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EXCITED STATE ELECTRON-TRANSFER REACTIONS OF TRANSITION METAL COMPLEXES

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Abstract - The properties of excited states of transition metal complexes are briefly reviewed. The outer-sphere electron transfer reactions of the excited states of complexes containing 2,2'-bipyridine or 1,10-phenanthroline ligands are discussed in detail, with particular reference to electron vs energy transfer quenching and conversion of light into chemical energy. The kinetic aspects of outer-sphere electron transfer reactions involving excited states are examined with particular reference to the so-called "Marcus inverted behavior" which is not observed in most of the systems studied. The extension of the kinetic formalism used for electron transfer reactions to energy transfer processes yields a unified view of "classical" and "non-classical" energy transfer behavior.

INTRODUCTION

The Werner-type transition metal complexes constitute an important family among chemical molecules. Until a few years ago, the photochemical studies in this field were mostly confined to unimolecular photochemical processes, such as homolytic and heterolytic metal-ligand bond breaking or isomerization reactions (1,2). In the last few years, however, the interest has moved towards bimolecular processes (3) with particular emphasis on electron transfer reactions (4). This last class of photochemical reactions is very interesting for at least three reasons: (i) they are very promising for the conversion of light energy (including solar energy) into chemical energy; (ii) they can lead to complexes having unusual oxidation states and thus unusual chemical (catalytic) properties; (iii) they allow us to check the theories of outer-sphere electron transfer reactions (5-7) over a broad range of free energy change. Some important features of transition metal complexes and their photochemical and photophysical implications, with particular reference to excited state bimolecular processes, are as follows:

- 1) The energy difference between different oxidation states is small, so that the excited states of these compounds can be easily involved in oxidation-reduction processes (1-4);
- 2) In most cases, the transition metal complexes have "spherical-type" symmetry, so that further association (e.g. exciplex

formation) is hindered;

3) Most transition metal complexes are ionic species, so that they are only soluble in polar solvents where exciplex formation is usually prevented;

4) Some excited states are localized on the central metal, and thus they are shielded by the ligands in bimolecular processes (3);

5) The energy difference between geometrical configurations is usually small, so that changes in the coordination geometry may often occur upon excitation (1,2);

6) The presence of the (heavy) metal atom causes a considerable degree of spin-orbit coupling; this has important consequences on the rates of the radiative and radiationless transitions and on the excited states lifetimes (8);

7) In some cases, the ground state of a transition metal complex has an open shell orbital configuration, which implies the presence of intra-configurational excited states at low energies (1,2);

8) Finally, the transition metal complexes have many types of orbitally different excited states (1) whose relative energy ordering is very sensitive to many factors (9). As a consequence, they exhibit a great variety of photophysical and photochemical properties (1-4, 8).

The important excited states of a molecule from the point of view of bimolecular photochemical processes in fluid solution are those with lifetime longer than 10^{-9} - 10^{-10} s. For many organic molecules, the lowest spin-allowed and/or the lowest spin-forbidden excited state satisfy this condition. In the field of transition metal complexes the lowest spin-allowed excited state has generally lifetime shorter than 10^{-10} s, owing to its chemical reactivity and/or fast intersystem crossing to the lowest spin-forbidden excited state (10). Thus, the only excited state of a transition metal complex that can be involved in bimolecular processes is the lowest spin-forbidden excited state. However, in several cases even this state is very short lived in fluid solution at room temperature owing to its strong chemical reactivity, lack of rigidity and strong spin-orbit coupling. In particular, the available data seem to indicate that when the lowest excited state is metal-centered (excluding intra-configurational excited states) or ligand-to-metal charge transfer (excluding UO_2^{2+} where the metal orbital involved is an inner f orbital) the excited state lifetime is too short to allow the participation of the excited state in bimolecular processes.

EXCITED STATE REDOX PROPERTIES OF BIPYRIDINE AND PHENANTHROLINE COMPLEXES

In the last few years it has been found that the transition metal complexes containing aromatic molecules such as bipyridine, phenanthroline or their derivatives as ligands are particularly suitable for excited state electron transfer reactions. The prototype of these complexes is the already famous tris-

bipyridine Ru(II) complex, $\text{Ru}(\text{bpy})_3^{2+}$. The properties of the lowest excited state of this and other analogous complexes are summarized in Table 1.

