

## Non-Adiabatic Electronic Energy Transfer from the ( $^3\text{CT}$ ) $\text{Ru}(\text{bpy})_2(\text{CN})_2$ Excited State to Cr(III) Complexes

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*The quenching of the luminescence lifetime of cis-Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> (bpy = 2,2'-bipyridine) by complexes of the cis- and trans-Cr(en)<sub>2</sub>(XY)<sup>+</sup> families (en = ethylenediamine; X and Y = F, Cl, Br, NCS, ONO) has been studied in aqueous solution and the results obtained have been discussed together with those previously reported for the quenching of the Ru(bpy)<sub>3</sub><sup>2+</sup> luminescence by the same Cr(III) complexes. Experimental results and theoretical considerations show that the quenching process occurs by exchange electronic energy transfer. Since in all cases the process is sufficiently exoergonic to make up for the small intrinsic barriers, the lowest diffusion values of the quenching constants indicate a non-adiabatic behavior. The degree of adiabaticity of the energy transfer process is larger for the neutral Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> donor than for the positively charged Ru(bpy)<sub>3</sub><sup>2+</sup> donor. The X and Y ligands can be ordered in the following adiabaticity series: ONO<sup>-</sup>, F<sup>-</sup> < Cl<sup>-</sup> < NCS<sup>-</sup> < Br<sup>-</sup>. The geometry of the acceptor is a discriminating parameter only for energy transfer from the charged donor. These results show that the electronic term of exchange energy transfer in non-adiabatic processes is governed by a delicate balance of factors related to the composition and structure of the encounter complex [1].*

### Introduction

Electronic energy transfer (hereafter called energy transfer) from an excited donor to an acceptor (eqn. 1) is a process of crucial importance in photochem-



istry [2–6]. In fluid solution, when transition metal complexes are involved as donors and/or acceptors, energy transfer generally occurs by an exchange mechanism which requires orbital overlap between the two partners. This type of energy transfer process must occur during a collision between donor and acceptor and it may be considered as being a very simple bimolecular chemical reaction where neither atoms nor electrons but electronic energy alone is transferred. In particular, a strict similarity exists

between bimolecular outer sphere electron transfer and exchange energy transfer processes, which are usually discussed on the basis of the same classical [7] or quantum mechanical [8] formalisms. In both types of approach, the rate constant of these processes is expressed as a product of an electronic term associated with the electronic interaction energy and a term associated with nuclear rearrangements.

While the role of the nuclear term (which includes changes in the inner vibrational coordinates of the two reaction partners and in the outer solvation spheres) in determining the rate variations is well documented [7–12], little is known about the role played by purely electronic effects. In most of the reactions studied so far, particularly in the field of electron transfer, the nuclear factor has been found to dominate and to mask, within the large uncertainty with which it can be evaluated, the role of electronic effects.

Recent work from several laboratories [13–21] has shown that there are families of energy transfer reactions where nuclear rearrangements are relatively unimportant and electronic factors dominate the rate variations. These systems offer a unique opportunity to disentangle the role of the electronic term from that of the nuclear term and to gain detailed information on those specific molecular properties (such as size and geometry of the complex, nature of the ligands, etc.) which determine the value of the electronic interaction energy.

Continuing our studies in this field, we report here the results of an investigation concerning the energy transfer quenching of the lowest excited state of cis-Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> (bpy = 2,2'-bipyridine) by 9 cis- or trans-Cr(en)<sub>2</sub>(XY)<sup>+</sup> complexes (en = ethylenediamine, X and Y = F, Cl, Br, NCS, ONO). The results obtained are discussed together with those previously reported for the quenching of the Ru(bpy)<sub>3</sub><sup>2+</sup> luminescence by the same Cr(III) complexes.

### Experimental

#### Materials

Cis-Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, hereafter called Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, was prepared as previously indicated [22].

The absorption and emission spectra and the luminescence lifetime were in agreement with the literature data [23]. The following salts of the  $\text{Cr}(\text{en})_2\text{-XY}^{2+}$  complexes (en = ethylenediamine) were prepared and purified as reported in the literature:  $[\text{t-Cr}(\text{en})_2(\text{F})_2]\text{Cl}$  [24],  $[\text{t-Cr}(\text{en})_2(\text{NCS})_2]\text{NCS}\cdot\text{H}_2\text{O}$  [25],  $[\text{t-Cr}(\text{en})_2\text{Br}_2]\text{Br}$  [26],  $[\text{t-Cr}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$  [27],  $[\text{t-Cr}(\text{en})_2(\text{NCS})\text{Cl}]\text{ClO}_4$  [26],  $[\text{t-Cr}(\text{en})_2(\text{ONO})\text{Cl}]\text{ClO}_4$  [26],  $[\text{c-Cr}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$  [25],  $[\text{c-Cr}(\text{en})_2(\text{NCS})\text{Cl}]\text{ClO}_4$  [28],  $[\text{c-Cr}(\text{en})_2(\text{NCS})_2]\text{NCS}\cdot\text{H}_2\text{O}$  [29].

