CH_2OH + MV^{2+} \tag{47}$$

and at alkaline pH, almost doubling due to the following reactions

$$R_2^{+}NCH_2CH_2OH \overset{pK_a=7.8}{\rightleftharpoons} R_2NCH_2CH^{\cdot}OH + H^{+} \tag{48}$$

$$R_2NCH_2\dot{C}HOH + MV^{2+} \rightarrow R_2NCH_2CHO + MV^{+} + H^{+} \tag{49}$$

One observes essentially similar behaviour with EDTA as the electron donor. In the presence of Pt catalysts, MV^{+} radical reduces water to H_2, according to the equation

$$2\,MV^{+} + 2\,H_2O \overset{\text{cat. Pt}}{\rightarrow} 2\,MV^{2+} + 2\,OH^{-} + H_2 \tag{50}$$

The H_2 yields are also pH dependent, being maximal around pH 4–5 with EDTA as the electron donor. At low pH values, the H_2 yields fall off due to fall off in the MV^{+} yields due to reactions such as (47). The fall off at pH > 6 presumably arises from the thermodynamic inability of MV^{+} radicals ($E_0 = -0.44$ V, vs. NHE, pH independent) to reduce water at these high

pH values. Reaction (50) is thermoneutral at pH 6.0. The maximal quantum yields for H_2 has been found to be ca. 15% [138,169]. Towards improving the efficiency of the system, quenching efficiencies and H_2 yields have been studied with various viologens and bpy, phen complexes with substituents covering a range of redox potentials. The other variations of this system include studies with polymeric systems with pendant viologen groups, surfactant derivatives of $Ru(bpy)_3^{2+}$ and MV^{2+}, redox partners incorporated in the organised media of micelles, synthetic surfactant vesicle systems, as adsorbed on cellulose etc. Some of these studies will be elaborated in later sections.

Lehn and co-workers [119,190] have reported efficient H_2 production on visible light photolysis of the $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$, TEOA system in aqueous solution in the presence of K_2PtCl_6 which turns into an active colloidal Pt catalyst during irradiation. The mechanism involved has been shown to be oxidative.

$$Ru(bpy)_3^{2+}* + Rh(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{3+} + Rh(bpy)_3^{2+} \qquad (51)$$

There has been some speculation as to whether or not the $Rh(bpy)_3^{3+}$ acts as a one electron relay like MV^{2+} or as a two electron relay undergoing a Rh(III)–Rh(I) cycle. Detailed studies by Sutin and co-workers [120,121] have shown that H_2 evolves mainly from Pt^0-catalysed reactions of Rh(II). As in the MV^{2+} system, the $Ru(bpy)_3^{3+}$ is reduced by the electron donor TEOA to the 2+ state. The oxidised, deprotonated $TEOA^+$ radical being a good reductant, reduces another molecule of $Rh(bpy)_3^{3+}$. In the absence of Pt, $Rh(bpy)_3^{2+}$ undergoes aquation and subsequent disproportionation yielding $Rh(bpy)_2^+$. The Rh(I) complex can exist in a variety of chemical forms depending on the Rh-complex concentration and pH: at low pH as $Rh(bpy)_2^+$ and the hydride $[Rh(bpy)_2(H_2O)H]^{2+}$ and at high pH as $[Rh(bpy)_2]^{2+}$ (dimer) and as $[Rhbpy_2]_2H^{3+}$. None of these species evolve H_2 in the dark by themselves. The cage escape yield for the Rh(II) species is 0.15 in reaction (51) and $\phi_{H_2} = 0.11$, a value close to $\phi_{Rh(I)}$ in the absence of Pt catalysis.

A number of heterogeneous catalysts such as colloidal metals [119,190], polymer supported metals [169,173,177], metals deposited on solid supports such as zeolites [190] and semiconductor powders [188,189,190a] phthalocyanine dispersions [189a] have been prepared and their efficiency to catalyse H_2 evolution tested with the two photoredox systems above. To date, the best efficiencies have been with Pt or Rh as colloids or as deposited on semiconductor powders of TiO_2 or $SrTiO_3$ [188,190a].

Physical descriptions of the redox catalysis step (reaction (50)) on the noble metals have been in terms of "microelectrode" concepts. Herein the Pt particles are pictured to behave as if they were electrodes polarised cathodically by the reduced MV^+ (or Rh(II)) radicals. With low overvoltages for H_2

evolution, they then catalyse water reduction efficiently. Miller and McLendon [183] have described the model in more quantitative terms and obtained experimental verification with various noble metals and with viologens of different redox potentials.

In addition to these popular systems based on the oxidative quenching of $Ru(bpy)_3^{2+}$*, systems involving reductive quenching of the excited state have been described by Sutin and co-workers [191,192] and Whitten and co-workers [193]. Here, the $Ru(bpy)_3^{2+}$ is converted to the more strongly reducing, long lived $Ru(bpy)_3^{+}$ state and the H_2 evolved directly from it with a Pt catalyst or via reduction of a metal complex yielding an unstable metal hydride. The latter systems involving Co(II) complexes, for example, are attractive, for they provide a means of homogeneous catalysis for the photoreduction of water. In the studies of Whitten and co-workers [193], hydrophobic, substituted bpy complexes of Ru(II) are photoreduced to the (+) state with TEA in H_2O–CH_3CN mixtures. In dry CH_3CN, the reaction

$$Ru(bpy)_3^{2+}* + TEA \rightarrow Ru(bpy)_3^{+} + TEA^{+} \tag{52}$$

is irreversible and $\phi_{Ru+} = 2.0$ due to reactions of the type outlined earlier (deprotonation and subsequent dark reduction of $Ru(bpy)_3^{2+}$ by the $TEOA^{\ddagger}$ radical). Crutchley and Lever [179] have described a similar system with $Ru(bpz)_3^{2+}$ as the sensitiser. With added MV^{2+}, $\phi_{MV^+} = 0.77$. In the presence of water and a Pt-catalyst, the Ru(2+) complex is regenerated

$$2\,Ru(bpy)_3^{+} + 2\,H_2O \xrightarrow[cat.]{Pt} 2\,Ru(bpy)_3^{2+} + 2\,OH^{-} + H_2 \tag{53}$$

In systems involving Co(II) either as a macrocyclic complex or as a labile bipyridine complex, $Co(bpy)^{2+}$ formed in situ and $Ru(bpy)_3^{+}$ (produced via reductive quenching with ascorbate or Eu^{2+} ions) reduced Co(II) to Co(I). The latter, as a coordinatively unsaturated d^8 complex, undergoes oxidative addition of H_3O^{+} to form a d^6-hydride. The hydrides of the Co system are unstable and undergo spontaneous decomposition to yield the parent complex and H_2. The quantum yields for H_2 production are significant, reaching as high as 13%. H_2 evolution via oxidative quenching of Ti^{3+} [96] has been proposed but the results have been questioned recently [97].

Photoreduction of other transition metal bipyridyl complexes is also known to lead to H_2 evolution, e.g. $Cr(bpy)_3^{3+}$ [194], $Rh(bpy)_3^{3+}$ [119] and $Rh(bpy)_2Cl_2$ [195]. However, these complexes have their long wavelength CT absorption bands in the 300–400 nm region and ϕ_{H_2} even where the Pt catalysts are quite low. The cage escape yields of redox products and quantum yields for H_2 for various bpy-based systems are compared in Table 12.

TABLE 12

Summary of various photoredox systems for the photoproduction of H_2 from water using $Ru(bpy)_3^{2+}$ as the sensitiser

Donor	Acceptor	Reductant	Catalyst	ϕ(cage)	Optimal pH	$\phi(H_2)$	Ref.
$Ru(bpy)_3^{2+*}$	MV^{2+}	EDTA/TEOA	Pt–PVA	0.30	5.0	0.13	138, 169
$Ru(bpy)_3^{2+*}$	$Rh(bpy)_3^{3+}$	TEOA	Pt^0 (in situ)	0.15	7.8	0.11	120, 121
$Ru(bpy)_3^{2+*}$	$Rh(bpy)_3^{3+}$	EDTA	Pt^0 (in situ)	0.15	5.0	0.04	121
Eu_{aq}^{2+}	$Ru(bpy)_3^{2+*}$		Co^{II} L	1.00	1.0	0.05	191
Ascorb.	$Ru(bpy)_3^{2+*}$		Co^{II}	0.5	3.1	0.0005	191
Ascorb.	$Ru(bpy)_3^{2+*}$		$Co(bpy)_n^{2+}$ (in situ)			0.13	192
TEA	$Ru(bpy)_3^{2+*}$		PtO_2	2.0	CH_3CN: H_2O	0.53	193
TEA	RuL_3^{2+*} (isopropyl ester)		PtO_2	0.4	CH_3CN: H_2O	0.44	193
TEOA	Rh $bpy_2Cl_2^+$		Pt^0 (in situ)			0.02	195
EDTA	Cr bpy_3^{3+*}		Pt–PVA		4.8	0.08	194
TEOA	$Ru(bpz)_3^{2+}$	MV^{2+}		0.77			179

(iii) Photooxidation of water to molecular oxygen

Prior to a discussion on the photooxidation of water, it is useful to review results obtained on the thermal oxidation of water with the oxidised forms of bpy, phen complexes of transition metals. Bpy, phen complexes in higher oxidation state, $M(LL)_3^{3+}$ e.g. $Ru(bpy)_3^{3+}$, are known to undergo rapid reduction upon addition of alkali (OH^-) and such reactions have been postulated to involve oxidation of water to oxygen [196–204,204a].

$$4\,M(LL)_3^{3+} + 4\,OH^- \rightarrow 4\,M(LL)_3^{2+} + 2\,H_2O + O_2 \qquad (54)$$

(M = Fe(III), Ru(III), Os(III), and LL = bpy or phen).
Nord and Weinberg [196,197]originally investigated kinetics of such reductions by stopped flow techniques and observed H_2O_2 and O_2 as oxidation products. Later Creutz and Sutin [198], and Shafirovich and co-workers [199–204], in detailed studies, found that the O_2 yields are strongly dependent on pH (maximal O_2 yields of over 75%, obtained in the pH range 8–10 for the $Ru(bpy)_3^{3+}$ complex and pH 13.0 for $Fe(bpy)_3^{3+}$) and on the complex concentration. However studies with more purified samples of $Ru(bpy)_3^{3+}$ [203] showed that O_2 yields are much lower (ca. 15%) but the O_2 yields increase significantly in the presence of small amounts of hydrolisable ions such as Co^{2+} or Fe^{3+} (10^{-5}–10^{-4} M). This form of catalysis of O_2 evolution from water; homogeneous with ions such as Fe^{3+}, Co^{2+}, Mn^{2+} [199–204], and heterogeneous with RuO_2 [205–210], IrO_2 (either as powders, colloids or on zeolite supports) in reaction (54) shown above, have advanced rapidly in the recent years. It has been clearly established that both the pH profile and O_2 yields can be influenced by the addition of redox catalysts.

Studies of redox-catalyst assisted reduction of $Fe(bpy)_3^{3+}$ in water with RuO_2 [205,215] show that maximal yields of oxygen are obtainable in the pH range 7–8 for powders, pH 9–10 for colloidal forms of RuO_2 and pH 13.0 for the unassisted process. With $Ru(bpy)_3^{3+}$, the maximal yields are obtained in the pH range 4–5. These optimal pH ranges for these two systems show that the overvoltages for oxygen evolution can be reduced to ca. 200 mV on catalysts such as RuO_2 or IrO_2. Parmon and co-workers [211] have also investigated $Fe(bpy)_3^{3+}$ reduction in the presence of various homogeneous forms of redox catalysts of Co(II) and obtained similar results.

A simple scheme for the photooxidation of water that has been widely studied involves oxidative quenching of $Ru(bpy)_3^{2+}*$ with suitable acceptor molecules. The sequence of reactions that take place is as follows

$$Ru(bpy)_3^{2+}* + A \rightarrow Ru(bpy)_3^{3+} + A^- \qquad (55)$$

$$A^- \rightarrow \text{irreversible products} \qquad (56)$$

$$4\,Ru(bpy)_3^{3+} + 2\,H_2O \xrightarrow[cat]{} 4\,Ru(bpy)_3^{2+} + 4H^+ + O_2 \qquad (57)$$

TABLE 13

$Ru(bpy)_3^{2+}$-based photoredox systems for the light induced O_2 evolution from water

Quencher	k_q (M^{-1} s^{-1})	$\phi(Ru^{3+})$	Photolysis medium	Catalyst forms	Ref.
$Co(NH_3)_5Cl^{2+}$	9.3×10^8	1.00	pH 4.7 buffer	RuO_2-as powder	206, 207, 210
				RuO_2-as colloid	206, 207, 211
				RuO_2-as electrode	212, 214
				RuO_2-as zeolite support	209
				IrO_2-powder	209, 210
$Co(C_2O_4)_3^{3-}$	6.7×10^9	0.70	pH 4.7 buffer	RuO_2-as colloid	206
				RuO_2-as powder	206
Tl^{3+}	4.9×10^8 ($1\ N\ H_2SO_4$)	2.00	pH 1.8	RuO_2-colloid	206
				RuO_2-electrode	212, 214
Ag^+	3.5×10^6		pH 4.7 buffer	RuO_2-on zeolite	99
$S_2O_8^{2-}$	8.0×10^8	2.00	pH 4.7 buffer	RuO_2-powder	212
				RuO_2-colloid	206, 216
				RuO_2-on zeolite support	209
				RuO_2-electrode	212

Several acceptors which upon reduction, undergo irreversible decomposition (in reactions such as disproportionation, dimerisation, photoaquation), and hence do not react back with the $Ru(bpy)_3^{3+}$, have been studied and these include $Co(NH_3)_5Cl^{2+}$ [206,209], $Co(C_2O_4)_3^{3-}$ [206], $S_2O_8^{2-}$ [212], Tl^{3+} [206] and Ag^+ [99]. Table 13 lists systems of this type that have been studied along with their quenching characteristics and redox catalyst forms employed. Co(III) complexes such as $Co(NH_3)_5Cl^{2+}$ decompose (aquate) rapidly upon reduction

$$Co(NH_3)_5Cl^{2+} + e^- \rightarrow Co_{aq}^{2+} + 5\,NH_3 + Cl^- \qquad (58)$$

and are used widely. With acceptors such as Tl^{3+} or $S_2O_8^{2-}$, in the reduced state A^-, they are strong oxidants capable of oxidising a second $Ru(bpy)_3^{2+}$ molecule in the dark and so $\phi_{Ru^{3+}} = 2.0$ with these systems. The above reaction can also be carried out in photoelectrochemical cells, as shown in the next section.

H. STUDIES IN PHOTOELECTROCHEMICAL CELLS

The wide variety of photoredox reactions exhibited by the $Ru(bpy)_3^{2+}$ complex has prompted its use in various forms of photoelectrochemical cells (PEC): photogalvanic cells, sensitisation of semiconductor electrodes as well as in photoelectric-catalytic/synthetic cell systems. In the latter redox products are produced in the bulk homogeneous solution and they are oxidised/reduced with catalytic electrodes to achieve net chemical processes (photoelectrosynthetic and photocatalytic cells).