TABLE 1. Properties of the lowest excited state of some bipyridine complexes (4)

Complex ^a	label ^b	lifetime (μs)	$E^{0-0}(\text{M}^*-\text{M})^c$ (eV)	$*E^0(\text{M}^+/*\text{M})^d$ (V)	$*E^0(*\text{M}/\text{M}^-)^d$ (V)
$\text{Ru}(\text{bpy})_3^{2+}$	³ CT	0.62	2.12	-0.86	0.84
$\text{Cr}(\text{bpy})_3^{3+}$	² MC	77	1.71	>-0.1	1.46
$\text{Os}(\text{bpy})_3^{3+}$	³ CT	0.019	1.85 ^e	-1.02	0.67
$\text{Ir}(\text{bpy})_3^{3+}$	³ LC	2.4 ^e	2.81 ^e	-0.64	2.05

a) aqueous solution, room temperature, unless otherwise noted.

b) CT = ligand-to-metal charge transfer; MC = metal centered; LC = ligand centered; the multiplicity label has scarce meaning for the Ru and Os complexes (8).

c) Energy of the zero-zero transition.

d) Reduction potential vs NHE.

e) in MeOH

The excited state redox potentials are obtained from the redox potentials of the corresponding ground state and the spectroscopic excited state energy (4), i.e. with the assumption that the excited state energy is all available as free energy for the excited state redox processes. This assumption is justified by the very small Stokes shift values (11,12) which indicate that the ground state has approximately the same shape, size and solvation (and thus entropy content) as the ground state. As we will see later, the experimental results confirm this assumption.

For both practical and theoretical purposes it is important to have a series of complexes which cover a wide range of values of the various excited state properties. For the complexes of the bpy and phen family it has been found that several excited state properties can be "tuned" by changing the nature of the central metal (Table 1) or the type of the ligands, or by appropriate substitutions on the ligand aromatic rings. Substitution of phen for bpy usually increases slightly the excited state lifetime and leaves almost unchanged the other excited state properties, but the introduction of different ligands may have profound consequences (4). Ligand substituents usually cause small changes in the excited state energy, but they can change significantly the excited state lifetime and the excited state reduction and oxidation potentials (13,14). It is important to note that in these complexes the excitation causes a crossing of the redox potentials (fig. 1). As a consequence, the excited state can be used as both an electron donor and an electron acceptor. For example, the excited Ru complex is a reductant strong enough to reduce water and at the same time an oxidant strong enough to oxidize water. In general, the presence of redox sites on both metal and ligands gives redox properties which cannot be present in either simple metal ions or organic molecules.