#### Apparatus

Absorption spectra were recorded with a Perkin Elmer 323 spectrophotometer. Luminescence spectra were measured with a Perkin-Elmer MPF 3 spectrofluorimeter equipped with an R 928 phototube. Emission lifetime measurements were carried out with a modified Applied Photophysics single photon counting equipment, or with a Molectron  $\text{N}_2$  pulsed laser.

#### Procedures

All the quenching experiments were carried out in aqueous solution. The temperature chosen was  $11.0 \pm 0.1$  C in order to reduce the rate of the aquation reaction of the Cr(III) complexes used as quenchers. The solutions were deaerated by bubbling  $\text{N}_2$ . When necessary, the ionic strength of the solution was controlled by KCl. The  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  concentration was usually  $1.0 \times 10^{-4}$  M and the quencher concentration was in the  $10^{-2}$ – $10^{-3}$  M range. Since the  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  emission ( $\lambda_{\text{max}} = 625$  nm) was partially absorbed by the quencher, the Stern–Volmer quenching constants were usually obtained by lifetime measurements ( $\lambda_{\text{exc}} = 337$  nm,  $\lambda_{\text{em}} = 607$  nm). In luminescence photosensitization experiments, excitation was carried out at 450 nm and the  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  emission was monitored at 727 nm. The emission spectra of the Cr(III) complexes at 77 K

were obtained in methylformamide (MF), which was the solvent yielding better glasses. For  $\text{t-Cr}(\text{en})_2\text{Br}_2^+$ , however, a dimethylformamide–water 1:3 (v/v) solution had to be used (for solubility reasons).

#### Results

In agreement with the results previously reported by Demas *et al.* [23],  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  was found to emit luminescence with maximum at 580 nm in MeOH–EtOH rigid matrix at 77 K and at 625 nm in aqueous solution at room temperature. This emission is known [22, 23] to be due to the lowest metal-to-ligand charge transfer excited state which may formally be considered as a triplet,  $^3\text{CT}$  (*vide infra*). In deaerated aqueous solution at 11.0 C the emission lifetime was  $300 \pm 10$  ns. The emission maxima of the Cr(III) complexes in MF rigid matrix at 77 K are reported in Table I. Among the Cr(III) complexes, only  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  was found to emit under the conditions of the quenching experiments (11 °C, aqueous solution), with maximum at 727 nm.

Absorption spectra of solutions containing  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and the quenchers were additive and did not change during the experiments. The Stern–Volmer quenching plots for lifetime quenching were linear in all the range of quencher concentrations used. Some of the plots obtained are shown in Fig. 1. Increasing ionic strength up to 1 M with KCl did not show any effect. The values of the bimolecular quenching constants (Table I) were obtained from the slopes of the Stern–Volmer quenching plots, using the reported value for the ( $^3\text{CT}$ ) $\text{Ru}(\text{bpy})_2(\text{CN})_2$  lifetime.

When  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  was used as a quencher, the quenching of the  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  emission was accompanied by the sensitized emission of the Cr complex, in agreement with the results previously reported by Sandrini *et al.* [30].

TABLE I. Quenching Constants,  $\text{M}^{-1} \text{s}^{-1}$ .

Quencher ( $E^{\circ\circ}$ , $10^3 \text{ cm}^{-1}$ ) <sup>a</sup>	( $^3\text{CT}$ ) $\text{Ru}(\text{bpy})_2(\text{CN})_2$ <sup>b</sup> $E^{\circ\circ} = 18.5 \times 10^3 \text{ cm}^{-1}$ c	( $^3\text{CT}$ ) $\text{Ru}(\text{bpy})_3^{2+}$ d $E^{\circ\circ} = 17.2 \times 10^3 \text{ cm}^{-1}$ c
$\text{t-Cr}(\text{en})_2\text{F}_2^+$ (14.9) <sup>e</sup>	$9.0 \times 10^7$	$3.5 \times 10^6$
$\text{t-Cr}(\text{en})_2\text{Cl}_2^+$ (14.3)	$8.2 \times 10^8$	$4.6 \times 10^7$
$\text{t-Cr}(\text{en})_2(\text{Cl})(\text{ONO})^+$ (14.5)	$5.3 \times 10^8$	–
$\text{t-Cr}(\text{en})_2(\text{Cl})(\text{NCS})^+$ (14.0)	$8.0 \times 10^8$	$7.1 \times 10^7$
$\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$ (13.8)	$9.1 \times 10^8$	$1.0 \times 10^8$
$\text{t-Cr}(\text{en})_2\text{Br}_2^+$ (14.5)	$1.1 \times 10^9$	$1.2 \times 10^8$
$\text{c-Cr}(\text{en})_2\text{Cl}_2^+$ (14.4)	$5.1 \times 10^8$	$5.0 \times 10^7$
$\text{c-Cr}(\text{en})_2(\text{Cl})(\text{NCS})^+$ (14.1)	$7.0 \times 10^8$	$1.4 \times 10^8$
$\text{c-Cr}(\text{en})_2(\text{NCS})_2^+$ (13.9)	$1.2 \times 10^9$	$5.0 \times 10^8$