(i) Photogalvanic cells

The potential changes produced upon illumination of dilute aqueous solutions of redox couples have been recognised for a number of years. These potentials are a consequence of the changed composition of the irradiated solution relative to the unirradiated one and such situations usually arise if there is a significant difference in the rates of forward and reverse electron transfer in a given photoredox process. A well characterised photogalvanic cell system is that composed of thionine and Fe^{3+}. Starting with the early studies of Rabinowitch [217] the system has been investigated by several workers, more recently by Albery and Foulds [218].

Rate differences of the order of 10^4 observed in the photoredox kinetics of the $Ru(bpy)_3^{2+}$–Fe^{3+} system suggests it to be a candidate for a photogalvanic cell.

$$Ru(bpy)_3^{2+} + Fe^{3+} \rightleftharpoons Ru(bpy)_3^{3+} + Fe^{2+} \qquad (59)$$

Upon visible light photolysis of $Ru(bpy)_3^{2+}$ in the photogalvanic cell, $Pt/Ru(bpy)_3^{2+}$, Fe^{3+}, 1 N H_2SO_4/Pt, Lin and Sutin [219] have observed significant photopotentials of ca. 160 mV. Calculations indicate that in the steady state, over 35% of the initial $Ru(bpy)_3^{2+}$ complex is converted to the (3 +) state. Ferraira and Harriman [89] have observed large differences in the electron transfer rates as a function of acidity and hence the steady state conversion yields depend upon the nature of the acid medium. CF_3SO_3H has been suggested to be the best medium for carrying out the photolysis. The quantum yield and the electrode selectivity aspects have been investigated by Albery et al. [220] by rotating ring disc electrode (RRDE) techniques. An essential requirement for the efficient performance of a photogalvanic cell is the ability of the electrodes to discriminate one redox couple from the other ($Ru(bpy)_3^{3+/2+}$ from $Fe^{3+/2+}$ or vice versa) and it appears that Pt electrodes covered with a thin layer of the thionine dye [221] have better selectivity for the system than naked Pt. Transient processes in the cell have been investigated by Zelewsky and co-workers [222,223] by measurement of the current–time, potential–time characteristics of the cell and the data explained in terms of a simple theoretical model.

DeGraff and Demas [110] have recently investigated $Ru(bpy)_3^{2+}$–Hg^{2+} photoredox system as a candidate for the photogalvanic cell. While there is hardly any separation of the redox products ($\phi_{redox} = 10^{-2}$) in HCl medium, in $HClO_4$ Hg^{2+} efficiently quenches $Ru(bpy)_3^{2+}*$ to give $Ru(bpy)_3^{3+}$ and Hg^+ ($\phi_{redox} > 0.6$). Dimerisation of Hg^+ to give Hg_2^{2+} competes with back electron transfer, leading to a biphasic type time profile for the decay of $Ru(bpy)_3^{3+}$.

$$Ru(bpy)_3^{2+}* + Hg^{2+} \rightleftharpoons Ru(bpy)_3^{3+} + Hg^+ \quad (60)$$

$$2\ Hg^+ \rightarrow Hg_2^{2+} \quad (61)$$

$$2\ Ru(bpy)_3^{3+} + Hg_2^{2+} \rightarrow 2\ Ru(bpy)_3^{2+} + 2\ Hg^{2+} \quad (62)$$

Irradiations in $HClO_4$ in a photogalvanic cell with Pt counter electrode lead to development of photopotentials in the range of 130–230 mV.

(ii) Sensitisation of semiconductor electrodes

For efficient capture of solar energy, there has been a sustained interest in the improvement of the photoresponse of wide band gap (> 3 eV) semiconductor materials by coating them with a thin layer of visible light absorbing dyes. A recent approach to the photodissociation of water in photoelectrochemical cells, is to use a dye, which upon excitation by visible light will transfer an electron to the conduction band of an n-type semiconductor and subsequently return to the ground state by oxidation of water. Provided the

conduction band of the semiconductor and the oxidation potential of the dye are suitably placed with respect to water reduction and oxidation respectively, one can then envisage a sustained cyclic cleavage of water. $Ru(bpy)_3^{2+}$ as the dye and semiconductors TiO_2 (rutile), $SrTiO_3$ are attractive candidates as they readily fulfil these requirements. The advantage of the method against homogeneous photoredox systems is that the electrons are exchanged between the semiconductor electrode and the excited dye molecule in solution only in one direction.

Towards understanding the factors that control redox reactions on semiconductor electrodes, Memming and co-workers in a series of studies [224–229] have investigated charge injection from the excited state of the dye $Ru(bpy)_3^{2+}$ to the conduction band of doped n-SnO_2 electrodes. The occurrence of charge injection has been verified by the observation of anodic photocurrents and its action spectrum similar to that of the dye. The question as to whether only the adsorbed dye molecules alone or those in the electrolyte also are involved in the charge transfer, is related to the excited state lifetime of the dye. With a lifetime of ca. 620 ns for the CT excited state for the $Ru(bpy)_3^{2+}$ complex, the diffusion length is ca. 210 Å ($L = (D\tau)^{1/2}$ with diffusion coefficient of ca. 10^{-5} cm^2 s^{-1}). This implies that only molecules very close to the semiconductor surface can participate in the reaction although they need not necessarily be absorbed. Oxidation of water to O_2 has been invoked as the reaction responsible for the regeneration of the dye

$$4\,Ru(bpy)_3^{3+} + 2\,H_2O \rightarrow 4\,Ru(bpy)_3^{2+} + 4\,H^+ + O_2 \qquad (63)$$

In the presence of reductants such as allylthiourea or OH^-, which rapidly react with the oxidised form of the dye, there is a significant increase in the anodic photocurrents (process known as "supersensitisation"), consistent with the above model. Similarly the presence of quenchers of the excited state of the dye in solution also quenches the photocurrent.

Electrode processes initiated by the excitation of adsorbed molecules as against those in solution are easily distinguished in experiments with insoluble dyes coated as monolayers on the semiconductor electrodes. In one study Memming and Schröppel examined sensitised photocurrents in monolayer assemblies of stearyl carboxy ester derivatives of $Ru(pby)_3^{2+}$ deposited on SnO_2 electrodes [228]. Quantum yield studies of photocurrents showed that only ca. 15% of the excited dye molecules charge transfer to the semiconductor conduction band. With highly conducting SnO_2 electrodes, cathodic photocurrents are also observed in the presence of oxygen at pH less than 8. Detailed examination revealed that the photochemical effects of the following type (reactions occurring in the electrolyte bulk) were involved: photoexcitation in the presence of oxygen leads to formation of $Ru(bpy)_3^{3+}$ which

diffuses to the electrode where it gets reduced.

$$Ru(bpy)_3^{2+} * + O_2 \rightarrow Ru(bpy)_3^{3+} + O_2^- \quad (64)$$

$$Ru(bpy)_3^{3+} + e_{(CB)}^- \rightarrow Ru(bpy)_3^{2+} \quad (65)$$

Since the cathodic photocurrents were observed only with highly doped SnO_2, the electrons are transferred to $Ru(bpy)_3^{3+}$, presumably by tunnelling through the space charge layer. Photoelectrochemical cells involving $Ru(bpy)_3^{2+}$ covalently attached to n-SnO_2 have been examined by Ghosh and Spiro [230]. The derivatised electrodes were prepared via a silination procedure involving Ru(4-($CH_2CHSiCl_3$)-4′-methyl 2,2′ bpy)(2,2′bpy)$(PF_6)_2$. A thick coating of ca. 1000 layers was produced which was stable to organic solvents as well to aqueous acids and bases. The anodic photocurrents were twice those observed for SnO_2 in contact with aqueous solutions of $Ru(bpy)_3^{2+}$.

Spectral sensitisation of n-TiO_2 electrodes by $Ru(bpy)_3^{2+}$ has been explored by Clark and Sutin [231] and followed quite recently by Goodenough and co-workers [232–234]. As with SnO_2-electrodes, upon irradiation with visible light ($\lambda \geqslant 400$ nm) an anodic photocurrent was observed, whose action spectrum was similar to that of the dye. A distinct feature of the work is to use a chopped light, and phase sensitive detection to measure the small photocurrents (ca. nA). Recent studies have revealed the existence of a slow risetime cathodic photocurrent in addition to the fast risetime anodic photocurrent observed earlier. The former is believed to arise from the surface O_2^- ions on the TiO_2 surface. Derivatised versions of $Ru(bpy)_3^{2+}$ on n-TiO_2 [233] with carboxy-ester derivatives have also been prepared and tested. With this derivatised electrode, only a d.c. anodic photocurrent was observed with no slow risetime cathodic component. Intriguingly, the photoresponse also did not show a peak around 450 nm in the action spectrum. Machor and Schoonman [235] have used the surfactant derivatives of the $Ru(bpy)_3^{2+}$ as the sensitisers for n-$SrTiO_3$ electrodes, and interpreted their results in terms of charge injection from the excited dye to the conduction band of the semiconductor followed by regeneration of the oxidised dye in a thermal water oxidation process. Redox catalysis by $Ru(bpy)_3^{2+}$ on n-MoS_2 has also been demonstrated by Tributsch [236]. For reference, Table 14 summarises all reported studies on $Ru(bpy)_3^{2+}$ sensitisation of semiconductor materials.

Grätzel and co-workers have recently reported on the photodecomposition of water sensitised by $Ru(bpy)_3^{2+}$ and derivatives in the presence of semiconductor dispersions loaded with two redox catalysts Pt and RuO_2 [181,188,189]. Finely reduced Pt^0 particles were deposited on n-TiO_2 powders (loaded with Nb) by a chemical reduction or photoplatinisation procedure and the $Ru(bpy)_3^{2+}$ complexes were photolysed with visible light in the presence of

TABLE 14

Sensitisation of semiconductor electrodes with $Ru(bpy)_3^{2+}$ and its derivatives

Semi-conductor	Ru-complex	Medium	Ref.
n-TiO_2	$Ru(bpy)_3^{2+}$, $Ru(4,7,Me_2phen)_3^{2+}$	0.5 M H_2SO_4	231
n-TiO_2	$Ru(bpy)_3^{2+}$	0.5 M H_2SO_4	232
n-TiO_2	$Ru(bpy)_3^{2+}$-derivatised on electrode	0.5 M H_2SO_4	233, 234
n-$SrTiO_3$	$Ru(bpy)_3^{2+}$ as hexadecyl ester monolayer		235
n-SnO_2	$Ru(bpy)_3^{2+}$	0.1 N H_2SO_4	224, 225
n-SnO_2	$Ru(bpy)_3^{2+}$	H_2O, pH 9.0	227
n-SnO_2	$Ru(bpy)_3^{2+}$ and as stearyl ester monolayer	H_2O, pH 9.0	228
n-SnO_2	$Ru(bpy)_3^{2+}$ and as covalently bound derivative	0.1 N H_2SO_4	230
n-ZnO	$Ru(bpy)_3^{2+}$		236
n-MoS_2	$Ru(bpy)_3^{2+}$	CH_3CN	236

these dispersions and colloidal RuO_2. Decomposition of water to hydrogen and oxygen is believed to occur by charge injection mechanisms referred to earlier.

There have also been several studies reported recently by Meyer and co-workers which concern synthesis and characterisation of bpy, phen complexes derivatised on electrode materials such as Pt [237–240], bis bpy derivatives with reactive ligands such as (NO) [241–244] as well as mixed valence Ru dimers composed of bis bpy, bis phen derivatives [245–247]. These newly synthesised materials have provided extensive spectral data to serve as a testing ground for various theories on electron-transfer phenomena in metal complexes. Photochemical properties of these complexes are yet to be explored. Derivatised electrode materials appear to be promising for use as catalytic electrodes.

(iii) Photoelectrochemical cells based on photoredox reactions

With the recent reports of light induced H_2, O_2 evolution from water sensitised by $Ru(bpy)_3^{2+}$ and its derivatives, there has been some interest in the study of such reactions in photoelectrochemical cells. The advantage of the PEC systems is that parts of cyclic water cleavage can be carried out in two separate compartments enabling spatial separation of the two gases H_2, O_2. In addition to being explosive in nature, H_2–O_2 are difficult to separate.

PEC versions of the homogeneous systems for the light induced H_2 [248,249] evolution from water discussed earlier in section G(ii), have been demonstrated. In the following cell

$$Pt/Ru(bpy)_3^{2+}, MV^{2+}, \text{TEOA, pH 9.0 buffer}//1\ N\ HCl/Pt \quad (66)$$

photolysis leads to permanent reduction of MV^{2+} to $MV^{+\cdot}$ radicals by reaction sequences outlined earlier. In the former system, H_2 evolution is catalysed by colloidal Pt particles while in PEC's, it occurs on the Pt electrode remote from the photolysis compartment. Photocurrents of the order of 200 μA stable over an hour were observed. Optimisation studies with EDTA as the reductant show that it is possible to increase the photocurrents to 2.0 mA, in a cell with no chemical bias, i.e. pH of the anode and cathode compartments the same [250].

The rapid reactivity of $MV^{+\cdot}$ radicals towards oxygen has been exploited in a PEC [251] involving the reversible photoredox system $Ru(bpy)_3^{2+}$–MV^{2+}. If one carries out the photolysis in the presence of O_2, $MV^{+\cdot}$ radicals are completely scavenged by O_2 to yield $O^{-\cdot}_2$ and $Ru(bpy)_3^{3+}$

$$Ru(bpy)_3^{2+} + MV^{2+} \rightleftharpoons Ru(bpy)_3^{3+} + MV^{+\cdot} \quad (67)$$

$$MV^{+\cdot} + O_2 \rightarrow MV^{2+} + O^{-\cdot}_2 \quad (68)$$

$$O^{-\cdot}_2 + H^+ \rightarrow HO_2\cdot \rightarrow H_2O_2 \quad (69)$$

Under acidic conditions, $O^{-\cdot}_2$ radicals rapidly protonate to give $HO^{-\cdot}_2$ (ultimately H_2O_2) and $Ru(bpy)_3^{3+}$ builds up as a stable product. Carried out in the cathode compartment, photogenerated $Ru(bpy)_3^{3+}$ is reduced to the (2+) state with concomitant oxidation of water to O_2 at the counter electrode. The overall reaction in such a cell, $Pt/Ru(bpy)_3^{2+}, MV^{2+}, O_2$, 1 N H_2SO_4//1 N NaOH/Pt, would be

$$2\ H_2O + O_2 \rightarrow 2\ H_2O_2 \quad (70)$$

a reaction driven uphill by the visible light absorbed by the Ru-complex. Cells of this type have come to be known to be as photoelectrosynthetic cells [252].

Photoelectrochemical cells leading to overall oxidation of water, halide ions etc., involving $Ru(bpy)_3^{2+}$-sensitised redox reactions have been assembled [212–214,253,254] and their efficiencies examined for various acceptor molecules.

Cell I [253,254]: $Pt/Ru(bpy)_3^{2+}, Co(C_2O_4)_3^{3-}$,

1 N H_2SO_4//1 N NaOH or Fe^{2+}/Pt

Cell II [212,214]: $C/Ru(bpy)_3^{2+}$, $S_2O_8^{2-}$,
pH 4.7 buffer//pH 4.7 buffer/RuO_2

Cell III [213]: $C/Ru(L)_3^{2+}$, $S_2O_8^{2-}$,
1 N H_2SO_4//H_2O (pH 1.8) or 1 N HCl/RuO_2
(L = isopropyl ester of carboxy bipyridine)

Cell IV [214]: $C/Ru(bpy)_3^{2+}$, A,
1 N H_2SO_4//H_2O or 1 N HCl or 1 N HBr/RuO_2
$\left(A = Co(NH_3)_5Cl^{2+}, Co(C_2O_4)_3^{3-}, S_2O_8^{2-} \text{ or } Tl^{3+}\right)$.