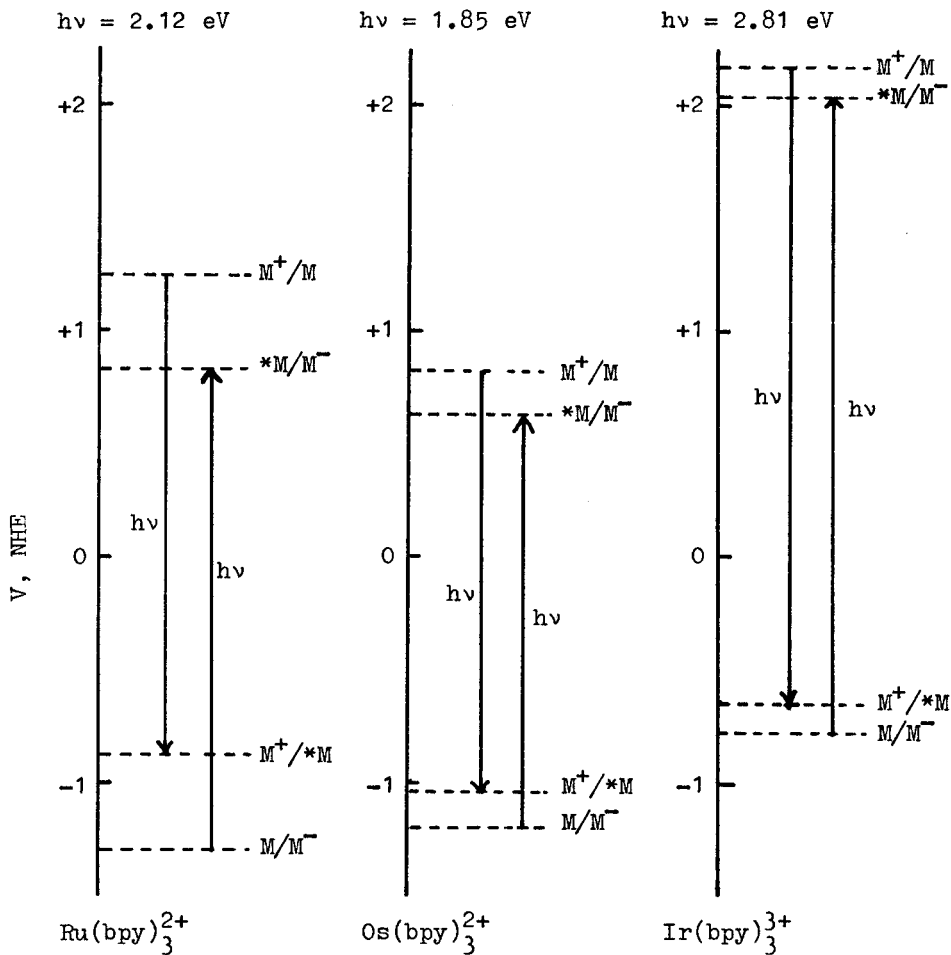
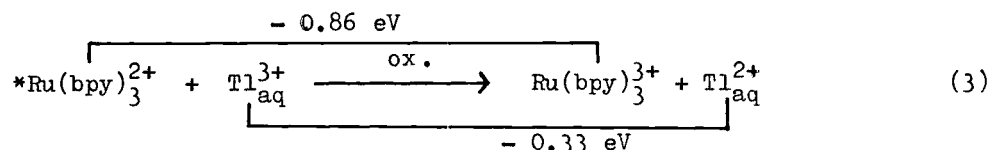
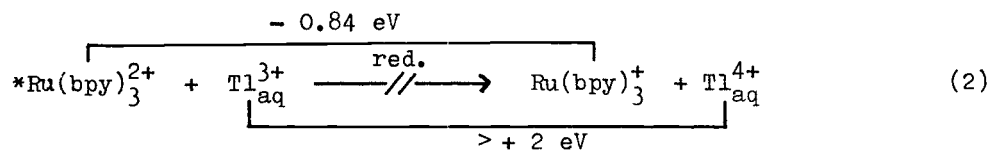
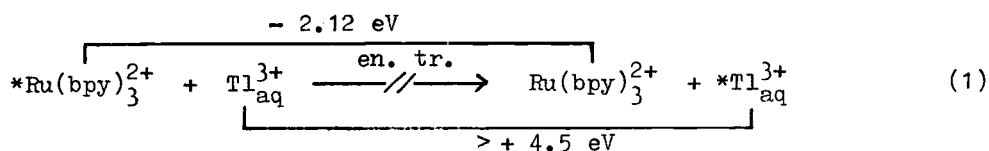


Fig. 1. Light-driven crossing of the redox potentials in $M(\text{bpy})_3^{2+}$ complexes.