<sup>a</sup>Maximum of the  $^2E_g$  luminescence emission in MF at 77 K, unless otherwise noted. <sup>b</sup>This paper (aqueous solution, 11 C,  $\mu = 0.1$ ). <sup>c</sup>Zero-zero spectroscopic energy of the donor excited state. <sup>d</sup>From ref. 21, extrapolated at  $\mu = 0$ ; aqueous solution, 20 C. <sup>e</sup>From: A. D. Kirk and G. B. Porter, *J. Phys. Chem.*, 84, 887 (1980).

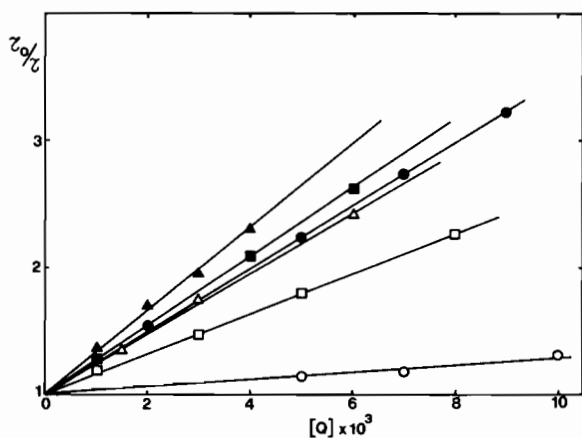


Fig. 1. Stern-Volmer plots for the quenching of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  emission lifetime by:  $\text{t-Cr}(\text{en})_2\text{F}_2^+$ ,  $\circ$ ;  $\text{t-Cr}(\text{en})_2\text{Cl}_2^+$ ,  $\bullet$ ;  $\text{t-Cr}(\text{en})_2(\text{Cl})(\text{ONO})^+$ ,  $\square$ ;  $\text{t-Cr}(\text{en})_2(\text{Cl})(\text{NCS})^+$ ,  $\triangle$ ;  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$ ,  $\blacksquare$ ;  $\text{t-Cr}(\text{en})_2\text{Br}_2^+$ ,  $\blacktriangle$ .

## Discussion

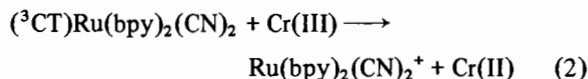
### Quenching mechanism

In fluid solution the quenching of an excited state may take place by several distinct mechanisms [2–6], the most important of which are (i) electronic energy transfer, (ii) electron transfer, (iii) chemical reaction involving atom transfer, (iv) exciplex formation, (v) spin catalyzed deactivation, and (vi) external heavy atom effect. In the specific case of the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  by Cr(III) complexes, the external heavy atom effect can obviously be excluded. Spin-catalyzed deactivation is possible in principle, because the ground state of the Cr(III) complexes is a quartet. This type of quenching process however is expected to be very slow; in fact, it is not yet clear whether there are cases in which such a mechanism has been experimentally observed [4].

Exciplex formation is not likely to occur in aqueous solution and it has never been observed between octahedral transition metal complexes [31]. Some quenching effect ( $k_q \sim 10^6\text{--}10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) by ground state  $\text{Cr}(\text{phen})_3^{3+}$  on excited  $(^2\text{E}_g)\text{Cr}(\text{phen})_3^{3+}$  has been observed [32], but only at very high ionic strength where an anion is thought to keep together an excited state and a ground state molecule. There is no reason why such associations should take place in our systems: no change in the absorption spectra has in fact been observed. Since both  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and the Cr(III) quenchers are kinetically inert complexes, quenching reactions involving transfer of ligands can be excluded. The only atom transfer reaction that can occur is the protonation of the nitrogen of the CN ligands. It is known, however, that such a reaction only takes place in highly acidic

conditions [33], while the Cr(III) amine complexes are very weak acids [34]. Thus our quenching results ( $k_q \geq 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , Table I) can only be accounted for by energy and/or electron transfer mechanisms.