The cells are based on the following reaction scheme.
At the cathode:

$$\left.\begin{array}{l} Ru(bpy)_3^{2+}* + A \rightarrow Ru(bpy)_3^{3+} + A^- \\ A^- \rightarrow \text{irreversible products} \end{array}\right\} \text{ (bulk)} \quad \begin{array}{l} (71) \\ (72) \end{array}$$

TABLE 15

$Ru(bpy)_3^{2+}$ sensitised anodic oxidations in photoelectrochemical cells

Ru-complex	Cathode compartment		
	Acceptor	Electrolyte conditions	Cathode
$Ru(bpy)_3^{2+}$	MV^{2+}, O_2	1 N H_2SO_4	Pt
$Ru(bpy)_3^{2+}$	$Co(C_2O_4)_3^{3-}$	1 N H_2SO_4	Pt
$Ru(bpy)_3^{2+}$	$S_2O_8^{2-}$	pH 4.7 buffer + 1 N Na_2SO_4	Carbon cloth
$Ru(bpy)_3^{2+}$	$S_2O_8^{2-}$	pH 4.7 buffer + 1 N Na_2SO_4	Carbon cloth
$Ru(bpy)_3^{2+}$	$S_2O_8^{2-}$	pH 4.7 buffer + 1 N Na_2SO_4	Carbon cloth
$Ru(bpy)_3^{2+}$	$Co(NH_3)_5Cl^{2+}$	pH 4.7 buffer + 1 N Na_2SO_4	Carbon cloth
$Ru(bpy)_3^{2+}$	Tl^{3+}	1 N H_2SO_4	Carbon cloth
RuL_3^{2+} (isopropyl ester)	$S_2O_8^{2-}$	1 N H_2SO_4	Carbon cloth
RuL_3^{2+} (isopropyl ester)	$S_2O_8^{2-}$	1 N H_2SO_4	Carbon cloth
RuL_3^{2+} (isopropyl ester)	$S_2O_8^{2-}$	1 N H_2SO_4	Carbon cloth
$Ru(bpy)_3^{2+}$	$Co(NH_3)_5Cl^{2+}$	pH 4.7 buffer + 1 N Na_2SO_4	Carbon cloth

$$Ru(bpy)_3^{3+} + e^{\prime} \rightarrow Ru(bpy)_3^{2+} \text{ (electrode)} \quad (73)$$

At the anode: one of the following reactions

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (74)$$

$$2\,H_2O \rightarrow 4\,H^+ + O_2 + 4\,e^- \quad (75)$$

$$2\,HX \rightarrow 2\,H^+ + X_2 + 2\,e^- \quad (X = Cl, Br) \quad (76)$$

A distinct feature of these studies is the utilisation of RuO_2-based electrodes as anodes for the oxidation of water and halide ions. These electrodes are known to have low over-voltage requirements for these difficult oxidations. Table 15 summarises observed photocurrents and potentials at the cathode for various acceptor systems at various incident photon fluxes. Oxidation of water at low pH values and of chloride ions requires generation of rather high photopotentials (> 1.35 V, vs. NHE) and these are easily reached if one employs the hydrophobic complexes of Ru(II) composed of di-isopropyl 4,4′-dicarboxy ester of 2,2′-bipyridine ligands. The oxidised forms of these complexes (in the 3+ state) are extremely reactive towards water. In order that one utilises all of the photogenerated oxidants in reduction on the

Anode compartment			Illum. source (λ 400 nm)	Photo-currents (mA cm^{-2})	Ref.
Electrolyte conditions	Oxidation process	Anode			
1 N NaOH	$H_2O \rightarrow O_2$	Pt		0.16	251
1 N NaOH	$H_2O \rightarrow O_2$	Pt		0.09	253, 254
pH 4.7 buffer +1 N Na_2SO_4	$H_2O \rightarrow O_2$	RuO_2	60 W	0.62	212, 214
1 N HBr	$Br^- \rightarrow Br_2$	RuO_2	60 W	1.40	212, 214
1 N HBr	$Br^- \rightarrow Br_2$		250 W	4.70	212, 214
pH 4.7 buffer +1 N Na_2SO_4	$H_2O \rightarrow O_2$	RuO_2	60 W	0.35	214
pH 4.7 buffer +1 N Na_2SO_4	$H_2O \rightarrow O_2$	RuO_2	250 W	0.32	214
1 N H_2SO_4	$H_2O \rightarrow O_2$	RuO_2	250 W	0.39	213
1 N HCl	$Cl^- \rightarrow Cl_2$	RuO_2	250 W	0.70	213
5 N NaCl	$Cl^- \rightarrow Cl_2$	RuO_2	250 W	0.80	213
1 N HBr	$Br^- \rightarrow Br_2$	RuO_2	250 W	2.40	214

electrode and not in the electrolyte bulk, it is advantageous to employ an additional relay species such as Ce^{4+} in such systems.

The observed photopotentials and photocurrents in photoelectrochemical cells of this type can be correlated in terms of a simple kinetic model [214] and utilisation of Evans-type diagrams: by the intersection of the current (i)–potential (E) curves for the respective redox processes at the cathode and the anode ($Ru(bpy)_3^{3+}$ reduction on the C cathode and $H_2O \rightarrow O_2$, $Cl^- \rightarrow Cl_2$ on the RuO_2 anode). For the $Ru(bpy)_3^{2+}$–acceptor systems under illumination, the steady state current vs. potential curve can be shown to be of the form

$$i_{ss} = -I_0 \cdot \phi_{eff.} \cdot F\left(1-10 \exp\left\{\epsilon \cdot C_0 \cdot d \cdot \left[f(e) - i_{ss}/i_d\right]\right\}\right) \tag{77}$$

where I_0 = incident photon flux, F = the faraday constant, C_0 = initial concentration of the Ru-complex, ϵ = the absorption coefficient of the complex and $f(e)$, a function which indicates the form of the oxidation wave for the Ru-couple and i_d the mass transfer limited photocurrent for the oxidant. ϕ_{eff} is the effective quantum yield for the formation of $Ru(bpy)_3^{3+}$

$$\phi_{eff} = \left[\frac{k_q[Q]}{k_q[Q] + 1/\tau}\right] \cdot \phi \tag{78}$$

where [Q] is the concentration of the quencher employed, k_q, the quenching rate constant and ϕ, the redox quantum yield for the quenching step. i_{ss} cannot be expressed explicitly but can be measured experimentally as a function of the potential. The intersection of this curve with that of the anode determines the cell current and the potentials. The experimentally measured photocurrents and potentials at the anode have been found to be in good agreement with these predictions.

I. PHOTOCHEMISTRY WITH SURFACTANT DERIVATIVES AND IN ORGANISED MOLECULAR ASSEMBLIES

(i) Photochemistry with surfactant derivatives in monolayers, micelles and vesicles

With the reports of Sprintschnik et al. in 1976 [255] that monolayer bound long chain surfactant derivatives of $Ru(bpy)_3^{2+}$ decomposed water to hydrogen and oxygen, there has been a growing interest in photochemical studies with surfactant derivatives, especially those of $Ru(bpy)_3^{2+}$ in several organised molecular assemblies such as monolayers, micelles, vesicles, polyelectrolytes, etc. Unfortunately, the original report could not be confirmed in subsequent detailed studies [256–259] and the failure has been attributed to some

adventitious impurities, probably some hydrolysis products that accumulated either during the synthesis or during the photochemical investigations. Since then, there have been several reports on the careful synthesis and characterisation of long chain surfactant derivatives of $Ru(bpy)_3^{2+}$ [260–265] both of the carboxy ester type ($Ru(bpy)_2 \cdot (bpy\text{-}COOR)_2$) and alkyl chain substituents on one or more of the bpy ligands. The carboxy ester derivatives are very susceptible to hydrolysis even under mild alkaline conditions. In Table 16 we have collected spectral data on some of these surfactant derivatives that have been reported.

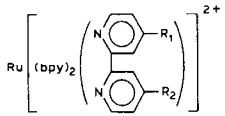
In their original work, deposited monolayers of di-octadecyl ester of the Ru-complex ($R_1 = R_2 = COOC_{18}H_{37}$) on glass slides were reported to decompose water to H_2, O_2 with a quantum yield of 0.1 upon exposure to visible light. The preparations gave good surface pressure–area isotherms with an area of ca. 40 $Å^2$ $molecule^{-1}$, both for the pure and for mixed layers with arachidic acid at a pressure of 30 dynes cm^{-1}. Subsequent preparations [256–259] gave much higher surface areas (ca. 85 $Å^2$ $molecule^{-1}$) at 30 dynes cm^{-1}. The carboxy esters are very susceptible to hydrolysis and HPLC analysis of the original samples showed presence of partially hydrolysed surfactant esters of the complex. Kuhn and co-workers [259], Valenty and co-workers [260] and others [262,263] have shown that mixtures of separately synthesised materials corresponding to these hydrolysed materials do indeed show this abnormally low surface area. The low surface-area data have thus been explained but the reasons for the absence of water oxidation remain obscure. Hydrolytically stable alkyl chain derivatives are better in this context and Sasse and co-workers [264], Gaines and co-workers [265] have reported on the synthesis and characterisation of several of these alkyl chain complexes. The monolayer absorption spectra of these are very similar to that in homogeneous solutions. π–A isotherms and luminescence spectra however showed significant dependence on the nature of the anion employed.

Intrigued by the results obtained in the monolayer experiments, these surfactant derivatives have been studied in a variety of other organised molecular assemblies of micelles and vesicles [266–284]. Solubilisation of the surfactant derivatives of the carboxy ester type in aqueous micellar solutions causes significant perturbations in absorption and emission spectra, relative to that in organic solvents. For example, the broad absorption peak around 450 nm with a shoulder in the shorter wavelength side observed in $CHCl_3$ changes to two well-resolved peaks (425, 490 nm), the one at longer λ being of lower intensity. The emission shows about 30–40 nm red shift. Similar behaviour is also observed in monolayers and mixed aqueous solvents. The alkyl chain derivatives do not show such differences.

Whitten and co-workers [10,285,286] have also reported on the synthesis

TABLE 16

Absorption, emission properties of hydrophobic surfactant derivatives of $Ru(bpy)_3^{2+}$

Ru complex 		Medium	Absorption		Emission		
			λ max (nm)	ε (mM)	λ max (nm)	τ (ns)	φ
A. Carboxy esters [256–263]							
R_1	R_2						
$COOCH_3$	$COOCH_3$	H_2O	475		660	615	0.045
Et	COOEt	H_2O	459	14.0			0.18
$COOC_{18}H_{37}$	$COOC_{18}H_{37}$	$CHCl_3$	482	13.1	665	900	0.18
$COOC_{18}H_{37}$	$COOC_{18}H_{37}$	EtOH	485			980	0.082
$COOC_{18}H_{37}$	$COOC_{18}H_{37}$	$NaLS/H_2O$	415, 505		695		
$COOC_{18}H_{37}$	$COOC_{18}H_{37}$	Monolayers	420, 490			900	
COOH	$COOC_{18}H_{37}$	$CHCl_3$	465	12.0	690		
B. Alkyl derivatives [264, 265]							
R_1	R_2						
CH_3	$C_{18}H_{37}$					850	0.06
$C_{18}H_{37}$	$C_{18}H_{37}$					850	0.06
$C_{19}H_{39}$	$C_{19}H_{39}$	$CHCl_3$	457	12.0	620		
$C_{19}H_{39}$	$C_{19}H_{39}$	NaLS (0.05 M)	452		625	500	
CH_3	CH_3	$CHCl_3$	457	11.0			

and photoredox properties of a series of substituted "hydrophobic" complexes RuL_3^{2+}, in which the polar, charged $Ru(bpy)_3^{2+}$ core is surrounded by aliphatic groups of varying size. Table 17 gives a summary of their absorption, emission and redox properties of CH_3CN. An interesting feature of these complexes is their selectivity to electron transfer reactions. In dry CH_3CN, there is efficient quenching by amines such as triethylamine (TEA) or dimethylaniline (DMA)

$$RuL_3^{2+}* + TEA \rightarrow RuL_3^{+} + TEA^{+} \tag{79}$$

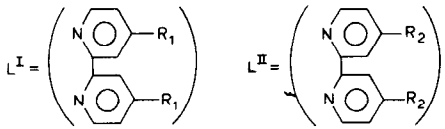
but, with di-isopropyl ester, for example, there is no back reaction and RuL_3^{+} builds up as a stable product upon photolysis. The ϕ_{redox} is 0.35 and the product is stable for a period of days in dry CH_3CN. However, in the presence of water or air, there is rapid return to the initial (2 +) species. The radical cations of amines presumably react in subsequent steps to give non-radical products (CH_3CHO has been identified as one of them). H_2 generation has been demonstrated in the thermal oxidation step in CH_3CN–H_2O mixtures in the presence of a Pt catalyst

$$2\,RuL_3^{+} + 2\,H_2O \xrightarrow{Pt^0} 2\,RuL_3^{2+} + 2\,OH^{-} + H_2 \tag{80}$$

Concurrent with the development of systems for the light induced H_2 evolution from water (section G) efficient photosensitised reduction of MV^{2+} in the presence of added electron donors in cationic micelles [266] has also been demonstrated. Herein the sensitiser Ru-complex was bound to the hydrophobic sites of the micellar interior. The donor, acceptor molecules being very water soluble are present in the bulk aqueous phase. More clear-cut examples of organisation of reactants at the molecular level are studies in vesicle systems. In single bilayer vesicles and multi-bilayer liposomes (these can be composed of naturally occurring lipids or of synthetic surfactant derivatives with two alkyl chains) there are distinct regions of hydrophobicity (made up of lipid chains arranged in the form of bilayer) and aqueous hydrophilic phase boundaries both in the interior and on the outside. With such systems it is possible to incorporate photoredox partners in spatially separated regions. Several studies involving surfactant derivatives of $Ru(bpy)_3^{2+}$ in such systems have been reported recently. In an elegant study, Calvin and co-workers [274] have examined photosensitised electron transport across phospholipid vesicle walls with di-C_{18} carboxy ester derivatives of $Ru(bpy)_3^{2+}$. By a suitable procedure of sonication and gel filtration, a photosystem was constructed wherein the Ru-complex is bound to the lipid phase, acceptor MV^{2+} located in the outer aqueous phase with donor EDTA being present in the inner aqueous phase. A kinetic model allowed derivation of an order of magnitude estimate for the rate constant

TABLE 17

Spectral, redox properties of a series of "hydrophobic" substituted bpy complexes of Ru(II) of the $Ru(L^I_2L^{II})^{2+}_3$ type [10,285,286]



Ru-complex	Absorption		Emission (298 K)		$E_{1/2}$ (oxid.) (vs. SCE) (V)	$E_{1/2}$ (red.) (vs. SCE) (V)
	λ_{max} (nm)	ϵ (mM)	λ_{max} (nm)	τ (μs)		
$R_1=R_2=H$	452	14.6	610	0.85	1.29	−1.32
$R_1=R_2=$-COOCH$(CH_3)_2$(4,4′)	468	19.4	629	2.39	1.59	−0.90
$R_1=R_2=$-COOCH$(CH_3)_2$(3,3′)	505		670			−0.72
$R_1=R_2=$-$COOC_5H_{11}$			630	2.21	1.56	−0.91
$R_1=R_2=$-$COOCH_2C_6H_5$			636	1.93	1.56	−0.95
$R_1=R_2=$-$COOC_{10}H_7$			631	2.19		
$R_1=R_2=$-$COOC_{10}H_{17}$			632	2.21		
$R_1=H$; $R_2=$-COODHC			660	2.00		
$R_1=$-COODHC; $R_2=H$			644	2.10		
$R_1=R_2=$-COODHC			638	2.14		