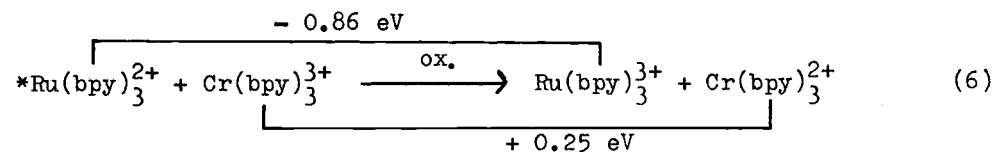
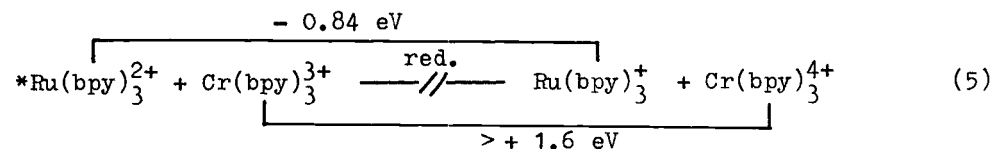
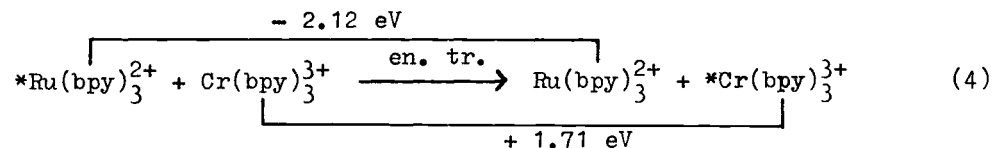
ENERGY VS ELECTRON TRANSFER PROCESSES

In bimolecular processes, the lowest excited state of these complexes can act as an energy donor, an electron acceptor and an electron donor. The actual quenching mechanism will be determined by thermodynamic and kinetic factors. From the thermodynamic point of view, the energy transfer ability of the excited state is related to its zero-zero spectroscopic energy, and the electron transfer ability is related to the excited state redox potentials. The kinetic factors are associated to the free activation energy needed to rearrange the inner and outer shells before energy or electron transfer takes place, as it will be discussed later.

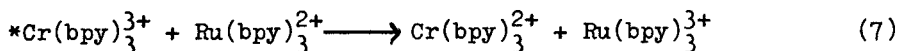
In some cases, the nature of the quenching mechanism can be straightforwardly predicted from simple thermodynamic arguments. For example, in the quenching of $*\text{Ru}(\text{bpy})_3^{2+}$ by $\text{Tl}_{\text{aq}}^{3+}$ only the oxidative electron transfer quenching is ther-



modynamically allowed and $Ru(bpy)_3^{3+}$ is actually obtained in the quenching reaction (15). In other cases, however, more than one quenching process are thermodynamically allowed. For example:



In this system, sensitized emission of $Cr(bpy)_3^{3+}$ is not observed (16), and flash experiments show that $Ru(bpy)_3^{3+}$ and $Cr(bpy)_3^{2+}$ are transiently produced (17). At first sight, these results seem to suggest that the quenching occurs via oxidative electron transfer (eq.6). However, a closer examination of this system shows that the same results could be obtained via quenching by energy transfer (eq.4) followed by reaction 7, whose occurrence can be independently



verified (16,17). Experiments carried out in the presence of I^- ions, which are known to be efficient and selective quenchers of $*Cr(bpy)_3^{3+}$, definitively showed that the quenching of $*Ru(bpy)_3^{2+}$ by $Cr(bpy)_3^{3+}$ occurs by reaction 6 (17). In other cases, however, the discrimination between different quenching mechanism is difficult (18). The available results seem to indicate that when energy and electron transfer are both thermodynamically allowed, electron transfer predominates.

ENERGY CONVERSION AND STORAGE

The $Ru(bpy)_3^{2+} - Cr(bpy)_3^{3+}$ system discussed above is also suitable for a discussion of the problems connected with energy conversion and storage (4,16,17). The energetic situation of this system is schematized in Fig. 2 where the zero