On the basis of the excited state spectroscopic energy ( $E^{00} = 2.29 \text{ eV}$ ) [23] and ground state potentials ( $E_{\text{red}}^0 = -1.30 \text{ V}$  and  $E_{\text{ox}}^0 = +1.09 \text{ V}$  in DMF vs. NHE) [35]  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  is a relatively strong reductant and oxidant species ( $E^0(\text{Ru}(\text{bpy})_2(\text{CN})_2^+ / (^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2) \approx -1.2 \text{ V}$ ,  $E^0(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2 / \text{Ru}(\text{bpy})_2(\text{CN})_2^- \approx +1.0 \text{ V}$ ). Since the Cr(III) complexes are extremely difficult to oxidize, the only likely electron transfer quenching is the following:



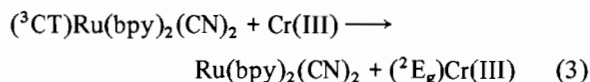
The Cr(III) complexes are known to undergo irreversible electrochemical reduction. Their standard reduction potentials are unknown and it is not possible to say whether (and in which cases) reaction 2 is thermodynamically allowed. For  $\text{t-Cr}(\text{en})_2\text{Br}_2^+$ ,  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$ ,  $\text{t-Cr}(\text{en})_2(\text{ONO})\text{Cl}^+$ , and  $\text{t-Cr}(\text{en})_2\text{F}_2^+$  irreversible reduction peaks have been found at about  $-0.6$ ,  $-0.8$ ,  $-1.0$  and  $-1.2 \text{ V}$ , respectively [14, 36]. Since irreversibility is most likely to be caused by a ligand dissociation reaction which follows the one-electron reduction of the complex [37], the reduction peak potentials can be taken as lower limiting values for the formal reduction potential. Thus, reaction 2 would be exoergic by  $\leq 0.4 \text{ eV}$  for  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  and  $\leq 0.6 \text{ eV}$  for  $\text{t-Cr}(\text{en})_2\text{Br}_2^+$ . The electron transfer quenching, however, is expected to exhibit a large intrinsic barrier because Cr(III) reduction involves the entering of an electron into the  $\sigma^*(e_g)$  antibonding orbitals with a consequent strong distortion in the molecular geometry [11]. In these cases, high rate constants can only be obtained for strongly exergonic reactions [9, 11, 38].

A quantitative evaluation of the problem is not possible because of the lack of data on self-exchange Cr(III)–Cr(II) reactions, but it seems likely that the exergonicities of the electron transfer process between  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  and Cr(III) complexes (reaction 2) can hardly account for the high quenching constants observed (Table I). From an experimental point of view, reaction 2 should cause a permanent change in the absorption spectrum of the solution because the Cr(II) complexes are very labile [34]. Although some change was observed after long irradiation periods (*vide infra*), it did not correspond to that expected for reaction 2. Even assuming that such a change cannot be observed because of a fast back electron transfer reaction, one would expect to find a transient spectral change in flash experiments.

Since  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  was found to undergo some photodecomposition in flash experiments even in the

absence of the quencher, the formation of a transient deriving from reaction 2 was not looked for. No transient spectral change however was observed in flash experiments carried out on solutions containing  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{c-Cr}(\text{en})_2\text{Cl}_2^+$  [39] or  $\text{Ru}(\text{phen})_2(\text{CN})_2$  and  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  [14]. This shows that quenching by electron transfer cannot be an important mechanism in these systems.

Thus, we remain with electronic energy transfer as being the most likely mechanism to account for the relatively high quenching constants of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  by  $\text{Cr}(\text{III})$  complexes (Table I). The effectiveness of this mechanism is indeed expected on a theoretical basis and substantiated by experimental results. For all the  $\text{Cr}(\text{III})$  complexes used as quenchers the lowest excited state ( $^2\text{E}_g$  in octahedral symmetry) lies at lower energy (see Table I) than the donor excited state, so that exchange energy transfer [40] (reaction 3) is thermodynamically allowed [41]:

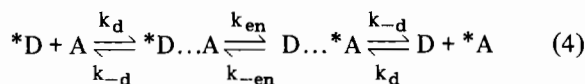


It should also be noted that reaction 3 is spin-allowed [2, 4] and is expected to exhibit a small intrinsic barrier because the  $^2\text{E}_g$  excited state of  $\text{Cr}(\text{III})$  complexes is known to have the same bond lengths and geometry as the ground state (*vide infra*). For  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$ , which is the only  $\text{Cr}(\text{III})$  complex among the quenchers used which is able to show photoluminescence in fluid solution, the quenching of the  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  emission was accompanied by the  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  sensitized emission. Previous experiments have also shown that sensitization by  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  gives the same quantum yields for en and  $\text{NCS}^-$  dissociation from  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  as does direct excitation of the Cr complex in its ligand field bands [30]. Finally, flash experiments based on the  $^2\text{E}_g$  absorption spectrum showed that the energy transfer efficiency from  $(^3\text{CT})\text{Ru}(\text{phen})_2(\text{CN})_2$  to yield  $(^2\text{E}_g)\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  is at least 0.8 [14]. It thus seems fair to conclude that the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  by the  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$  occurs by energy transfer (reaction 3). For the other quenchers direct evidence for energy transfer quenching is not available because they exhibit neither photoluminescence nor excited state absorption. However, lacking also any evidence for electron transfer quenching, on the basis of the above discussion it seems fair to assume that the quenching mechanism is the same as that demonstrated for  $\text{t-Cr}(\text{en})_2(\text{NCS})_2^+$ , i.e. electronic energy transfer. This is also in agreement with the conclusions reached in previous papers, where the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$  [21] and  $(^3\text{CT})\text{Ru}(\text{phen})_2(\text{CN})_2$  [14] by  $\text{Cr}(\text{III})$  complexes was attributed to electronic energy transfer. The data concerning the  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$

quenching are shown in Table I for comparison purposes.