TABLE 18

Photoredox reactions of $Ru(bpy)_3^{2+}$ and its derivatives in multiphase systems of micelles, vesicles and liposomes

Medium	Ru-complex type	Photoredox partners	Ref.
Micelles			
NaLS	Ru-C_{18} carboxyester	MV^{2+}, cysteine	266
NaLS, DTAB, CO-630	Ru-C_{18} carboxyester		267
	Ru-C_{18} alkyl dvt.	MV^{2+}, *p*-anisidine $Ni(CN)_4^{2-}$	
CTAC	Ru-C_{12}carboxyamide	DMA	268
NaLS, CTAC, Tx-100	Ru-C_{12}carboxyamide	C_{12}-MV^{2+}, AQS, EDTA	269
CTAC	Ru-C_{12}carboxyamide	n-Butyl PTH, NTA, TEA	270
CTAC	$Ru(bpy)_3^{2+}$	C_{12}-MV^{2+}, C_{14}-MV^{2+}, C_{18}-MV^{2+}	287, 288
NaLS	$Ru(bpy)_3^{2+}$	MV^{2+}, C_7-MV^{2+}	289
CTAB, NaLS	$Ru(bpy)_3^{2+}$	MV^{2+}	283, 284
NaLS	$Ru(bpy)_3^{2+}$	Zn, Co^+, Cd^+, e_{aq}^-	290
NaLS	$Ru(bpy)_3^{2+}$	$Ru(bpy)_3^{2+}$	291, 292
NaLS	$Ru(bpy)_3^{2+}$	MPTH	293
Vesicles & liposomes			
(a) Natural lipids			
DPC	Ru-C_{12}carboxyamide	C_{12}-MV^{2+}, AQS, EDTA, NTA, TEA	269, 271
DMPC	Ru-C_{12}carboxyamide	n-Butyl PTH	270
Egg DPC	Ru-C_{16}carboxyamide	MV^{2+}, EDTA	273, 274
DPC	Ru-C_{16}carboxyamide	C_7-MV^{2+}, EDTA, vanilomycin	279
(b) Synthetic lipids			
C_{16}NB	Ru-C_{12}carboxyamide	n-Butyl PTH	270
C_{16}NB	Ru-C_{12}carboxyamide	DMA	271
C_{16}NB	Ru-C_{12}carboxyamide	C_{16}-MV^{2+}, EDTA	272
DODAC	Ru-C_{18} alkyl dvt.	PTH, C_{12}-PTH	278
DODAC	Ru-C_{18}alkyl dvt.	MV^{2+}, EDTA	280
DODAC	$Ru(bpy)_3^{2+}$	Ag^+	281
DODAC	$Ru(bpy)_3^{2+}$	C_{14}-MV^{2+}	282

for the electron transport across the lipid vesicle walls. Analogous experiments of photosensitised electron transport across vesicle bilayers of various photoredox couples have been reported recently by Matsuo and co-workers [269–272] and Fendler and co-workers [278,280]. Flash photolysis data on the growth and decay of the redox products in these systems are of considerable assistance in the assignment of mechanisms, as has been demonstrated by Fendler and co-workers. Table 18 provides a summary of various photoredox systems that have been examined, in micelles, natural lipid liposomes and synthetic bilayer vesicles.

(ii) Luminescence and photoredox processes of $Ru(bpy)_3^{2+}$ in micellar media and in polyelectrolytes

Solubilisation of molecules in aqueous micelle-forming surfactant solutions alter distinctly their photophysical, photochemical properties in many ways, and interest in the exploitation of this phenomenon has been growing rapidly in recent years [294–296]. The ability of micelles to solubilise a wide variety of water-insoluble molecules and the presence of a charged interface region provide in these systems a unique opportunity to study the influence of spatial separation of reactants and charged interfaces on the efficiency of charge separation in photoredox processes [297]. Several studies of luminescence behaviour of $Ru(bpy)_3^{2+}$ and its quenching by additives in micelles have been reported.

Lachish et al. [291] examined the emission decay of $Ru(bpy)_3^{2+}$ in aqueous anionic micellar solutions of sodium lauryl sulphate (NaLS) and observed a biphasic behaviour in the decay time profile: a fast initial part followed by a slower component having the normal lifetime of ca. 600 ns. The fast component became more pronounced at sub-c.m.c. (c.m.c. ca. 8.0×10^{-3} M) concentrations of NaLS and it was attributed to the association of $Ru(bpy)_3^{2+}$ to the negatively charged micelles. Recently [292] the fast component has been interpreted as due to, "self-quenching" resulting from the high local concentrations of $Ru(bpy)_3^{2+}$ in the clusters of NaLS containing several $Ru(bpy)_3^{2+}$.

Kinetic measures of quenching of $Ru(bpy)_3^{2+}*$ by *N*-methylphenothiazine [293], methyl viologen [283,284,287,288] and 2-methylanthracene [292,298,299] in micellar media have been examined in some detail. Maestri et al. [293] have described a phenomenological model for describing the kinetics of fast intramicellar redox reactions. It takes into account the influence of compartmentation and of statistical distribution of reactants and the derived kinetic equations differ from the rate laws of homogeneous kinetics. The distribution of water-insoluble solutes in micelles is adequately described by a Poisson distribution. According to this, the probability P_n of

finding n solute molecules in a given micelle is given by

$$P_n = m^n \cdot e^{-m}/n! \tag{81}$$

where m is the mean (average) number of solute molecules per micelle.

In cases where both the excited state and the quencher are exclusively bound to the micelle, a Poisson distribution of quenching species results, e.g. quenching by 2-methyl anthracene. The luminescence decay in such cases shows multiexponential character and consists of components of emission of excited states in micelles containing varying number of quencher molecules. The decay at long times (often a single exponential) corresponds to the emission of the unquenched Ru-complex. A method for determination of the micellar aggregation number is also described [298,300]. A second case arises where the quencher is partially water-solubilised. Here again, multiexponential decay is observed but the decay at long times corresponds to quenching by quencher molecules present in water. An example of the latter situation in MV^{2+} quenching of surfactant $Ru(bpy)_3^{2+}$-complex (a C_{18} dialkyl derivative) in anionic NaLS micelles [283,284]. Kinetic analysis of this intramicellar quenching enables determination of the binding constant of MV^{2+} onto the micellar surface as well as rates of binding and dissociation. The exchange of MV^{2+} molecules has been found to be very rapid relative to the decay of the Ru-complex excited state. The quenching rates and the association constants are strongly influenced by the presence of added electrolytes [284]. The model also allows analysis of these specific electrolyte effects on the quenching kinetics.

An interesting variation of the above situation is provided in the quenching of $Ru(bpy)_3^{2+}*$ by a series of surfactant viologen salts C_nMV^{2+} ($n = 11$, 13, 15, 17) in water and in aqueous cationic micellar solutions [287,288].

$$Ru(bpy)_3^{2+}* + C_nMV^{2+} \rightarrow Ru(bpy)_3^{3+} + C_nMV^{+} \tag{82}$$

The forward electron transfer occurs with the viologens present in the aqueous phase with $k_q = 6.7 \times 10^8\ M^{-1}\ s^{-1}$. (Evidence in support comes from the observation that the specific rate for quenching increases linearly with C_nMV^{2+} concentration until c.m.c. is reached where one observes a plateau. This implies that only monomers of C_nMV^{2+} are effective in quenching.) Upon reduction, the relay acquires hydrophobic properties leading to rapid solubilisation in the micelle. The subsequent thermal back reaction is impaired by the positive surface potential of the micelles and is reflected in a 500-fold drop in the rate constant.

Polyelectrolytes such as polyvinylsulphate (PVS) are also an interesting class of systems for the study of the influence of molecular organisation and of electronic forces on reaction kinetics. Photoredox quenching by Cu^{2+}, Fe^{3+} or $Ru(bpy)_3^{2+}*$ in PVS has been studied by Meisel and co-workers

[301–303] Rabani and co-workers [304,305]. In negatively charged polyelectrolytes such as PVS, cations like Cu^{2+}, Fe^{3+} and even $Ru(bpy)_3^{2+}$ adsorb strongly onto the surface, resulting in relatively high local concentrations of these species on the surface. At moderate Cu^{2+} concentrations, it quenches the Ru-excited state with Stern–Volmer constants 2000 times higher than in the absence of PVS. With a limited number of binding sites on the polyelectrolyte, further increase in adsorbing quenchers results in the displacement of previously adsorbed sensitiser complex. This results in the phenomenon of "quenching reversal". Similar behaviour was observed for Fe^{3+} quenching. A linear increase in quenching rate with Fe^{3+} concentration was observed up to 25% coverage of the sites. At higher concentrations, the rate dropped, presumably due to some configurational changes of the polymer caused by the adsorbed cations.

(iii) $Ru(bpy)_3^{2+}$ photochemistry in other multiphase systems of clays, zeolites, polymers and membranes

Van Damme and co-workers [306,307] have investigated the absorption, emission properties of $Ru(bpy)_3^{2+}$, $Cr(bpy)_3^{3+}$ as exchangeable cations in clay membranes of the Smectite and Hectorite type. These are layer lattice silicates of very high surface area (up to 800 $m^2\ g^{-1}$) and are known to show excellent catalytic properties due to the high degree of dissociation of adsorbed water and due to the presence of Lewis acid sites. The absorption spectrum of adsorbed $Ru(bpy)_3^{2+}$ showed large differences with respect to the spectrum in water (intensity of π–π^* bands near 290 nm significantly reduced with new bands developing near 320 nm) and the results interpreted as due to the formation of covalently hydrated or slightly distorted bpy ligands. Based on IR, XPS data, the adsorbed Ru-complex is pictured to be slightly distorted with weaker Ru–N bonds but with stronger Ru–H_2O interactions [307]. The efficiency of quenching by various M^{3+} quenchers (Eu^{3+}, Cr^{3+} and Fe^{3+}) and of oxygen were also examined. $Ru(bpy)_3^{2+}$–Hectorite samples were found to be photoinert at room temperature but irradiations at higher temperatures (70°C) led to the formation of Ru^{III}-oxo-bridged dimers, via photoaquation followed by thermal redox dimerisation.

Synthesis and spectral properties of $Ru(bpy)_3^{2+}$ incorporated in Y-zeolites have been reported by DeWildes et al. [308]. The bpy complex was synthesised by reacting the ligand with a $Ru(NH_3)_6$–Y form of the zeolite. The resulting complexes are characterised by absorption, emission bands similar to those in aqueous solutions. The relatively high concentration of the adsorbed dye results in "concentration quenching" of the excited state. The role of adsorbed water on the luminescence has also been investigated.

Lee and Meisel [309] and Thornton and Laurence [310] have provided an

interesting study of the effects of the morphology of perfluorosulphonate membranes of the Nafion type on the excited state quenching kinetics of $Ru(bpy)_3^{2+}$. The loading of the Ru-complex and that of quenchers was carried out by equilibrating a well-stirred solution of the former with the membrane samples for about 12 h. While the absorption spectrum of the adsorbed complex is very similar to that in aqueous solution, the emission spectrum showed a more pronounced effect (ca. 12 nm blue shift and ca. 10 nm narrowing of the width at half height as compared to aqueous solution). By comparison of spectral properties in various micelles, polyelectrolytes, the environment in the membranes is pictures as close to that in Na-perfluorooctanoate micelles. The quenching of excited states by various metal ions (Cu^{2+}, Cr^{3+} and Eu^{3+}) all occur by a dynamic process but the detailed nature of the process was found to be very similar to the inhomogeneous quenching as observed in micellar systems. Rubenstein and Bard [162] also adsorbed $Ru(bpy)_3^{2+}$ on Nafion-type membranes and studied chemiluminescence processes.

The possibility of photoinduced charge separation at the solid–liquid interfaces utilising a polystyrene pendant $Ru(bpy)_3^{2+}$ has been explored by Kaneko et al. [311,312]. The polystyrene complex is insoluble in water or methanol but soluble in DMF, $CHCl_3$, THF as well as in DMF–water mixtures. Light induced formation of MV^+ in the presence of EDTA, MV^{2+} as well as formation of H_2 in the presence of added Pt-black were observed. These authors also adsorbed MV^{2+} on a cellulose and studied photoreduction of MV^{2+} in the solid phase sensitised by $Ru(bpy)_3^{2+}$ present in the aqueous phase. A significant feature of this system is the accumulation of MV^+ even in the presence of oxygen [313].

Earlier, Clear et al. [314] have reported on the synthesis and properties of polyvinyl pyridine-bound $Ru(bpy)_3^{2+}$. The polymer supported complex however was found to be unstable, undergoing photochemical ligand substitution reactions. Recently, a similar report appeared [315] concerned with the synthesis and properties of the $Ru(bpy)_2$(terpy) moiety attached to poly-4-vinylpyridine. Absorption and emission studies showed that, in these metallo-polymers, at low degree of metallation, the optical properties of polymer-bound sites are essentially those of the related monomer but at a high degree of metallation, evidence for interaction between sites has been obtained.

J. PHOTOSUBSTITUTION AND RACEMISATION REACTIONS OF $Ru(bpy)_3^{2+}$

One of the main attractions of the $Ru(bpy)_3^{2+}$ complex for photochemical studies is its ability to retain its chemical identity as a tris-chelated complex when it undergoes a wide variety of photochemical reactions. For studies in

aqueous media at room temperature, it behaves strictly as a photosensitiser. However, several studies in recent years indicate that the Ru-complex does undergo photosubstitution reactions especially at elevated temperatures, in strongly acidic, alkaline conditions and also in a few selected organic solvents such as DMF or CH_2Cl_2 [74,316–319].

Van Houten and Watts [317] have investigated photoaquation behaviour of $Ru(bpy)_3^{2+}$ in 0.1 M HCl in the temperature range 40–95°C. Photolysis with visible light ($\lambda = 436$ nm) led to significant changes in the absorption spectrum of the complex. Analysis of the photoproducts showed the presence of two main products: a possible Cl^--anation product where one Cl^- and one monodentate bpy ligand are bound to Ru(II): $[Ru(bpy)_2 \cdot (bpy)(Cl)]^+$ and another, based on its pH dependence of absorbance formulated as $[Ru(bpy)_2 \cdot (OH)(bpy)]^+$. The monodentate bpy hypothesis has been proposed to explain the recovery of the starting tris-bipyridine complex in CH_3CN. Similar complexes with monodentate bpy ligands have been proposed as intermediates in the thermal reduction of $Ru(bpy)_3^{3+}$ in water to give $Ru(bpy)_3^{2+}$ [204a]. The photosubstitution reactions are thermally activated with quantum yields in the range 10^{-3}–10^{-5}. A kinetic model has been proposed which assumes that the photochemical reactions occur from a set of ligand field (LF) levels located at about 3560 cm^{-1} above the CT levels and are in thermal equilibrium with them.