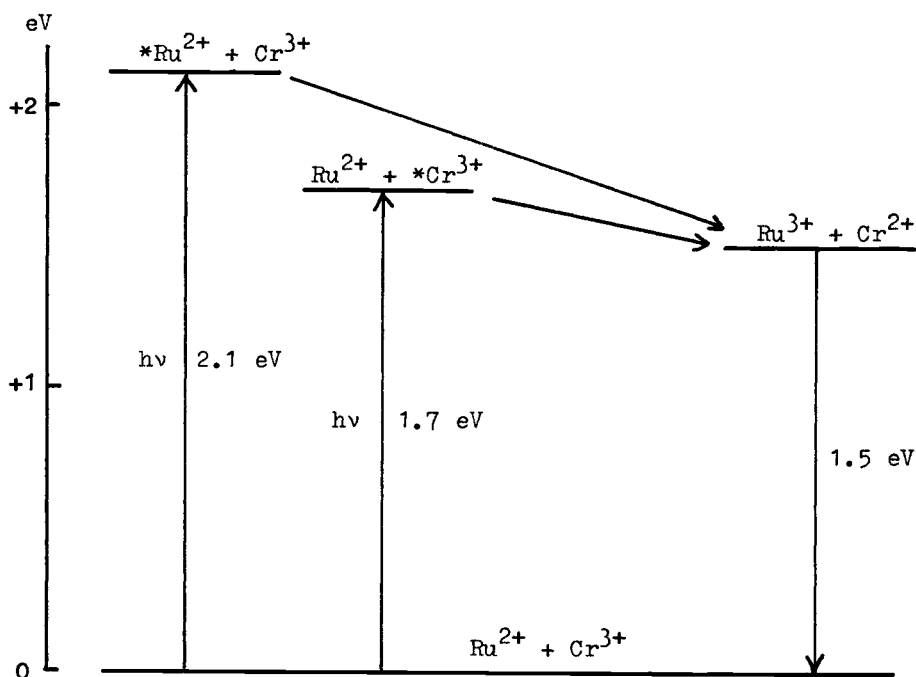


Fig. 2. Energetics of the $Ru(bpy)_3^{2+} - Cr(bpy)_3^{3+}$ system. For the sake of simplicity the ligands have been omitted.

energy level has been taken to correspond to the two complexes in their normal oxidation state and spectroscopic ground state. Excitation of the ruthenium or chromium complexes ultimately leads to the lowest excited state of these species, whose energy content is 2.12 and 1.71 eV, respectively. Quenching of the excited state of one complex by the ground state of the other leads in both cases to oxidized ruthenium and reduced chromium complexes which are

high energy species whose (back) electron transfer reaction can give back 1.5 eV. Thus, a substantial amount of "spectroscopic" energy has been converted into "chemical" energy in this system, but unfortunately this converted energy is only transiently stored because the back electron transfer reaction is very fast. Effective storage would be possible if the back reaction can be slowed down in some way or if one of the two high energy species can be rapidly scavenged. Studies in these directions are under way in several laboratories (see for example, ref. 19).

KINETIC ASPECTS OF EXCITED STATE ELECTRON TRANSFER REACTIONS

The outer-sphere electron transfer reactions are uniquely amenable to theoretical attack because they only involve the transfer of an electron without any bond breaking or bond making processes. The most detailed treatment of outer-sphere electron transfer reactions has been given by Marcus (5). A point which is still the object of many discussions is whether the expected decrease of the rate constant when electron transfer reaction becomes more and more favoured thermodynamically (Marcus inverted region) really occurs (4-7). When both reactants are in their ground state, few opportunities arise for systematic exploration of the inverted region because ΔG° is not sufficiently negative. Excited state systems, on the contrary, provide excellent probes of this region.

For excited state electron transfer reactions, a kinetic scheme like that shown in Fig. 3 can be used. Using steady-state approximations and assuming

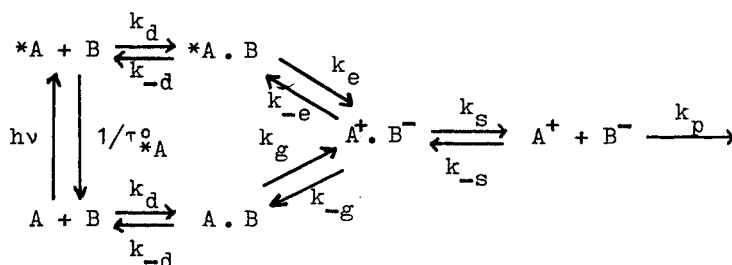


Fig. 3. Kinetic scheme for quenching by electron transfer.

that the k_p path is negligible compared to the k_s path or viceversa, this scheme leads to the following equation for the experimental quenching constant

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d} k_{-e}}{k_x k_e}} \quad (8)$$

where $k_x = k_g$ when the k_p path is negligible, and $k_x = k_g + k_s$ when the k_s path is negligible.