#### Theoretical Approach

For an exchange energy transfer reaction such as reaction 3 the following mechanism can be used [7]:



where  $^*\text{D}\dots\text{A}$  and  $\text{D}\dots^*\text{A}$  represent the precursor and successor complex in the encounter,  $k_d$  is the diffusion rate constant,  $k_{-d}$  is the dissociation rate constant of the encounter, and  $k_{en}$  and  $k_{-en}$  are the unimolecular rate constants for the forward and back energy transfer within the encounter. The experimental bimolecular rate constant is given by

$$k_q = \frac{k_d}{1 + \frac{k_{-en}}{k_{en}} + \frac{k_{-d}}{k_{en}}} \quad (5)$$

The key step in eqn. 4 is the uni-molecular exchange of excitation energy between donor and acceptor within the encounter. This step can be dealt with using either classical or quantum mechanical models originally developed for outer sphere electron transfer processes.

In the quantum mechanical approach, the energy transfer step is considered as a radiationless transition between two states of the 'supermolecule' consisting of donor, acceptor and solvent [8]. The uni-molecular rate constant  $k_{en}$  may be indicated by

$$k_{en} = E \cdot N \quad (6)$$

where the electronic term  $E$  contains the electronic interaction energy  $H_{if}$  and the nuclear term  $N$  is a complex thermally averaged Franck-Condon factor. The quantum mechanical approach cannot be applied to our systems because of the lack of knowledge of the relevant molecular parameters.

In the classical formalism [7], eqn. 5 can be written as

$$k_q = \frac{k_d}{1 + \exp(\Delta G/RT) + \frac{k_{-d}}{k_{en}}} \quad (7)$$

where

$$\Delta G = -E^{00}(*\text{D},\text{D}) + E^{00}(*\text{A},\text{A}) \quad (8)$$

is the difference between the zero-zero spectroscopic energy of the donor and the acceptor and  $k_{en}$  is given by:

$$k_{en} = k_{en}^0 \exp(-\Delta G^\ddagger/RT) = k \frac{kT}{h} \exp(-\Delta G^\ddagger/RT) \quad (9)$$

where  $k_{\text{en}}^0$  is the pre-exponential factor,  $k$  is the electronic transmission coefficient,  $kT/h$  is the universal frequency of the transition state theory (which should more correctly be replaced by an effective frequency for nuclear motion [10–12]) and  $\Delta G^\ddagger$  is the free activation energy which can be expressed by the free energy relationship given by eqn. 10 [42]:

$$\Delta G^\ddagger = \Delta G + \frac{\Delta G^\ddagger(0)}{\ln 2} \ln\left(1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^\ddagger(0)}\right)\right) \quad (10)$$

In this equation,  $\Delta G$  is the previously seen free energy change, and  $\Delta G^\ddagger(0)$  is the so-called intrinsic barrier to energy transfer, a parameter related to the amount of distortion of both the inner coordination spheres and the outer solvation shells accompanying the energy transfer. It is thus apparent that the classical equation, like the quantum mechanical one (in the high temperature limit) [44] expresses the rate constant as a product of an electronic term, associated with  $k$ , and a nuclear term associated with  $\exp(-\Delta G^\ddagger/RT)$ .

In current terminology, a reaction is said to be adiabatic when the electronic interaction is sufficiently strong to make  $k \approx 1$ , and non-adiabatic when the electronic interaction is small and thus  $k < 1$ .

The classical approach predicts that for sufficiently exoergic processes the nuclear factor is equal to unity, so that  $k_{\text{en}}$  is equal to  $kT/h$  for adiabatic processes and smaller than  $kT/h$  for non-adiabatic processes. Since  $kT/h \gg k_{-d}$ , for sufficiently exoergic and adiabatic processes eqn. 7 predicts  $k_q \approx k_d$ , whereas for sufficiently exoergic but strongly non-adiabatic ( $k \ll 1$ ) processes it predicts  $k_q = (k_d/k_{-d})k_{\text{en}} = (k_d/k_{-d})k(kT/h)$ .