Concurrent to these investigations, Gleria et al., [316] have reported that $Ru(bpy)_3Cl_2$ is photolabile in chlorinated solvents such as CH_2Cl_2 giving $Ru(bpy)_2Cl_2$ as the major product. In CH_2Cl_2, $\phi = 0.02$, a value much higher than that (ca. 10^{-3}) observed in DMF or EtOH. In low-polarity solvents, factors such as ion-pairing and solvation effects appear to play an important role in the substitutional photochemical behaviour. Detailed investigations by Meyer et al. (unpublished results quoted in ref. 74), showed that the reactions involve ion-pairs and photosubstitutions occur through an upper, probably *d–d* excited state which is thermally populated from the emitting CT state, such as proposed by Van Houten and Watts [317]. The lack of significant entering group dependence suggests that the substitution step is largely dissociative. The absence of any significant net substitutional photochemistry in DMF or water at ambient temperature is attributed to possible, efficient, rapid re-chelation of the intermediates such as $[Ru(bpy)_2 \cdot (bpy) \cdot (H_2O)]^{2+}$. $[Ru(bpy)_2Cl_2]$ is formed as a substitution product in CH_2Cl_2 only with $[Ru(bpy)_3]Cl_2$ and not from $[Ru(bpy)_3][PF_6]_2$, [74,320] indicating that the chloride source for the dichloro complex in chlorinated hydrocarbons is the counter anion rather than the solvent. Efficient formation of substitutional products such as $Ru(bpy)_2X_2$ (X = Cl or Br) and $Ru(bpy)_2(DMF)(X)^+$ upon photolysis of $Ru(bpy)_3X_2$ in DMF have also been observed [74]. Ion-pair formation has been implicated as the primary

TABLE 19

Substitution products in the photolysis of $Ru(bpy)_3^{2+}$-derivatives in various solvents

Ru complex	Photolysis conditions	Photoproducts and their absorption spectral features (λ_{max} and ϵ_{mM})	$\phi_{prod.}$	Ref.
$[Ru(bpy)_3](SCN)_2$	DMF, 25°C $[SCN^-]=0.1$ M	$[Ru(bpy)_2(SCN)_2]^0$ 515 (9.3), 360 (9.8)	5.0×10^{-4}	318
		$[Ru(bpy)_2(DMF)(SCN)]^+$ 498 (9.8), 353 (9.8)	3.0×10^{-4}	318
$[Ru(bpy)_3](Cl)_2$	CH_2Cl_2, 25°C	$[Ru(bpy)_2Cl_2]^0$ 556 (9.4), 380 (9.4)	0.02	316
$[Ru(bpy)_3](Br)_2$	DMF, 25°C $[Br^-]=0.017$ M	$[Ru(bpy)_2Br_2]^0$ 551 (12.2), 373 (13.3)	6.8×10^{-5}	319
		$[Ru(bpy)_2(DMF)(Br)]^+$ 524 (8.2), 360 (7.7)	2.1×10^{-4}	319
$[Ru(bpy)_3](Cl)_2$	0.1 M HCl, 80°C	$[Ru(bpy)_2(OH)(bpy)]^+$ 510 at pH=8.0 and 485 at pH=1.0	4.4×10^{-4}	317
		$[Ru(bpy)_2(Cl)(bpy)]^+$ 495		317
$[Ru(bpy)_3](Cl)_2$	CH_3CN, 25°C	$[Ru(bpy)_2(CH_3CN)(Cl)]^+$ 476, 342	$<10^{-2}$	320
	CH_3NO_2, 25°C	$[Ru(bpy)_2(CH_3NO_2)(Cl)]^+$ 485	$<10^{-2}$	320
$[Ru(bpy)_2(py)_2]^+ + X^-$ ($X^-=F^-$, Cl^-, Br^-, SCN^-)	CH_2Cl_2, 25°C	$[Ru(bpy)_2(X)_2]+2$ py $X^-=Cl^-$: 556, 380	0.18 for loss of first py	74
$[Ru(bpy)_2(py)_2]^+ + Y^-$ ($Y^-=NO_3^-$, CH_3COO^-, ClO_4^-)	CH_2Cl_2, 25°C	$[Ru(bpy)_2(py)(Y)]^+ + py$ $Y^-=NO_3^-$: 488, 346	0.18 for loss of first py	74

photoactive species during photolysis. Table 19 summarises available data on the photosubstitution reactions of $Ru(bpy)_3^{2+}$ and its analogues.

Another photoreaction of $Ru(bpy)_3^{2+}$ that has been investigated is photoracemisation [321]. In aqueous solutions at neutral pH, the Δ-complex racemises upon irradiation with visible light and the reaction readily monitored by following the decrease in the circular dichroism spectrum. The racemisation, like photosubstitution, is thermally activated, has a quantum yield in the range of 10^{-3}–10^{-4}, and occurs via the luminescent excited state. Competitive (photodecomposition versus photoracemisation) studies implicate again a common five-coordinated achiral intermediate involving a monodentate bpy.

TABLE 20

Absorption, emission and quenching properties of dicyanocomplexes, $Ru(bpy)_2(CN)_2$ and $Ru(phen)_2(CN)_2$ [322,324]

Property	Medium	$Ru(bpy)_2(CN_2)$	$Ru(phen)_2(CN)_2$
Absorption			
λ_{max} (nm) and ϵ (mM)	CH_3OH	458 (8.9)	452 (10.1)
		325 (7.8)	415 (9.2)
	H_2O	432 (6.0)	435 (9.0)
			395 (9.3)
Emission			
λ_{max} (nm)/77 K	CH_3OH–H_2O	570, 605	568, 610
λ_{max} (nm)/298 K	CH_3OH	660	628
λ_{max} (nm/298 K	H_2O	638	613
τ (μs)/298 K	CH_3OH	0.40	1.58
τ (μs)/298 K	H_2O	0.27	0.71
τ (μs)/298 K	DMF	0.22	0.09
pK_a (ground state)	H_2O-/HCl	0.13, −0.07	0.13, −0.07
pK_a^* (excited state)	H_2O/HCl	5.0, 2.0	6.0, 2.0
Quenching rate constants, k_q (M^{-1} s^{-1})			
$Co(NH_3)_5Cl^{2+}$	H_2O	3.3×10^9	3.9×10^9
$Co(NH_3)_6^{3+}$	H_2O	1.39×10^9	2.3×10^9
$Ni(CN)_6^{2-}$	H_2O	4.38×10^9	5.6×10^9
$Fe(CN)_6^{4-}$	H_2O	0.61×10^9	0.51×10^9
$Fe(CN)_6^{3-}$	H_2O	6.9×10^9	6.54×10^9
$Co(C_2O_4)_3^{3-}$	H_2O	2.98×10^9	3.24×10^9

TABLE 21

Comparison of spectral properties of protonated, deprotonated forms in $Ru(L_2(4,7(OH)_2phen))^{2+}$ complexes [323]

Property		L=2,2′-bpy		L=1,10-phen	
		Protonated (pH 1.0)	Deprotonated (pH 13.0)	Protonated (pH 1.0)	Deprotonated (pH 13.0)
Absorption in water					
λ_{max} (nm) and ϵ (mM)		460 (12.6)	495 (10.0)	455 (15.0)	490 (12.4)
		445 (12.9)	458 (9.7)	425 (16.7)	428 (15.6)
		288 (65.3)	370 (18.7)	263 (78.8)	385 (14.7)
Emission					
In water (298 K)	λ_{max} (nm)	652	730	635	719
	τ (ns)	455	38	1250	175
		0.01	0.001	0.04	0.003
In D_2O (298 K)	λ_{max} (nm)	652	730	635	719
	τ (ns)	800	76	2100	310
		0.02	0.002	0.07	0.006
In EtOH (77 K)	λ_{max} (nm)	597, 645	656, 725	590, 629	649
	τ (μs)	3.9	1.2	3.0	1.0
		0.27	0.02	0.38	0.01
pK_a (ground state)		10.1		10.0	
pK_a^* (excited state)		5.1		4.7	

K. ACID–BASE PROPERTIES OF EXCITED STATES IN SUBSTITUTED bpy, phen COMPLEXES OF Ru(II)

Excited state acid–base reactions of organic molecules have long been known and studied by luminescence methods. There have been a few cases of distinct changes in the acid–base properties on excitation to higher excited states in substituted bis bpy, phen complexes of Ru(II) [322–327].

Demas and co-workers have investigated in some detail excited state acid–base reactions in $Ru(bpy)_2(CN)_2$ and $Ru(phen)_2(CN)_2$. Like the tris-chelated complexes, the dicyanocomplexes are good luminescence donors, with long lived CT emission in fluid solution and undergo a variety of photoredox reactions [322–324]. Table 20 gives a summary of selected data on the absorption, emission and quenching properties of the two dicyano complexes. The cyanide is sufficiently basic to be protonated at low pH to exist in two acid forms: $[Ru(bpy)_2(CN)(CNH)]^+$ (HD^+) and $[Ru(bpy)_2(CNH_2)]^{2+}$ (H_2D^{2+}). At room temperature, at 0.3 M $> H^+ <$ 3 M, substantial amounts of HD^+ and H_2D^{2+} can co-exist with D but on excitation $HD^{+}*$ and $H_2D^{2+}*$ are such strong acids that they deprotonate very rapidly, and only CT emission from D* is observed

$$H_2D^{2+}* \rightleftharpoons HD^{+}* + H^+ \tag{83}$$

$$HD^{+}* \rightleftharpoons D* + H^+ \tag{84}$$

The deprotonation reactions thus occur with 100% efficiency.

Introduction of substituents such as hydroxyl or carboxyl in one of the bpy, phen ligands also alters the absorption, luminescence properties of the resulting complex upon changes in the pH of the solution, as has been

TABLE 22

Excited state acid–base properties in substituted, mixed ligand bpy, phen complexes of Ru(II)

Ru complex	pK_a		Ref.
	Ground state	Excited state	
$Ru[bpy_2\cdot(4,7\text{-}(OH)_2phen)]^{2+}$	10.1	5.1	326
$Ru[(4,4'\text{-}Me_2bpy)_2\cdot(4,7\text{-}(OH)_2phen)]^{2+}$	10.0	5.4	326
$Ru[phen_2\cdot(4,7\text{-}(OH)_2phen)]^{2+}$	10.1	4.7	326
$Ru[(3,4,7,8\text{-}Me_4phen)_2(4,7\text{-}(OH)_2phen)]^{2+}$	9.8	5.6	326
$Ru(bpy)_2\cdot(CN)_2$	0.13, −0.07	5.0, 2.0	322, 324
$Ru(phen)_2(CN)_2$	0.13, −0.07	5.0, 2.0	322, 324
$Ru(bpy_2(4,4'\text{-}(HOOC)_2bpy))^{2+}$	1.75, 2.80	8.5	325, 327

demonstrated by Wrighton and co-workers [325,326]. Table 21 presents data on the absorption, emission properties of acidic, basic forms of the hydroxyl-substituted bpy, phen complexes of Ru(II). As the pK_a^* values indicate, the complexes are stronger acids in the excited state compared to the ground state. Upon deprotonation, the absorption and emission spectra are red shifted, suggesting the deprotonated forms are strong π-donors. Similar results have been obtained for carboxyl-substituted derivatives [326,327]. For these complexes at pH 3.5, the deprotonated form is almost exclusively excited while luminescence is observed from the protonated form. pK_a values in the ground and excited states for these various substituted bpy, phen complexes are collected in Table 22.

ADDENDUM

Since the completion and submission of the manuscript, several publications dealing with various aspects of $Ru(bpy)_3^{2+}$ photochemistry have appeared and we briefly review them here.

Tinnemans et al. [328] have described the synthesis and properties of several binuclear 1:10 phen/2,2'bpy complexes of Ru(II). Electrochemical studies indicate that the redox reactions of these complexes involve two electron transfer. Similarly Belser and co-workers [329,330] have described properties of Ru-complexes of the type $Ru(bpy)_{3-n}(LL)_n^{2+}$ (where $n = 0$–3, LL = di-t-butylbpy, dimethylbpy or a diquinoyl derivative DMCH). The DMCH derivative, in particular, appear to have some interesting visible light absorption, redox properties well suited for solar energy conversion. Careful luminescence measurements by Demas and co-workers [331] on $Ru(bpy)_3^{2+}$ dispersed in either polyvinylalcohol or polyvinylpyrrolidone solid films suggest that the Ru-complex can serve as a luminescence counter.

Reductive quenching of $Ru(bpy)_3^{2*}$ by benzenethiolate (PhSH) in acetonitrile has been shown to be efficient [332] ($k_q = 5.7 \times 10^9$ M^{-1} s^{-1}) and the back reaction is suppressed by rapid dimerisation of the thiyl radicals (PhS·). Such systems also exhibit significant photogalvanic effects [333]. Similarly reductive quenching of RuL_3^{2+}* (L = carboxy esters of bpy) by amines, quinone and aromatic ethers and subsequent reactions of the redox products have been examined by laser flash photolysis by Monserrat et al. [334]. The mechanism of H_2 evolution with photoreduced RuL_3^+ species and colloidal Pt catalyst is explored in some detail. $Ru(bpy)_3^{2+}$-mediated photoreduction with olefins and nicotinamide derivatives via reductive quenching have also been demonstrated [335,336].

$Ru(bpy)_3^{2+}$ sensitised H_2 evolution from water with methyl viologen (MV^{2+}) and colloidal redox catalysts continue to receive special attention [337–351]. Pt catalysts produced via citrate reduction and protected by

carbowax evolves H_2 from MV^+ in quantitative yield [337,338]. Quantitative description of "microelectrode" concepts for the action of the redox catalysts has been presented by McLendon and co-workers [339,340]. Irreversible photoreduction of the viologen relay with inefficient Pt catalysts limit long term performance of the photosystem [341]. As expected, the H_2 yields vary as a function of the viologen redox potential [342]. The role of functionalised viologen relays, of micelle and of colloids such as SiO_2 in effecting charge-separation in the $Ru(bpy)_3^{2+}$–viologen system have been elaborated by various authors [343–347]. Interesting photceffects have been shown with Nb-doped TiO_2 catalyst particles [348,349]. In the presence of EDTA, the H_2 yields are maximal and the system evolves H_2 from water even in the absence of EDTA by direct charge injection from MV^+ to the conduction bands of TiO_2. Studies have been reported also on the oxidation of water by photogenerated $Ru(bpy)_3^{3+}$, mediated by heterogeneous [352,353] or homogeneous [354,355] catalysts. Sensitisation of metal, semiconductor electrodes by derivatised versions of $Ru(bpy)_3^{2+}$ continue to receive some attention [356–358]. The photodecomposition of $Ru(bpy)_3^{2+}$ complex in very acidic HCl solutions has been the subject of a report by Giro et al. [359]. Kurimura et al. [360] have described light induced oxidation of ascorbic acid and formation of H_2O_2, via oxidative quenching with molecular O_2.

CONCLUDING REMARKS

It is encouraging to note that in just a decade since the report of Demas and Adamson in 1971 on the possible use of $Ru(bpy)_3^{2+}$ as a photosensitiser, the Ru-complex and its derivatives have established themselves clearly as superior sensitisers especially for photoredox processes. Its recent use in studies on the photodissociation of water tempt many authors to call it "an inorganic substitute for chlorophyll-*a* in in vitro photosynthesis". Clearly many more interesting studies on this and related complexes are bound to come. It should also be mentioned that considerable progress has been made in recent years in the photochemistry of bpy, phen complexes of other transition metals, especially those of Cr, Ir, Rh and Co. Cr and Rh complexes have already shown good promise for possible use in studies of solar energy conversion and storage.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the continued encouragement and fruitful discussions on materials covered in this review with Prof. M. Grätzel. Our thanks are also due to the Swiss National Funds for Scientific Research for financial support. We would also like to thank the referees for their constructive criticisms.