In most of the systems studied, the quenching process is not accompanied by permanent chemical changes, indicating that the excited state electron transfer reaction is reversed in the dark. Under such conditions, the experimental quenching constant can thus be expressed by eq.9:

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d} k_{-e}}{k_{-g} k_e}} \quad (9)$$

The rate constants of the three electron transfer steps which appear in eq.9 have to obey equation 10, where Z_i is the frequency factor and ΔG_i^\ddagger is the free

$$k_i = Z_i \exp(-\Delta G_i^\ddagger / RT) \quad (10)$$

activation energy of the step. The ratio of the back and forward excited state electron transfer rate constants is given by eq. 11 where ΔG_e^0 is the free

$$\frac{k_{-e}}{k_e} = \exp(\Delta G_e^0 / RT) \quad (11)$$

energy change associated with the forward excited state electron transfer step. Using relationships 10 and 11 and assuming that the frequency factor is the same in all cases, eq. 9 can be transformed in eq. 12. In his classical papers (20) on the electron transfer quenching of aromatic hydrocarbons fluorescence,

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{Z \exp(-\frac{\Delta G_e^\ddagger}{RT})} + \frac{k_{-d}}{Z \exp(-\frac{\Delta G_g^\ddagger}{RT})} \exp(\frac{\Delta G_e^0}{RT})} \quad (12)$$

Weller assumed that the back electron transfer reaction leading to the ground state has no activation energy ($k_{-g} = Z$) because the free energy loss in this step is exceedingly large. With this assumption, eq.12 simplifies into eq. 13.

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{Z} \left(\exp \frac{\Delta G_e^\ddagger}{RT} + \exp \frac{\Delta G_e^0}{RT} \right)} \quad (13)$$

This equation can be used, and actually it has been often used (20-22), to calculate the dependence of the experimental quenching constant on the free energy change provided that the free activation energy can be expressed as a function of the free energy change. In this regard, two options are available: (i) the classical relationship of the Marcus theory (5) (eq. 14), or the empirical relationship proposed by Weller (20) (eq. 15). In both equations λ represents the reorganizational energy which is related to intrinsic properties of the two reactants (4-6).

$$\Delta G_e^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G_e^0}{\lambda} \right)^2 \quad (14)$$

$$\Delta G^\ddagger = \frac{\Delta G_e^0}{2} + \left[\left(\frac{\Delta G_e^0}{2} \right)^2 + \left(\frac{\lambda}{4} \right)^2 \right]^{\frac{1}{2}} \quad (15)$$

In the quenching of an excited state by a homogeneous family of quenchers having variable redox potential, the reorganizational parameter λ is constant, as are the diffusion and separation rate constants that appear in eq. 13. Thus, the quenching constant is only a function of the free energy change which, in its turn, changes with the redox potential of the quencher. Depending on whether one uses the Marcus (eq. 14) or Weller (eq. 16) relationship to express the dependence of ΔG_e^\ddagger on ΔG_e^0 , curves M and W of Fig. 4 are obtained for

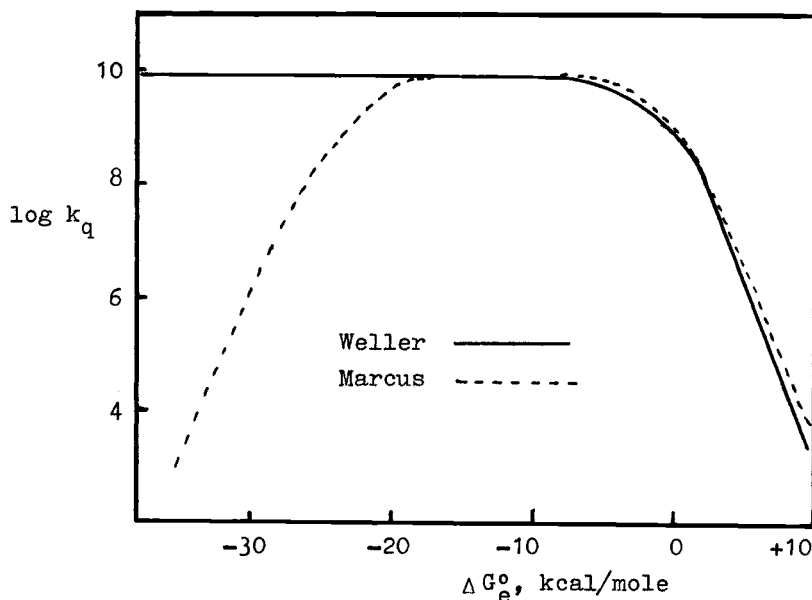


Fig. 4. Plot of the logarithm of the experimental quenching constant vs the free energy change of the electron transfer reaction calculated from eq. 13 using the Marcus (eq. 14) or Weller (eq. 15) relationships (see note a).