For the  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ –Cr(III) systems, taking an encounter distance of 10 Å, the following values can be obtained for the diffusion and dissociation rate constants:  $k_d = 7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-d} = 2.9 \times 10^9 \text{ s}^{-1}$ . As one can see from Table I, the rate constants for the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  by the Cr(III) complexes are lower than the diffusion rate constant and are also different from one another. Similar results were previously found for the  $\text{Ru}(\text{bpy})_3^{2+}$ –Cr(III) systems (Table I) [21], whose  $k_d$  and  $k_{-d}$  value (at  $\mu = 0$ ) are  $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.5 \times 10^9 \text{ s}^{-1}$ , respectively. We now examine the reasons for such a behavior.

### Spin Statistics

Energy transfer processes via an exchange mechanism obey the Wigner spin statistics for collisional processes. This problem has been recently discussed by Wilkinson and Tsiamis [16, 17] with particular reference to energy transfer from organic triplets to Cr(III) complexes. The validity of the triplet spin label for the lowest excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  (and, by analogy, for the lowest excited state of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ ) has been the object of some con-

trovery [46–51]. Assuming that the donor excited state can be considered as a triplet, spin statistics show that reaction 3 has a spin statistical factor of 1/6, which means that the upper limiting value for the quenching constant would be  $k_d/6$ , i.e.  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Thus, the rate constants for the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  by  $\text{t-Cr}(\text{en})_2\text{Br}_2^+$  and  $\text{c-Cr}(\text{en})_2(\text{NCS})_2^+$  (Table I) would be diffusion controlled. It seems more likely however that spin statistics cannot be applied to our reactions because of the strong spin-orbit coupling induced by the heavy Ru atom. The reasons why the rate constants for the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  by the other Cr(III) complexes are lower than  $k_d/6$  and differ from one another must be found in limiting nuclear and/or electronic factors. A similar type of reasoning applies to the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ , where only  $\text{c-Cr}(\text{en})_2\text{Cl}_2^+$  approaches the spin-statistics corrected diffusion limit,  $3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

### Nuclear Factors

The effect of nuclear factors is contained in the  $\exp(-\Delta G^\ddagger/RT)$  term of eqn. 9, where  $\Delta G^\ddagger$  is a function of the intrinsic barrier  $\Delta G^\ddagger(0)$  and the free energy change  $\Delta G$  according to eqn. 10. The intrinsic barrier is related to changes in the inner nuclear coordinates of the molecules ('inner sphere' reorganizational energy) and to changes in the solvent arrangement around the molecule ('outer sphere' reorganizational energy). For the Cr(III) quenchers, both the inner and outer sphere reorganizational energies are expected to be very small because the  $^2E_g$  excited state has practically the same size, charge distribution, vibrational frequencies and solvation arrangement as the ground state [52].

As far as the donors are concerned, the upper limit for the reorganizational energy of the self-exchange  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ – $\text{Ru}(\text{bpy})_3^{2+}$  energy transfer reaction is estimated to be  $200 \text{ cm}^{-1}$  [10]. For the corresponding self-exchange reaction of  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ , the reorganizational energy is certainly higher because of contributions coming from the asymmetric spatial redistribution of the electric charge (the excited state is obtained by a  $\text{Ru} \rightarrow \text{bpy}$  charge transfer transition). It is unlikely, however, that such a reorganizational energy exceeds  $1000 \text{ cm}^{-1}$  [53]. As one can see from Table I, the minimum exergonicity for energy transfer is  $2300 \text{ cm}^{-1}$  when the donor is  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$  and  $3600 \text{ cm}^{-1}$  when the donor is  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ . Using the above values for exergonicities and intrinsic barriers, eqn. 10 gives values lower than  $5 \text{ cm}^{-1}$  for  $\Delta G^\ddagger$ . It follows that the term  $\exp(-\Delta G^\ddagger/RT)$  is not far from unity ( $>0.97$ ) [54]. In other words, energy transfer is in all cases sufficiently exoergic to make up for the intrinsic barrier. This means that nuclear factors cannot be responsible for the observed lower than

diffusion quenching constants and for the differences in the  $k_q$  values for the various complexes.

#### Electronic Factors

From the above discussion it is apparent that the quenching constants are controlled by small values of the transmission coefficient  $k$ , *i.e.* by electronic factors. When  $\Delta G$  is large and negative and  $\Delta G^\ddagger$  is small, eqn. 7 reduces to

$$k_q = \frac{k_d k k T / h}{k_{-d} + k k T / h} \quad (11)$$

Using this equation,  $k$  values ranging from  $9 \times 10^{-7}$  to  $\sim 10^{-4}$  [55] can be obtained for the quenching of  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ , showing that the energy transfer process is strongly non-adiabatic. For  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  as a donor, the process appears to be slightly more adiabatic since  $k$  varies from  $6 \times 10^{-6}$  to  $\sim 10^{-4}$  [55].

