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- (14) (a) A. D. Walsh, *J. Chem. Soc.*, 2260–2266 (1953); (b) *ibid.*, 2262 (1953).

## Free Energy Correlation of Rate Constants for Electron Transfer Quenching of Excited Transition Metal Complexes

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**Abstract:** The quenching of the emitting excited states of Cr(bpy)<sub>3</sub><sup>3+</sup>, Ru(bpy)<sub>3</sub><sup>2+</sup>, and Ir(Me<sub>2</sub>phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> (bpy, 2,2'-bipyridine; Me<sub>2</sub>phen, 5,6-dimethyl-1,10-phenanthroline) by some 30 amines or methoxybenzenes having variable oxidation potentials has been studied in acetonitrile solution. Flash photolysis experiments showed that the quenching process takes place with formation of the one-electron oxidation product of the quencher. The bimolecular quenching constants obtained from the Stern–Volmer constants and the excited-state lifetimes have been found to be related to the free-energy change of the electron transfer process. The plots of log *k<sub>q</sub>* vs. *E*<sub>1/2</sub>(Q/Q<sup>+</sup>) show a region of linear increase at high *E*<sub>1/2</sub> values and reach a plateau at low *E*<sub>1/2</sub>. With aromatic amines and methoxybenzenes as quenchers, the comparison between theoretical curves<sup>14,16</sup> and experimental plots indicates that the kinetically estimated value of the excited-state reduction potential is in reasonable agreement with that expected on spectroscopic grounds. The results also indicate that the intrinsic barrier for the excited-state self-exchange reaction is comparable with that of the ground-state self-exchange reaction. For Cr(bpy)<sub>3</sub><sup>3+</sup> and Ir(Me<sub>2</sub>phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, no evidence of *k<sub>q</sub>* decrease with  $-\Delta G$  is present even for free-energy changes which are two to three times larger than that expected for the onset of the Marcus "inverted" region. The difference between the electron transfer quenching properties of aromatic and aliphatic amines is also briefly discussed.

### Introduction

Electronic excitation decreases the ionization potential and increases the electronic affinity of a molecule.<sup>2</sup> As a consequence, those electronically excited states which live long enough to encounter other species can easily be involved in intermolecular electron transfer reactions. The extraordinary redox properties of electronically excited molecules are currently drawing the attention of many workers for at least two reasons: (1) they can be used for the conversion of light energy (including solar energy) into chemical energy<sup>3–5</sup> and (2) they allow us to check the theories of outer-sphere electron transfer reactions<sup>6,7</sup> over a broad range of free-energy change.<sup>8–11</sup>

The electron transfer reactions of electronically excited organic molecules have been extensively studied in the past decade,<sup>12–37</sup> particularly by Weller et al.<sup>12–19</sup> A quantitative analysis was given by Rehm and Weller,<sup>14,16</sup> who established an equation on the relationship between the rate constant and the free-energy change of the electron transfer process. Such an equation was found to be obeyed by a number of systems consisting of fluorescent aromatic hydrocarbons and various quenchers (amines, methoxybenzenes, nitriles). In the last few years it has been shown that transition metal complexes containing bpy (2,2'-bipyridine) or phen (1,10-phenanthroline) as ligands are very suitable for excited-state electron transfer reactions. Several theoretical and practical aspects (including solar energy conversion<sup>3,4</sup>) of these reactions have been studied<sup>3–5,38–56</sup> but with few exceptions<sup>41,51,52</sup> the correlation between rate constants and free-energy change has not yet been investigated.

We report here the results of a systematic study on the electron transfer quenching of excited Cr(bpy)<sub>3</sub><sup>3+</sup>, Ru-

(bpy)<sub>3</sub><sup>2+</sup>, and Ir(Me<sub>2</sub>phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> by some 30 quenchers having variable oxidation potentials.