$\log k_q$ vs ΔG_e^0 . These curves almost coincide for positive or slightly negative ΔG_e^0 values, but they are different for large and negative free energy changes, where the Marcus model predicts a sharp decrease of k_q (Marcus inverted region). No evidence of this inverted region has been found in the electron transfer quenching of fluorescent aromatic molecules (20), thionine and lumiflavine acid and basic triplet forms (23), duroquinone triplet state (21),

Note a. The calculation has been performed using a set of parameters ($k_d = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; $k_{-d} = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $Z = 1 \times 10^{11} \text{ s}^{-1}$; $\lambda/4 = 12 \text{ kcal/mole}$) that are appropriate to the quenching of $^* \text{Cr}(\text{bpy})_3^{3+}$ by aromatic amines and methoxybenzenes (22).

and the lowest excited state of $\text{Cr}(\text{bpy})_3^{3+}$ and $\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$ (22). However, "vestiges" (i.e. a very small decrease of k_q) of the inverted region have been found in the quenching of polypyridine Ru(II) complexes (24). Recently it has been noted (25) that the ability of the Marcus or Weller relationships to interpret the experimental quenching results cannot be tested by introducing these relationships in eq. 13, since it derives from the "anti-Marcus" assumption that the back electron transfer step is very fast being highly exoergonic. Rather, eq. 12, which is "neutral" in this regard, should be used. If this is done, the discrepancy between the correlations predicted by the Marcus (eq. 14) and Weller (eq. 15) relationships is even more dramatic than that shown in Fig. 4, since different results are also predicted in the "normal" free energy region (Fig. 5). The reason why the Marcus relationship

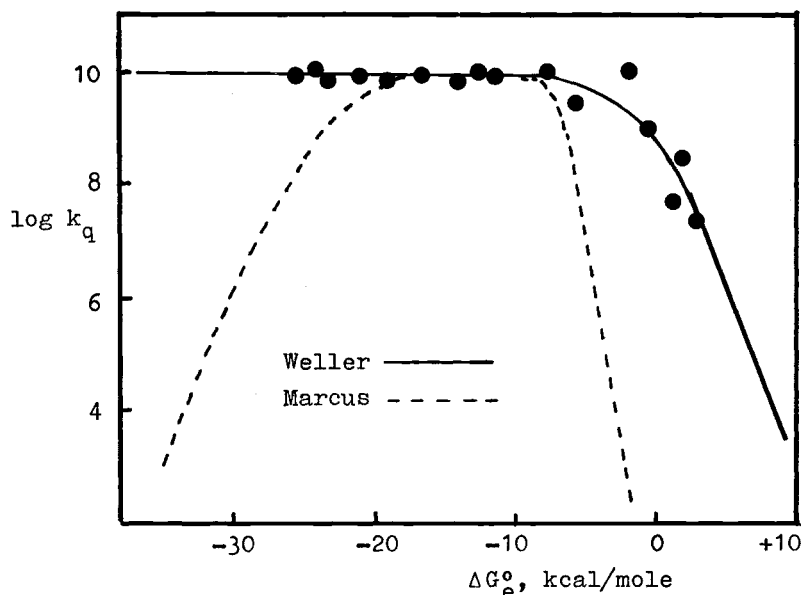


Fig. 5. Plot of the logarithm of the experimental quenching constant vs the free energy change of the electron transfer reaction calculated from eq. 12 using the Marcus (eq. 14) or Weller (eq. 15) relationships (see note a). The points indicate the experimental values for the quenching of $^*\text{Cr}(\text{bpy})_3^{3+}$ by aromatic amines and methoxybenzenes (22).