The non-adiabatic behavior of energy transfer processes involving metal centered orbitals of transition metal complexes has already been observed [13–20]. It has been shown that the nature of the ligands is a fundamental factor governing the adiabaticity character because of their ability to delocalize the metal orbitals, allowing a better overlap with the donor orbitals. This phenomenon has been discussed in the frame of Jørgensen's nephelauxetic effect [13, 14] or Mulliken's charge transfer perturbation [11, 20, 56]. All these results show that the ligands can be arranged in a series of increasing adiabaticity which, however, is not exactly coincident for different donors because the electronic interaction energy is a specific property of each donor–acceptor couple.

In fact, the results reported in this paper reveal some finer details concerning the factors which govern the degree of adiabaticity. For  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$  as a donor, it is clear that the *cis* isomers are better quenchers than the *trans* isomers. As discussed in a previous paper [19], the most likely explanation of this effect is the following.

The *cis* quenchers have a dipolar distribution of their electric charge, with their less positive region corresponding to the XY ligands which are better 'mediators' than *en*. Thus, in the encounter the *cis* isomers offer their more adiabatic face to a positively charged donor. Such a preferential orientation cannot be imposed by a neutral donor such as  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ , and thus the *cis* isomers are no longer favoured. It should also be noted that with the neutral donor the degree of adiabaticity is larger for all quenchers. This presumably reflects a closer distance of approach, which facilitates donor–acceptor orbital overlap. The quenching rates are thus closer to the diffusion limit, which causes a levelling-off effect.

#### Conclusion

The rate constant of energy transfer from  $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$  or  $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$  to Cr(III) complexes of the *cis* and *trans*  $\text{Cr}(\text{en})_2(\text{XY})^+$  families is governed by electronic factors which are related to the charge of the donor, the nature of the X and Y ligands, and the geometry of the acceptor. The positive charge of the donor increases the non-adiabatic character of the process, presumably keeping the (positive) acceptors at longer distances. The X and Y ligands can be ordered in the following series of increasing adiabatic character:  $\text{F}^-$ ,  $\text{ONO}^-$ ,  $\text{Cl}^-$ ,  $\text{CNS}^-$ ,  $\text{Br}^-$ . Finally, a geometry effect (*cis* isomers more adiabatic than *trans* isomers) is important only for the charged donor. These results show that the electronic term of exchange energy transfer in non-adiabatic processes is governed by a delicate balance of factors related to the composition and structure of the encounter complex.

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#### References

- 1 Part of the experimental work was carried out by F.B. at the Wayne State University, Detroit, Michigan.
- 2 A. A. Lamola, in 'Energy Transfer and Organic Photochemistry', A. A. Lamola and N. J. Turro, Eds., Interscience, New York, 1969, p. 17.
- 3 F. Wilkinson, *Pure Appl. Chem.*, **41**, 661 (1975).
- 4 V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
- 5 V. L. Ermolaev, E. G. Sveshnikova and T. A. Shakhverdov, *Russ. Chem. Rev.*, **44**, 26 (Engl. Transl.) 1975.
- 6 F. Scandola and V. Balzani, *J. Chem. Educ.*, **60**, 814 (1983).
- 7 V. Balzani, F. Bolletta and F. Scandola, *J. Am. Chem. Soc.*, **102**, 2152 (1980).
- 8 N. R. Kestner, J. Logan and J. Jortner, *J. Phys. Chem.*, **78**, 2148 (1974).
- 9 R. D. Cannon, 'Electron Transfer Reactions', Butterworths, London, 1980.
- 10 N. Sutin, *Accounts Chem. Res.*, **15**, 275 (1982).
- 11 J. F. Endicott, K. Kumar, T. Ramasani and F. P. Rotzinger, *Prog. Inorg. Chem.*, **30**, 141 (1983).
- 12 N. Sutin, *Prog. Inorg. Chem.*, **30**, 441 (1983).
- 13 V. Balzani, M. T. Indelli, M. Maestri, D. Sandrini and F. Scandola, *J. Phys. Chem.*, **84**, 852 (1980).
- 14 M. Maestri and D. Sandrini, *J. Phys. Chem.*, **85**, 2050 (1981).
- 15 J. F. Endicott, M. J. Heeg, D. C. Gaswick and S. C. Pyke, *J. Phys. Chem.*, **85**, 1777 (1981).
- 16 F. Wilkinson and C. Tsiamis, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1681 (1981).