REFERENCES

1 A. Adamson and P.D. Fleischauer (Eds.), Concepts in Inorganic Photochemistry, Wiley, New York, 1975.
2 V. Balzani, L. Moggi, M.F. Manfrin, F. Boletta and G.S. Laurence, Coord. Chem. Rev., 15 (1975) 321.
3 G.A. Crosby, Acc. Chem. Res., 8 (1975) 231.
4 T.J. Meyer, Isr. J. Chem., 15 (1977) 200.
5 T.J. Meyer, Acc. Chem. Res., 11 (1978) 94.
6 N. Sutin and C. Creutz, Adv. Chem. Ser., 168 (1978) 1.
7 V. Balzani, F. Boletta, M.T. Gandolfi and M. Maestri, Topics Curr. Chem., 75 (1978) 1.
8 R.J. Watts, J.S. Harrington and J. van Houten, Adv. Chem. Ser., 168 (1978) 57.
9 P.J. DeLaive, J.T. Lee, H. Abruna, H.W. Sprintschnik, T.J. Meyer and D.G. Whitten, Adv. Chem. Ser., 168 (1978) 28.
10 P.J. DeLaive, D.G. Whitten and C. Giannoti, Adv. Chem. Ser., 173 (1979) 236.
11 V. Balzani, F. Boletta, F. Scandola and R. Ballardini, Pure Appl. Chem., 51 (1979) 299.
12 N. Sutin, J. Photochem., 10 (1979) 19.
13 T.J. Kemp, Prog. Reaction Kinet., 10 (1980) 301.
14 D.G. Whitten, Acc. Chem. Res., 13 (1980) 83.
15 N. Sutin and C. Creutz, Pure Appl. Chem., 52 (1980) 2717.
16 J.P. Paris and W.W. Brandt, J. Am. Chem. Soc., 81 (1959) 5001.
17 G.B. Porter and H.L. Schläfer, Ber. Bunsenges. Phys. Chem., 68 (1964) 316.
18 G.A. Crosby, W.G. Perkins and D.M. Klassen, J. Chem. Phys., 43 (1965) 1498.
19 R.A. Palmer and T.S. Piper, Inorg. Chem., 5 (1966) 864.
20 D.M. Klassen and G.A. Crosby, Chem. Phys. Lett., 1 (1967) 127.
21 P. Day and N. Sanders, J. Chem. Soc. A, (1967) 1536.
22 D.M. Klassen and G.A. Crosby, J. Chem. Phys., 48 (1968) 1853.
23 J.N. Demas and G.A. Crosby, J. Mol. Spectrosc., 26 (1968) 72.
24 F. Zuloaga and M. Kasha, Photochem. Photobiol., 7 (1968) 549.
25 I. Hanazaki and S. Nagakura, Inorg. Chem., 8 (1968) 648; Bull. Chem. Soc., Jpn., 44 (1971) 2312.
26 F.E. Lytle and D.M. Hercules, J. Am. Chem. Soc., 91 (1969) 253.
27 J.N. Demas and G.A. Crosby, J. Am. Chem. Soc., 92 (1970) 7262.
28 J.N. Demas and G.A. Crosby, J. Am. Chem. Soc., 93 (1971) 2841.
29 I. Fujita and H. Kobayashi, Inorg. Chem., 12 (1973) 2758.
30 R.W. Harrigan and G.A. Crosby, J. Chem. Phys., 59 (1973) 3468.
30a R.W. Harrigan, G.D. Hager and G.A. Crosby, Chem. Phys. Lett., 21 (1973) 487.
30b R.J. Watts and G.A. Crosby, J. Am. Chem. Soc., 94 (1972) 2606.
31 G.A. Crosby, K.W. Hipps and W.H. Elfring, J. Am. Chem. Soc., 96 (1974) 629.
31a D.C. Baker and G.A. Crosby, Chem. Phys., 4 (1974) 428.
32 G.D. Hager and G.A. Crosby, J. Am. Chem. Soc., 97 (1975) 7031.
33 G.D. Hager, R.J. Watts and G.A. Crosby, J. Am. Chem. Soc., 97 (1975) 7037.
34 K.W. Hipps and G.A. Crosby, J. Am. Chem. Soc., 97 (1975) 7042.
35 J. van Houten and R.J. Watts, J. Am. Chem. Soc., 97 (1975) 3843.
36 J. van Houten and R.J. Watts, J. Am. Chem. Soc., 98 (1976) 4853.
36a G.A. Crosby and W.H. Elfring, J. Phys. Chem., 80 (1976) 2206.
37 S.R. Allsopp, A. Cox, S.A. Jenkins, T.J. Kemp and S.M. Tunstall, Chem. Phys. Lett., 43 (1976) 135.
38 S.R. Allsopp, A. Cox, T.J. Kemp and W.J. Reed, J. Chem. Soc. Faraday Trans. 1, 74 (1978) 1275.

39 M. Forster and R.E. Hester, Chem. Phys. Lett., 81 (1981) 42.
39a R.F. Dallinger and W.H. Woodroff, J. Am. Chem. Soc., 101 (1979) 4391.
40 F. Felix, J. Ferguson, H.U. Güdel and A. Ludi, Chem. Phys. Lett., 62 (1979) 153.
41 F. Felix, J. Ferguson, H.U. Güdel and A. Ludi, J. Am. Chem. Soc., 102 (1980) 4096.
42 K.W. Hipps, Inorg. Chem., 19 (1980) 1390.
43 M.K. DeArmond and C.M. Carlin, Abstr. IUPAC Conf. Photochem., Seefeld, Austria, 1980, p. 146.
43a R.H. Fabian, D.M. Klassen and R.W. Sanntag, Inorg. Chem., 19 (1977) 80.
43b D.M. Klassen, Inorg. Chem., 15 (1976) 3166.
44 P.D. Belser, C. Daul and A. von Zelewsky, Chem. Phys. Lett., 79 (1981) 596.
45 W.H. Elfring and G.A. Crosby, J. Am. Chem. Soc., 103 (1981) 2683.
46 M.K. DeArmond, C.M. Carlin and W.L. Huang, Inorg. Chem., 19 (1980) 62.
47 M.L. Stone and G.A. Crosby, Chem. Phys. Lett., 79 (1981) 169.
48 K. Mandel, T.D.L. Pearson and J.N. Demas, Inorg. Chem., 20 (1981) 786.
49 D.M. Krol and G. Blasse, Chem. Phys. Lett., 77 (1981) 253.
50 A.G. Motten, K. Hanck and M.K. DeArmond, Chem. Phys. Lett., 79 (1981) 541.
51 G.A. Heath, L.J. Yellowlees, P.S. Braterman, J. Chem. Soc. Chem. Commun., (1981) 287.
52 A. Ceulemans and L.G. van Quickenborne, J. Am. Chem. Soc., 103 (1981) 2238.
52a R.J.H. Clark, P.C. Turtle, D.P. Strummen, B. Streusand, J. Kincaid and K. Nakamoto, Inorg. Chem., 16 (1977) 84.
53 M. Kràl, Theor. Chim. Acta, 43 (1977) 273.
54 M. Kràl, Naturwissenschaften, 64 (1977) 385.
55 B. Mayoh and P. Day, Theor. Chim. Acta, 49 (1978) 259.
56 R.V. Bensasson, C. Salet and V. Balzani, J. Am. Chem. Soc., 98 (1976) 3722.
57 D. Meisel, M.S. Matheson, W.A. Mulac and J. Rabani, J. Phys. Chem., 81 (1977) 1445.
58 U. Lachish, P.P. Infelta and M. Grätzel, Chem. Phys. Lett., 62 (1979) 317.
59 R.V. Bensasson, C. Salet and V. Balzani, C. R. Acad. Sci. Ser. B, 289 (1979) 41.
60 C. Creutz, M. Chou, T.L. Netzel, M. Okumura and N. Sutin, J. Am. Chem. Soc., 102 (1980) 1309.
60a Q.A. Mulazzani, S. Emmi, P.G. Fuochi, M. Venturi, M.Z. Hoffmann and M.G. Simic, J. Phys. Chem., 83 (1979) 1562.
60b A. Harriman, J. Photochem., 8 (1978) 205.
61 N.E. Tokel-Takvoryan, R.E. Hemingway and A.J. Bard, J. Am. Chem. Soc., 95 (1973) 6582.
62 T. Saji and S. Aoyagui, J. Electroanal. Chem., 58 (1975) 401.
63 T. Saji and S. Aoyagui, J. Electroanal. Chem., 60 (1975) 1.
64 T. Saji and S. Aoyagui, J. Electroanal. Chem., 63 (1975) 405.
65 T. Saji and S. Aoyagui, J. Electroanal. Chem., 66 (1975) 81.
66 T. Saji and S. Aoyagui, J. Electroanal. Chem., 108 (1980) 223.
67 C.-T. Lin, W. Böttcher, M. Chou, C. Creutz and N. Sutin, J. Am. Chem. Soc., 98 (1976) 6536.
68 C.R. Bock, J.A. Connor, A.R. Gutierrez, T.J. Meyer, D.G. Whitten, B.P. Sullivan and J.K. Nagle, J. Am. Chem. Soc., 101 (1979) 4815.
69 T. Matsurmara-Inoue, H. Tomono, M. Kasai and T. Torminaga-Morimoto, J. Electroanal. Chem., 95 (1979) 109.
70 H.D. Abruna, A.Y. Teng, G.E. Samuels and T.J. Meyer, J. Am. Chem. Soc., 101 (1979) 6745.
71 P. Belser and A. von Zelewsky, Helv. Chim. Acta., 63 (1980) 1675.

72 Y. Ohsawa, T. Saji and S. Aoyagui, J. Electroanal. Chem., 106 (1980) 327.
72a R.J. Crutchley and A.B.P. Lever, J. Am. Chem. Soc., 102 (1980) 7128.
73 R.H. Fabian, D.M. Klassen and R.W. Sonntag, Inorg. Chem., 19 (1980) 1977.
74 B. Durham, J.L. Walsh, C.L. Carter and T.J. Meyer, Inorg. Chem., 19 (1980) 860.
75 J.H. Baxendale and M. Fiti, J. Chem. Soc. Dalton Trans., (1972) 1995.
75a Q.G. Mulazzani, S. Emmi, P.G. Fuochi, M.Z. Hoffman and M. Venturi, J. Am. Chem. Soc., 100 (1978) 981.
76 C. Creutz and N. Sutin, J. Am. Chem. Soc., 98 (1976) 6384.
77 C. Creutz, Inorg. Chem., 17 (1979) 1046.
78 M. Maestri and M. Grätzel, Ber. Bunsenges, Phys. Chem., 81 (1977) 504.
79 C.P. Anderson, D.J. Salmon, R.C. Young and T.J. Meyer, J. Am. Chem. Soc., 99 (1977) 1980.
80 D. Rehm and A. Weller, Ber. Bunsenges, Phys. Chem., 73 (1969) 834.
81 D. Rehm and A. Weller, Isr. J. Chem., 8 (1970) 259.
82 R.A. Marcus, Discuss. Faraday Soc., 29 (1960) 21; Ann. Rev. Phys. Chem., 15 (1964) 155; J. Chem. Phys., 43 (1965) 679.
83 N.S. Hush, Prog. Inorg. Chem., 8 (1967) 391; Electrochim. Acta., 13 (1968) 1005.
84 C.-T. Lin and N. Sutin, J. Am. Chem. Soc., 97 (1975) 3543.
85 R.C. Young, F.R. Keene and T.J. Meyer, J. Am. Chem. Soc., 99 (1977) 2468.
86 G.S. Laurence and V. Balzani, Inorg. Chem., 13 (1974) 2976.
87 C.R. Bock, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc., 96 (1974) 4710.
88 C. Creutz and N. Sutin, Inorg. Chem., 15 (1976) 496.
89 M.I.C. Ferreira and A. Harriman, J. Chem. Soc. Faraday Trans. 2, 75 (1979) 874.
90 D.G. Taylor and J.N. Demas, J. Chem. Phys., 71 (1979) 1032.
91 M.A. Hazelton, C.-T. Lin, H.A. Schwarz and N. Sutin, J. Am. Chem. Soc., 100 (1978) 2383.
92 J.E. Baggott and M.J. Pilling, J. Phys. Chem., 84 (1980) 3012.
93 J.N. Demas and J.W. Addington, J. Am. Chem. Soc., 98 (1976) 5800.
94 E. Sutcliffe, M. Neumann-Spallart and K. Kalyanasundaram, (1980) unpublished results.
95 B.S. Brunschwig and N. Sutin, Inorg. Chem., 18 (1979) 1731.
96 G. Giro, G. Casalbore and P.G. Di Marco, Chem. Phys. Lett., 71 (1981) 476.
97 B.S. Brunschwig and N. Sutin, Chem. Phys. Lett., 77 (1981) 63.
98 T.K. Foreman, C. Gianotti and D.G. Whitten, J. Am. Chem. Soc., 102 (1980) 1170.
99 K. Chandrasekaran, T.K. Foreman and D.G. Whitten, Nouv. J. Chim., 5 (1981) 275.
100 F. Boletta, A. Juris, M. Maestri and D. Sandini, Inorg. Chim. Acta, 44 (1980) L175.
101 M. Neumann-Spallart, K. Kalyanasundaram, C. Grätzel and M. Grätzel, Helv. Chim. Acta, 62 (1980) 1111.
102 J.S. Winterle, D.S. Kliger and G.S. Hammond, J. Am. Chem. Soc., 98 (1976) 3719.
103 V.S. Srinivasan, D. Podolski, N.J. Westrick, D.C. Neckers, J. Am. Chem. Soc., 100 (1978) 6513.
104 J.N. Demas, D. Diemente and E.W. Harris, J. Am. Chem. Soc., 95 (1973) 6865.
105 J.N. Demas, E.W. Harris and R.P.M. McBride, J. Am. Chem. Soc., 99 (1977) 3547.
106 J.N. Demas, R.P.M. McBride and E.W. Harris, J. Phys. Chem., 80 (1976) 2248.
107 Y. Kurimura and R. Onimura, Inorg. Chem., 19 (1980) 3516.
108 C. Creutz, N. Sutin and B.S. Brunschwig, J. Am. Chem. Soc., 101 (1979) 1297.
109 E. Pelizzetti, E. Mentasti and E. Pramauro, Inorg. Chem., 15 (1976) 2898.
110 B.A. DeGraff and J.N. Demas, J. Am. Chem. Soc., 102 (1980) 6169.
111 H.D. Gafney and A.W. Adamson, J. Am. Chem. Soc., 94 (1972) 8238.