predicts low k_q values in the "normal" region is that for positive or slightly negative ΔG_e^0 values, ΔG_{-g}^0 is exceedingly large and negative (see note b), so that the back electron transfer reaction leading to the ground state lies in

Note b. Note that $\Delta G_e^0 + \Delta G_{-g}^0 = -\Delta E_{0-0}^{\text{sp}}$, where $\Delta E_{0-0}^{\text{sp}}$ is the zero-zero spectroscopic energy of the excited state. The entropy changes associated with excitation are assumed to be small (see above).

its "Marcus inverted region" and thus its rate is expected to be very small. Under these conditions, the back electron transfer leading to the excited state (k_{-e} in Fig. 3) should prevail, with a consequent regeneration of excited states and thus a small quenching effect. In conclusion, from the left-hand side of a diagram like that in Fig. 5 one can learn which free energy relationship is obeyed by the excited state electron transfer reaction, whereas from the right-hand side one can learn which relationship is obeyed by the back electron transfer reaction leading to the ground state.

The results obtained in the quenching of the lowest excited state of $\text{Cr}(\text{bpy})_3^{3+}$ by aromatic amines and methoxybenzenes in acetonitrile (22) are compared in Fig. 5 with the predictions of the Marcus and Weller relationships. One can see that neither the excited state electron transfer reaction nor the back electron transfer reaction follow the Marcus relationship.

EXTENSION OF THE MARCUS-WELLER FORMALISM TO ENERGY TRANSFER PROCESSES

The formalism used for excited state electron transfer processes has been recently extended to energy transfer (collisional) quenching processes (26). There is in fact a very close analogy between the quenching of an excited state by outer-sphere electron transfer and exchange energy transfer. In both cases, spatial overlap of the donor and acceptor wave functions is required, no bond breaking or bond making processes take place, and Franck-Condon restrictions have to be obeyed because the electronic rearrangement with or without the net transfer of an electron between donor and acceptor occurs in a time short compared to that required for nuclear motions. Using a normal kinetic scheme (Fig. 6) and assuming that $1/\tau_{*B}^0 \gg k_{-S}$ [A], the treatment given before

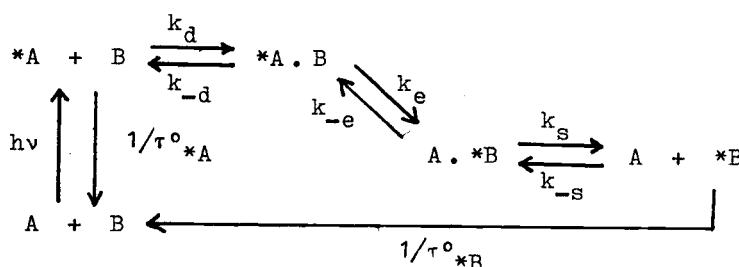


Fig. 6. Kinetic scheme for excited state quenching by collisional energy transfer.

for electron transfer quenching leads to the following equation for the experimental quenching constant:

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d}k_{-e}}{k_s k_e}} \quad (16)$$

where k_e and k_{-e} are now the rate constants for the energy transfer steps and k_{-d} is equal to k_s . Using relationships 10 and 11, where Z , ΔG_e^\ddagger and ΔG_e^0 are now the frequency factor, the free energy change, and the free activation energy of the energy transfer step, eq. 16 can be transformed into eq. 17:

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{Z} \exp(\Delta G_e^\ddagger/RT) + \exp(\Delta G_e^0/RT)} \quad (17)$$

The free activation energy and the free energy change are related by eq. 15 where the reorganizational parameter λ associated to the energy transfer reaction can be expressed by means of the free activation energies of the corresponding "self-exchange" energy transfer reactions (26). Eq. 17 yields a unified view of "classical" and "non-classical" (27) energy transfer processes. Actually it accounts well for the literature data concerning energy transfer from aromatic triplets to a "classical" acceptor like biacetyl (26) and "non-classical" acceptors like *o*-anisil (26), ferrocene (28) and ruthenocene (28) and it can also yield important pieces of information on the excited state energy and excited state distortion.

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