- 17 F. Wilkinson and C. Tsiamis, *J. Phys. Chem.*, **85**, 4153 (1981).
- 18 F. Wilkinson and C. Tsiamis, *J. Am. Chem. Soc.*, **105**, 767 (1982).
- 19 M. T. Gandolfi, M. Maestri, D. Sandrini and V. Balzani, *Inorg. Chem.*, **22**, 3435 (1983).
- 20 J. F. Endicott, T. Ramasani, D. C. Gaswick, R. Tamilasaran, M. J. Heeg, G. R. Brubaker and S. C. Pyke, submitted for publication.
- 21 F. Bolletta, M. Maestri, L. Moggi and V. Balzani, *J. Am. Chem. Soc.*, **95**, 7864 (1973).
- 22 J. N. Demas, T. F. Turner and G. A. Crosby, *Inorg. Chem.*, **8**, 674 (1969).
- 23 J. N. Demas, J. W. Addington, S. H. Peterson and E. W. Harris, *J. Phys. Chem.*, **81**, 1039 (1977).
- 24 J. W. Vaughn, O. J. Stvan, Jr. and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).
- 25 C. L. Rollinson and J. C. Bailar, *Inorg. Synth.*, **2**, 200 (1946).
- 26 W. W. Fee, J. N. Mac, B. Harrowfield and W. G. Jackson, *J. Chem. Soc.*, **A**, 2612 (1970).
- 27 G. Brauer, 'Handbook of Preparative Inorganic Chemistry', Vol. 2, 2nd Ed., Academic Press., New York, 1965, p. 1357.
- 28 D. A. House and C. S. Garner, *J. Inorg. Nucl. Chem.*, **28**, 904 (1966).
- 29 W. W. Wendlandt and L. K. Sveum, *J. Inorg. Nucl. Chem.*, **28**, 393 (1966).
- 30 D. Sandrini, M. T. Gandolfi, L. Moggi and V. Balzani, *J. Am. Chem. Soc.*, **100**, 463 (1978).
- 31 V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, *Top. Curr. Chem.*, **75**, 1 (1978).
- 32 N. Serpone, M. A. Jamieson, R. Sriram and M. Z. Hoffman, *Inorg. Chem.*, **20**, 3983 (1981).
- 33 S. H. Peterson and J. N. Demas, *J. Am. Chem. Soc.*, **101**, 6571 (1979).
- 34 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd Ed., Wiley & Sons, New York, 1967.
- 35 S. Roffia and M. Ciano, *J. Electroanal. Chem.*, **77**, 349 (1977).
- 36 M. Ciano, unpublished results.
- 37 Cr(II) complexes are known to undergo very fast ligand dissociation [34].
- 38 F. Scandola, V. Balzani and G. B. Schuster, *J. Am. Chem. Soc.*, **103**, 2519 (1981).
- 39 J. F. Endicott, unpublished results.
- 40 Energy transfer by the so-called trivial mechanism [2, 6] can be ruled out because our results refer to lifetime quenching. Coulombic energy transfer [2, 6] can also be ruled out because the electronic transitions in the acceptor are spin and/or symmetry forbidden.
- 41 In the case of t-Cr(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup>, energy transfer leading to the low lying quartet excited state is also energetically allowed.
- 42 Eqn. 10 is preferred to the classical Marcus equation, because it can better account for the behavior of highly exoergonic reactions [43]. In the case of slightly endoergonic or slightly exoergonic reactions like those dealt in this paper, the two equations give practically equivalent results [43].
- 43 F. Scandola and V. Balzani, *J. Am. Chem. Soc.*, **101**, 6140 (1979).
- 44 For a comparison between the classical and quantum mechanical models, see ref. 12.
- 45 P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); M. Z. Eigen, *Phys. Chem.*, **1**, (Frankfurt am Main), 176 (1954).
- 46 G. A. Crosby, *Accounts Chem. Res.*, **8**, 231 (1975).
- 47 G. A. Crosby, *Adv. Chem. Ser.*, **150**, 149 (1976).
- 48 F. Felix, J. Ferguson, H. U. Gudel and A. Ludi, *Chem. Phys. Letters*, **62**, 153 (1979); *J. Am. Chem. Soc.*, **102**, 4096 (1980).
- 49 M. K. De Armond, C. M. Carlin and W. L. Huang, *Inorg. Chem.*, **19**, 62 (1980).
- 50 K. Mandal, T. D. L. Pearson, W. P. Krug and J. N. Demas, *J. Am. Chem. Soc.*, **105**, 701 (1983).
- 51 E. M. Kober and T. J. Meyer, *Inorg. Chem.*, **21**, 3967 (1982).
- 52 V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds', Academic Press, London, 1970.
- 53 The reorganizational energy for the self-exchange Ru(bpy)<sub>3</sub><sup>3+</sup>/Ru(bpy)<sub>3</sub><sup>2+</sup> reaction, which involves the net transfer of one electron, is estimated to be 1150 cm<sup>-1</sup> [10].
- 54 Using the Marcus quadratic equation instead of eqn. 10 [42] one obtains quite similar values.
- 55 When the quenching constant approaches the diffusion limit, there is a strong uncertainty on the estimated *k* values.
- 56 J. F. Endicott and R. Ramasani, *J. Am. Chem. Soc.*, **104**, 5252 (1982).