112 I. Fujita and H. Kobayashi, J. Chem. Phys., 52 (1970) 4904.
113 I. Fujita and H. Kobayashi, J. Chem. Phys., 59 (1972) 2902.
114 I. Fujita and H. Kobayashi, Ber. Bunsenges. Phys. Chem., 76 (1972) 115.
115 G. Navon and N. Sutin, Inorg. Chem., 13 (1974) 2159.
116 P. Natarajan and J.F. Endicott, J. Phys. Chem., 77 (1973) 971.
117 P. Natarajan and J.F. Endicott, J. Phys. Chem., 77 (1973) 1823.
118 J.N. Demas and A.W. Adamson, J. Am. Chem. Soc., 93 (1971) 1800.
119 M. Kirsch, J.-M. Lehn and J.-P. Sauvage, Helv. Chim. Acta, 62 (1979) 1345.
120 G.M. Brown, S.F. Chan, C. Creutz, H.A. Schwarz and N. Sutin, J. Am. Chem. Soc., 101 (1979) 7638.
121 S.-F. Chan, M. Chan, C. Creutz, M. Matsubara and N. Sutin, J. Am. Chem. Soc., 103 (1981) 369.
122 F. Boletta, M. Maestri, L. Moggi and V. Balzani, J. Chem. Soc. Chem. Commun., (1975) 901.
123 R. Ballardini, G. Varani, M.A. Scandola and V. Balzani, J. Am. Chem. Soc., 98 (1976) 7432.
123a A. Juris, M.T. Gandolfi, M.F. Manfrin and V. Balzani, J. Am. Chem. Soc., 98 (1976) 1047.
124 N. Sabbatini, M.A. Scandola and V. Carassiti, J. Phys. Chem., 77 (1973) 1307.
125 N. Sabbatini, M.A. Scandola and V. Balzani, J. Phys. Chem., 78 (1974) 541.
126 F. Boletta, M. Maestri and V. Balzani, J. Phys. Chem., 80 (1976) 2499.
127 A. Juris, M.F. Manfrin, M. Maestri and N. Serpone, Inorg. Chem., 17 (1978) 2258.
128 H.E. Toma and C. Creutz, Inorg. Chem., 16 (1977) 545.
128a F. Boletta, M. Maestri, L. Moggi and V. Balzani, J. Phys. Chem., 78 (1974) 1374.
129 P. Natarajan and J.F. Endicott, J. Am. Chem. Soc., 94 (1972) 3635.
130 P. Natarajan and J.F. Endicott, J. Am. Chem. Soc., 95 (1973) 2470.
131 W. Böttcher and A. Haim, J. Am. Chem. Soc., 102 (1980) 1564.
132 K.R. Leopold and H. Haim, Inorg. Chem., 17 (1978) 1753.
133 K. Chandrasekaran and P. Natarajan, Inorg. Chem., 19 (1980) 1714.
134 K. Chandrasekaran and P. Natarajan, J. Chem. Soc. Dalton Trans., (1981) 478.
135 K. Chandrasekaran and P. Natarajan, J. Chem. Soc. Chem. Commun., (1977) 774.
136 J.N. Demas and A.W. Adamson, J. Am. Chem. Soc., 95 (1973) 5159.
137 C.R. Bock, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc., 97 (1975) 2909.
137a R.C. Young, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc., 97 (1975) 4781.
138 K. Kalyanasundaram, J. Kiwi and M. Grätzel, Helv. Chim. Acta, 61 (1978) 2720.
139 G.L. Gaines, J. Phys. Chem., 83 (1979) 3088.
140 K. Takuma, M. Kajiwara and T. Matsuo, Chem. Lett., (1977) 1199.
141 E. Amouyal, B. Zidler, P. Keller and A. Moradpour, Chem. Phys. Lett., 74 (1980) 314.
142 J.K. Nagle, J.S. Bernstein, R.C. Young and T.J. Meyer, Inorg. Chem., 20 (1981) 1760.
143 J.K. Nagle, R.C. Young and T.J. Meyer, Inorg. Chem., 16 (1977) 3366.
144 J.R. Darwent and K. Kalyanasundaram, J. Chem. Soc. Faraday Trans. 2, 77 (1981) 373.
145 R. Ballardini, G. Varani, M.T. Indelli, F. Scandola and V. Balzani, J. Am. Chem. Soc., 100 (1978) 7219.
146 A. Deronzier and T.J. Meyer, Inorg. Chem., 19 (1980) 2912.
146a T. Miyashita and M. Matsuda, Bull. Chem. Soc. Jpn., 54 (1981) 1740.
147 M.S. Wrighton and J. Markham. J. Phys. Chem., 77 (1973) 3042.
148 G. Favaro and F. Masetti, J. Phys. Chem., 83 (1979) 2129.
149 M.S. Wrighton, L. Pdungzap and D.L. Morse, J. Phys. Chem., 79 (1975) 66.
149a L.R. Faulkner, Int. Rev. Sci. Phys. Chem., 9 (1975) 213.

149b A.J. Bard and L.R. Faulkner, in A.J. Bard (Ed.), Electroanal. Chem., Vol. 10, Marcel Dekker, New York, 1977, Chap. 1.
150 D.M. Hercules and F.E. Lytle, J. Am. Chem. Soc., 88 (1966) 4795.
151 F.E. Lytle and D.M. Hercules, Photochem. Photobiol., 13 (1971) 123.
152 N.E. Tokel and A.J. Bard, J. Am. Chem. Soc., 94 (1972) 2862.
153 N.E. Tokel-Takvoryan, R.E. Hemingway and A.J. Bari, J. Am. Chem. Soc., 95 (1973) 6582.
154 C.D. Jonah, M.S. Matheson and D. Meisel, J. Am. Chem. Soc., 100 (1978) 1449.
155 J.E. Martin, E.J. Hart, A.W. Adamson, H. Gafney and J. Alpern, J. Am. Chem. Soc., 94 (1972) 9238.
156 H.D. Gafney and A.W. Adamson, J. Chem. Educ., 52 (1975) 480.
157 W. Wallace and A.J. Bard, J. Phys. Chem., 83 (1979) 1350.
158 K. Itoh and K. Honda, Chem. Lett., (1979) 99.
159 J.R. Luttmer and A.J. Bard, J. Phys. Chem., 85 (1981) 1155.
160 R.S. Glass and L.R. Faulkner, J. Phys. Chem., 85 (1981) 1160.
161 I. Rubenstein and A.J. Bard, J. Am. Chem. Soc., 103 (1981) 512.
162 I. Rubenstein and A.J. Bard, J. Am. Chem. Soc., 102 (1980) 6641.
163 S. Markiewicz, M.S. Chan, R.H. Sparks, C.A. Evans and J.R. Bolton, Paper presented at 1st Int. Conf. Solar Energy, London, Ontario, 1976.
164 A. Moradpour, E. Amouyal, P. Keller and H. Kagan, Nouv. J. Chim., 2 (1978) 547.
165 K. Takuma, M. Kajiwara and T. Matsuo, Chem. Lett., (1977) 1199.
166 J. Kiwi and M. Grätzel, Angew. Chem. Int. Ed. Engl., 18 (1979) 624.
167 K. Takuma, Y. Shuto and T. Matsuo, Chem. Lett., (1978) 983.
168 J. Kiwi and M. Grätzel, Nature (London), 281 (1979) 657.
169 J. Kiwi and M. Grätzel, J. Am. Chem. Soc., 101 (1979) 7214.
170 M. Gohn and N. Getoff, Z. Naturforsch. Teil A, 34 (1979) 1135.
171 I. Okura and N. Kim-Thuan, J. Mol. Catal., 5 (1979) 311.
172 I. Okura, S. Nakamura, N. Kim-Thuan and K.I. Nakamura, J. Mol. Catal., 6 (1979) 261.
173 P. Keller, A. Moradpour, E. Amouyal, H.B. Kagan, Nouv. J. Chim., 4 (1980) 377.
174 P. Keller, A. Moradpour, E. Amouyal and H.B. Kagan, J. Mol. Catal., 7 (1980) 539.
175 A.I. Krasna, Photochem. Photobiol., 31 (1980) 75.
176 E. Amouyal, P. Keller and A. Moradpour, J. Chem. Soc. Chem. Commun., (1980) 1019.
177 P. Keller and A. Moradpour, J. Am. Chem. Soc., 102 (1980) 7193.
178 Y. Okuno and O. Yonemitsu, Chem. Lett., (1980) 959.
179 R.J. Crutchley and A.B.P. Lever, J. Am. Chem. Soc., 102 (1980) 7128.
180 O. Johansen, A. Launikonis, A.W.H. Mau and W.H.F. Sasse, Aust. J. Chem., 33 (1980) 1643.
181 E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Grätzel, J. Am. Chem. Soc., 103 (1981) 6324.
182 D. Duonghong, E. Borgarello and M. Grätzel, J. Am. Chem. Soc., 103 (1981) 4685.
183 D. Miller and G. McLendon, Inorg. Chem., 20 (1981) 950.
184 I. Okura and N. Kim-Thuan, J. Chem. Soc. Faraday Trans. 1, 77 (1981) 1411.
185 I. Okura, N. Kim-Thuan and M. Takeuchi, Inorg. Chim. Acta, 53 (1981) L149.
186 T. Nishijima, T. Nagamura and T. Matsuo, J. Polym. Sci. Polym. Lett., 19 (1981) 65.
187 K. Ageishi, T. Endo and M. Okawara, J. Polym. Sci. Polym. Chem., 19 (1981) 1085.
188 J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca and M. Grätzel, Angew. Chem. Int. Ed. Engl., 19 (1980) 646.
189 E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Grätzel, Nature (London), 289 (1981) 158.

189a K. Kalyanasundaram, D. Duonghong and M. Grätzel, 1980, unpublished results.
190 J.M. Lehn, J.-P. Sauvage and R. Ziessel, Nouv. J. Chim., 5 (1981) 291.
190a J.-M. Lehn and J.-P. Sauvage, Nouv. J. Chim., 1 (1977) 449.
191 G.M. Brown, B.S. Brunschwig, C. Creutz, J.F. Endicott and N. Sutin, J. Am. Chem. Soc., 101 (1979) 1298.
192 C.V. Krishnan and N. Sutin, J. Am. Chem. Soc., 103 (1981) 2141.
193 P.J. DeLaive, B.P. Sullivan, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc., 101 (1979) 4007.
194 R. Ballardini, A. Juris, G. Varani and V. Balzani, Nouv. J. Chim., 4 (1980) 563.
195 K. Kalyanasundaram, Nouv. J. Chim., 3 (1979) 511.
196 G. Nord and O. Weinberg, J. Chem. Soc. Dalton Trans., (1972) 866.
197 G. Nord and O. Weinberg, J. Chem. Soc. Dalton Trans., (1975) 845.
198 C. Creutz and N. Sutin, Proc. Nat. Acad. Sci. U.S.A., 72 (1975) 2858.
199 V.Ya. Shafirovich, A.P. Moravskii, T.S. Dzhabiev and A.E. Shilov, Kinet. Catal., 18 (1977) 509.
200 V.V. Strelets, O.N. Efimov and V.Ya. Shafirovich, Kinet. Catal., 18 (1977) 646.
201 V.Ya. Shafirovich and A.E. Shilov, Kinet. Catal., 20 (1979) 1156.
202 V.Ya. Shafirovich and V.V. Strelets, Izv. Akad. Nauk. SSSR, 1 (1980) 7.
203 V.Ya. Shafirovich, N.K. Khannanov and V.V. Strelets, Nouv. J. Chim., 4 (1980) 81.
204 V.Ya. Shafirovich, N.K. Khannanov and V.V. Strelets, Dokl. Akad. Nauk SSSR, 250 (1980) 1197.
204a J.A.A. Sagnes, R.D. Gillard, R. Lancashire and P.A. Williams, J. Chem. Soc. Dalton Trans., (1979) 193.
205 J. Kiwi and M. Grätzel, Angew. Chem., Int. Ed. Engl., 18 (1979) 624.
206 K. Kalyanasundaram and M. Grätzel, Angew. Chem. Int. Ed. Engl., 18 (1979) 701.
207 K. Kalyanasundaram, O. Micic, E. Pramauro and M. Grätzel, Helv. Chim. Acta, 62 (1979) 2532.
208 J.M. Lehn, J.-P. Sauvage and R. Ziessel, Nouv. J. Chim., 3 (1979) 423.
209 J.-M. Lehn, J.-P. Sauvage and R. Ziessel, Nouv. J. Chim., 4 (1980) 355.
210 J. Kiwi and M. Grätzel, Chimia, 33 (1979) 289.
211 A.L. Elizasova, L.A. Matvienko, V.N. Parmon and K.I. Zamaraev, Dokl. Akad. Nauk SSSR, 249 (1979) 863.
212 M. Neumann-Spallart, K. Kalyanasundaram, C. Grätzel and M. Grätzel, Helv. Chim. Acta, 62 (1980) 1111.
213 M. Neumann-Spallart and K. Kalyanasundaram, J. Chem. Soc. Chem. Commun., (1981) 437.
214 M. Neumann-Spallart and K. Kalyanasundaram, Ber. Bunsenges Phys. Chem., 85 (1981) 704.
215 E. Pramauro and E. Pelizzetti, Inorg. Chim. Acta, 45 (1980) 2131.
216 A. Harriman, G. Porter and P. Walters, J. Chem. Soc. Faraday Trans. 2, in press.
217 E. Rabinowitch, J. Chem. Phys., 8 (1940) 551, 560.
218 W.J. Albery and A.W. Foulds, J. Photochem., 10 (1979) 41.
219 C.-T. Lin and N. Sutin, J. Phys. Chem., 80 (1976) 97.
220 W.J. Albery, M.D. Archer and R.D. Egdell, J. Electroanal. Chem., 82 (1977) 199.
221 W.R. Bowen, Acta Chem. Scand. Part A, 311 (1980) 437.
222 C. Daul, O. Haas, A. Lottaz, A. von Zelewsky and H.R. Zumbrennen, J. Electroanal. Chem., 112 (1980) 51.
223 A. Lottaz and A. von Zelewsky, Chimia, 31 (1977) 180.
224 M. Gleria and R. Memming, Z. Phys. Chem. (Frankfurt am Main), 98 (1975) 303.

225 M. Gleria and R. Memming, Z. Phys. Chem. (Frankfurt am Main), 101 (1976) 171.
226 R. Memming, in E. Kay and P. Bagus (Eds.), Topics in Surface Chemistry, Plenum Press, 1978, p. 19.
227 R. Memming, F. Schröppel and U. Bringmann, J. Electroanal. Chem., 100 (1979) 307.
228 R. Memming and F. Schröppel, Chem. Phys. Lett., 62 (1979) 207.
229 R. Memming, Surf. Sci., 101 (1980) 551.
230 P.K. Ghosh and T.G. Spiro, J. Am. Chem. Soc., 102 (1980) 5543.
231 W.D.K. Clark and N. Sutin, J. Am. Chem. Soc., 99 (1977) 4676.
232 A. Hamnett, M.P. Dare-Edwards, R.D. Wright, K.R. Seddon and J.B. Goodenough, J. Phys. Chem., 83 (1979) 3280.
233 S. Anderson, E.C. Constable, M.P. Dare-Edwards, J.B. Goodenough, A. Hamnett, K.R. Seddon and R.D. Wright, Nature (London), 280 (1979) 571.
234 J.B. Goodenough, A. Hamnett, M.P. Dare-Edwards, G. Campett and R.D. Wright, Surf. Sci., 101 (1980) 531.
235 A. Mackor and J. Schoonman, Rec. Trav. Chim. Pays-Bas, 99 (1980) 71.
236 H. Tributsch, Z. Naturforsch. Teil A, 32 (1977) 972.
237 H.D. Abruna, T.J. Meyer and R.W. Murray, Inorg. Chem., 11 (1979) 3233.
238 H.D. Abruna, P. Denisevich, M. Umana, T.J. Meyer and R.W. Murray, J. Am. Chem. Soc., 103 (1981) 1.
239 H.D. Abruna, J.L. Walsh, T.J. Meyer and R.W. Murray, Inorg. Chem., 20 (1981) 1481.
240 O. Haas and J.A. Vos, J. Electroanal. Chem., 113 (1980) 139.
241 B.A. Moyer, M.S. Thompson and T.J. Meyer, J. Am. Chem. Soc., 102 (1980) 2310.
242 B.A. Moyer and T.J. Meyer, Inorg. Chem., 20 (1981) 436.
243 B.A. Moyer, B.K. Sipe and T.J. Meyer, Inorg. Chem., 20 (1981) 1475.
244 R.A. Brinstead, B.A. Moyer, G.J. Samuels and T.J. Meyer, J. Am. Chem. Soc., 103 (1981) 2897.
245 M.A. Powers and T.J. Meyer, J. Am. Chem. Soc., 102 (1980) 1289.
246 B.P. Sullivan and T.J. Meyer, Inorg. Chem., 19 (1980) 752.
247 J.C. Curtis, J.S. Bernstein, R.H. Schmehl and T.J. Meyer, Chem. Phys. Lett., 81 (1981) 48.
248 B. Durham, W.J. Dressick and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1979) 381.
249 K. Chandrasekaran and D.G. Whitten, J. Am. Chem. Soc., 102 (1980) 5119.
250 M. Neumann-Spallart and K. Kalyanasundaram, J. Phys. Chem., 86 (1982) in press (June issue).
251 S.O. Kobayashi, N. Furuta and O. Simamura, Chem. Lett., (1976) 503.
252 A.J. Bard, J. Photochem., 10 (1979) 59.
253 B. Durham and T.J. Meyer, J. Am. Chem. Soc., 100 (1978) 6286.
254 D.P. Rillemma, B. Durham and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1980) 247.
255 G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch and D.G. Whitten, J. Am. Chem. Soc., 98 (1976) 2337.
256 G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch and D.G. Whitten, J. Am. Chem. Soc., 99 (1977) 4947.
257 A. Harriman, J. Chem. Soc. Chem. Commun., (1977) 777.
258 S.J. Valenty and G.L. Gaines, J. Am. Chem. Soc., 99 (1977) 1285.
259 K.-P. Seefeld, D. Möbius and H. Kuhn, Helv. Chim. Acta, 60 (1977) 2608.
260 G.L. Gaines, P.E. Behnken and S.J. Valenty, J. Am. Chem. Soc., 100 (1978) 6549.
261 S.J. Valenty and P.E. Behnken, Anal. Chem., 50 (1978) 834.
262 L.Y. Yellowlees, R.G. Dickinson, C.S. Halliday, J.S. Bonham and L.E. Lyons, Aust. J. Chem., 31 (1978) 431.

263 J. Ferguson, A.W.H. May and W.H.F. Sasse, Chem. Phys. Lett., 68 (1979) 21.
264 O. Johansen, C. Kowala, A.W.H. Mau and W.H.F. Sasse, Aust. J. Chem., 32 (1979) 1453.
265 S.J. Valenty, D.E. Behnken and G.L. Gaines, Inorg. Chem., 18 (1979) 2160.
266 K. Kalyanasundaram, J. Chem. Soc. Chem. Commun., (1978) 628.
267 G.L. Gaines, Inorg. Chem., 19 (1978) 1710.
268 Y. Tsutsui, K. Takuma, T. Nishijima and T. Matsuo, Chem. Lett., (1979) 617.
269 T. Matsuo, K. Takuma, Y. Tsutsui and T. Nishijima, J. Coord. Chem., 10 (1980) 187.
270 T. Takayanaghi, T. Nagamura and T. Matsuo, Ber. Bunsenges. Phys. Chem., 84 (1980) 1125.
271 T. Nagamura, K. Takuma, Y. Tsutsui and T. Matsuo, Chem. Lett., (1980) 503.
272 K. Takuma, T. Sakamoto and T. Matsuo, Chem. Lett., (1981) 815.
273 W.E. Ford, J.W. Otvos and M. Calvin, Nature (London), 274 (1978) 507.
274 W.E. Ford, J.W. Otvos and M. Calvin, Proc. Nat. Acad. Sci. U.S.A., 76 (1979) 3590.
275 W.E. Ford and M. Calvin, Chem. Phys. Lett., 76 (1980) 105.
276 T. Sugimoti, J. Miyazaki, T. Kokubo, S. Tanimoto, M. Okano and M. Matsumoto, J. Chem. Soc. Chem. Commun., (1981) 210.
277 I. Willner, W.E. Ford, J.W. Otvos and M. Calvin, Nature (London), 280 (1979) 823.
278 P.P. Infelta, M. Gratzel and J.H. Fendler, J. Am. Chem. Soc., 102 (1980) 1479.
279 C. Laane, W.E. Ford, J.W. Otvos and M. Calvin, Proc. Nat. Acad. Sci. U.S.A., 78 (1981) 2017.
280 M.S. Tanuli and J.H. Fendler, J. Am. Chem. Soc., 103 (1981) 2507.
281 K. Monserrat, M. Grätzel and P. Tundo, J. Am. Chem. Soc., 102 (1980) 5527.
282 K. Monserrat and M. Grätzel, J. Chem. Soc. Chem. Commun., (1981) 183.
283 R.H. Schmehl and D.G. Whitten, J. Am. Chem. Soc., 102 (1980) 1938.
284 R.H. Schmehl, L.G. Whiteshell and D.G. Whitten, J. Am. Chem. Soc., 103 (1981) 3761.
285 P.J. DeLaive, J.T. Lee, W.H. Sprintschnik, H.D. Abruna, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc., 99 (1977) 7094.
286 P.J. DeLaive, T.K. Foreman, C. Giannotti and D.G. Whitten, J. Am. Chem. Soc., 102 (1980) 5627.
287 P.A. Brugger and Grätzel, J. Am. Chem. Soc., 102 (1980) 2461.
288 P.A. Brugger, P.P. Infelta, A.M. Braun and M. Grätzel, J. Am. Chem. Soc., 103 (1981) 320.
289 M.A.J. Rodgers and J.C. Becker, J. Phys. Chem., 84 (1980) 2762.
290 D. Meisel, M.S. Matheson and J. Rabani, J. Am. Chem. Soc., 100 (1978) 117.
291 U. Lachish, M. Ottolenghi and J. Rabani, J. Am. Chem. Soc., 99 (1977) 8062.
292 J.H. Baxendale and M.A.J. Rodgers, Chem. Phys. Lett., 72 (1980) 424.
293 M. Maestri, P.P. Infelta and M. Grätzel, J. Chem. Phys., 69 (1978) 1522.
294 K. Kalyanasundaram, Chem. Soc. Rev., 7 (1978) 453.
295 N.J. Turro, A.M. Braun and M. Grätzel, Angew. Chem. Int. Ed. Engl., 19 (1980) 675.
296 J.K. Thomas, Chem. Rev., 80 (1980) 283.
297 J. Kiwi, K. Kalyanasundaram and M. Grätzel, Struct. Bond., 49 (1982) 37.
298 A. Yekta and N.J. Turro, J. Am. Chem. Soc., 100 (1978) 5951.
299 M.A.J. Rodgers and J.H. Baxendale, Chem. Phys. Lett., 81 (1981) 347.
300 P.P. Infelta, Chem. Phys. Lett., 61 (1979) 88.
301 D. Meisel and M.S. Matheson, J. Am. Chem. Soc., 99 (1977) 6577.
302 D. Meisel, J. Rabani, D. Meyerstein and M.S. Matheson, J. Phys. Chem., 82 (1978) 985.
303 C.D. Jonah, M.S. Matheson and D. Meisel, J. Phys. Chem., 83 (1979) 257.
304 R.E. Sasson and J. Rabani, J. Phys. Chem., 84 (1980) 1319.

305 S. Kelder and J. Rabani, J. Phys. Chem., 85 (1981) 1637.
306 D. Krenske, S. Abdo, H. Van Damme, M. Cruz and J.J. Fripiat, J. Phys. Chem., 84 (1980) 2447.
307 S. Abdo, P. Canesson, M. Cruz, J.J. Fripiat and H. Van Damme, J. Phys. Chem., 85 (1981) 797.
308 W. DeWildes, G. Peeters and J.H. Lunsford, J. Phys. Chem., 84 (1980) 2306.
309 P.C. Lee and D. Meisel, J. Am. Chem. Soc., 102 (1980) 5477.
310 A. Thornton and G.S. Laurence, J. Chem. Soc. Chem. Commun., (1978) 408.
311 M. Kaneko, S. Nemoto, A. Yamada and Y. Kurimura, Inorg. Chim. Acta, 44 (1980) L289.
312 M. Kaneko, A. Yamada, E. Tsuchida and Y. Kurimura, Paper presented at the 3rd Int. Conf. Photochemical Conversion Solar Energy, Colorado, August 1980.
313 M. Kaneko and A. Yamada, Photochem. Photobiol., 33 (1981) 793.
314 J.M. Clear, J.M. Kelly, D.C. Pepper and J.G. Vos, Inorg. Chim. Acta, 33 (1979) L139.
315 J.M. Calvert and T.J. Meyer, Inorg. Chem., 20 (1981) 27.
316 M. Gleria, F. Minto, G. Beggiato and P. Bortolus, J. Chem. Soc. Chem. Commun., (1978) 285.
317 J. Van Houten and R.J. Watts, Inorg. Chem., 17 (1978) 3387.
318 P.E. Hoggard and G.B. Porter, J. Am. Chem. Soc., 100 (1978) 1457.
319 W.M. Wallace and P.E. Hoggard, Inorg. Chem., 19 (1980) 2141.
320 R.F. Jones and D.J. Cole-Hamilton, Inorg. Chim. Acta, 53 (1981) L3.
321 G.B. Porter and R.H. Sparks, J. Photochem., 13 (1980) 123.
322 S.H. Peterson and J.M. Demas, J. Am. Chem. Soc., 98 (1976) 7880.
323 J.N. Demas, J.W. Addington, S.H. Peterson and E.W. Harris, J. Phys. Chem., 81 (1977) 1039.
324 S.H. Peterson and J.N. Demas, J. Am. Chem. Soc., 101 (1979) 6571.
325 P.J. Giordano, C.R. Bock, M.S. Wrighton, L.V. Interrante and R.F.S. Williams, J. Am. Chem. Soc., 99 (1977) 3187.
326 P.J. Giordano, C.R. Bock and M.S. Wrighton, J. Am. Chem. Soc., 100 (1978) 6960.
327 J. Ferguson, A.W.-H. Mau and W.H.F. Sasse, Chem. Phys. Lett., 68 (1979) 21.
328 A.H.A. Tinnemans, K. Timmer, M. Reinben, J.G. Kraaijkamp, A.H. Alberts, J.G.M. van der Linden, J.E.J. Schmitz and A.A. Saaman, Inorg. Chem., 20 (1981) 3698.
329 A. Juris, V. Balzani, P. Belser and A. von Zelewsky, Helv. Chim. Acta, 64 (1981) 2175.
330 P. Belser, A. von Zelewsky and M. Zehnder, Inorg. Chem., 20 (1981) 3098.
331 K. Mandel, T.D.L. Pearson and J.N. Demas, Inorg. Chem., 20 (1981) 787.
332 T. Miyashita and M. Matsuda, Bull. Chem. Soc. Jpn., 54 (1981) 1740.
333 T. Miyashita and M. Matsuda, J. Phys. Chem., 85 (1981) 3122.
334 K. Monserrat, T.K. Foreman, M. Grätzel and D.G. Whitten, J. Am. Chem. Soc., 103 (1981) 6667.
335 J. Kiwi, J. Photochem., 16 (1981) 193.
336 C. Pac, M. Ikama, M. Yasuda, Y. Miyaguchi and H. Sakurai, J. Am. Chem. Soc., 103 (1981) 6495.
337 A.J. Frank and K.L. Stevenson, J. Chem. Soc. Chem. Commun., (1981) 593.
338 N. Toshima, M. Kuriyama, Y. Yamada and H. Hirai, Chem. Lett., (1981) 793.
339 D.S. Miller, A.J. Bard, G. McLendon and J. Ferguson, J. Am. Chem. Soc., 103 (1981) 5336.
340 D.S. Miller and G. McLendon, J. Am. Chem. Soc., 103 (1981) 6791.
341 O. Johansen, A. Launikonis, J.W. Loder, A.W.-H. Mau, W.H.F. Sasse, J.D. Swift and D. Wells, Aust. J. Chem., 34 (1981) 981.

342 P. Keller, A. Moradpour, E. Amouyal and B. Zidler, J. Mol. Catal., 12 (1981) 261.
343 P.A. Brugger, P. Cuendet and M. Grätzel, J. Am. Chem. Soc., 103 (1981) 2923.
344 P.P. Infelta and P.A. Brugger, Chem. Phys. Lett., 82 (1981) 462.
345 T.K. Foreman, W.M. Sobol and D.G. Whitten, J. Am. Chem. Soc., 103 (1981) 5333.
346 I. Willner, J-M. Yang, C. Laane, J.W. Otvos and M. Calvin, J. Phys. Chem., 85 (1981) 3277.
347 T. Matsuo, T. Sakamoto, K. Takuma, K. Sakura and T. Ohsako, J. Phys. Chem., 85 (1981) 1277.
348 E. Borgarello, J. Kiwi, E. Pelizetti, M. Visca and M. Grätzel, J. Am. Chem. Soc., 103 (1981) 6324.
349 D. Duonghong, E. Borgarello and M. Grätzel, J. Am. Chem. Soc., 103 (1981) 4685.
350 A. Harriman and A. Mills, J. Chem. Soc. Faraday Trans. 2, 77 (1981) 2111.
351 I. Okura and N. Kim-Thuan, Inorg. Chim. Acta, 54 (1981) L56.
352 H. Nijs, M. Cruz, J.J. Fripiat and H. van Damme, J. Chem. Soc. Chem. Commun., (1981) 1026.
353 A. Mills and M.L. Zeeman, J. Chem. Soc. Chem. Commun., (1981) 948.
354 G.L. Elizarova, L.G. Matvienko, N.V. Lozhkina, V.N. Parmon and K.I. Zamaraev, Reaction Kinet. Cat. Lett., 16 (1981) 191.
355 G.L. Elizarova, L.G. Matvienko, N.V. Lozhkina, V.E. Maizlish and V.N. Parmon, Reaction Kinet. Cat. Lett., 16 (1981) 285.
356 P.K. Ghosh and T.G. Spiro, J. Electrochem. Soc., 128 (1981) 1281.
357 H.B. Mark, A. Vougaropoulous and C.A. Meyer, J. Chem. Soc. Chem. Commun., (1981) 1021.
358 N. Alonso, V.M. Beley, P. Chartier and V. Ern, Rev. Phys. Appl., 16 (1981) 5.
359 G. Giro, P.G. DiMarco and G. Casalbore, Inorg. Chim. Acta, 50 (1981) 201.
360 Y. Kurimura, H. Yokoto and Y. Muraki, Bull. Chem. Soc. Jpn, 54 (1981) 2450.