### Experimental Section

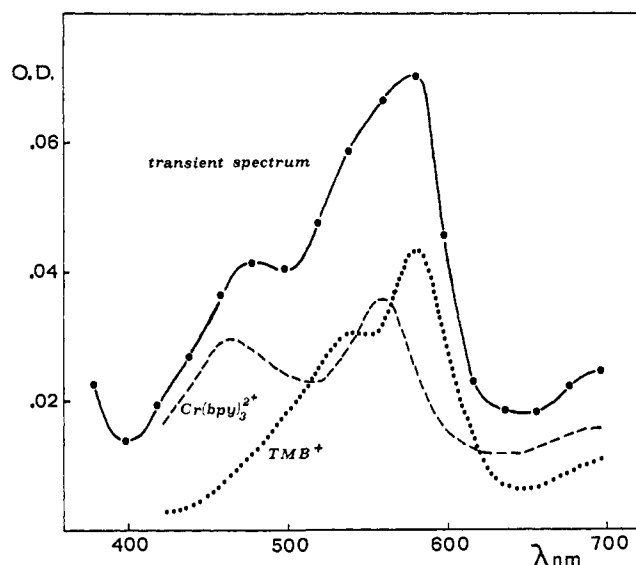
**Materials.** Tris(2,2'-bipyridine)chromium(III) perchlorate hemihydrate, [Cr(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O, was prepared and purified according to the procedure indicated by Baker and Mehta.<sup>57</sup> Tris(2,2'-bipyridine)ruthenium(II) chloride tetrahydrate, [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O, was prepared and purified as indicated by Burstall.<sup>58</sup> A pure sample of *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride trihydrate, [Ir(Me<sub>2</sub>phen)<sub>2</sub>Cl<sub>2</sub>]Cl·3H<sub>2</sub>O, was obtained as previously reported.<sup>59</sup> The quenchers were of the highest purity commercially available and were used without further purification. Tetraethylammonium perchlorate (TEAP) was C. Erba RS grade for polarography and was dried before use. Acetonitrile (Merck Uvasol) was used without further purification.

**Apparatus.** The emission spectra were measured with a Perkin-Elmer MPF 3 spectrofluorimeter equipped with an R-446 Hamamatsu tube for the experiments with the chromium complex and an R-106 Hamamatsu tube for those with the ruthenium and iridium complexes. The excitation wavelengths were 350 nm for Cr(bpy)<sub>3</sub><sup>3+</sup>, 450 nm for Ru(bpy)<sub>3</sub><sup>2+</sup>, and 400 nm for Ir(Me<sub>2</sub>phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>; the monitoring wavelengths were those corresponding to the maxima of the respective emission bands (Cr(bpy)<sub>3</sub><sup>3+</sup>, 727 nm; Ru(bpy)<sub>3</sub><sup>2+</sup>, 610 nm; Ir(Me<sub>2</sub>phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, 495 nm). The lifetime of the emitting state of Cr(bpy)<sub>3</sub><sup>3+</sup> was obtained by measuring the decay of the doublet–doublet absorption ( $\lambda_{\text{max}}$  390 nm) with an Applied Photophysics ruby laser apparatus. The emission lifetimes of the ruthenium and iridium complexes were measured by means of a modified Applied Photophysics apparatus based on the single photon counting technique. The excitation wavelength was 337 nm. The emission decay was monitored at the maxima of the respective emission bands. Transient absorption spectra were obtained by using an Applied Photophysics KR-10 flash photolysis apparatus.

**Table I.** Spectroscopic and Electrochemical Properties of the Complexes Used

complex ( $M^{n+}$ )	excited state <sup>a</sup>	$\Delta E_{0-0}$ , <sup>b</sup> $\mu\text{m}^{-1}$	$\tau$ , <sup>c</sup> $\mu\text{s}$	$E_{M^{n+}/M^{(n-1)+}}$ , <sup>d</sup> V	$E^*_{M^{n+}/M^{(n-1)+}}$ , <sup>e</sup> V
$\text{Cr}(\text{bpy})_3^{3+}$	<sup>2</sup> MC	1.38 <sup>f</sup>	50	-0.26 <sup>g</sup>	+1.45
$\text{Ru}(\text{bpy})_3^{2+}$	<sup>3</sup> MLCT	1.71 <sup>h</sup>	0.153	-1.35 <sup>i</sup>	+0.79
$\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$	<sup>3</sup> LC	2.05 <sup>j</sup>	0.490	-1.16 <sup>k</sup>	+1.38

<sup>a</sup> The formal multiplicity and the orbital nature of the emitting state are shown (MC = metal centered; MLCT = metal to ligand charge transfer; LC = ligand centered). <sup>b</sup> Energy of the emitting excited state (0-0 transition at 77 K). <sup>c</sup> Lifetime of the emitting excited state in aerated acetonitrile solution. <sup>d</sup> Half-wave reduction potential vs. SCE in acetonitrile solution unless otherwise noted. <sup>e</sup> "Theoretical" (see eq 12) half-wave reduction potential of the excited state vs. SCE. <sup>f</sup> Reference 72. <sup>g</sup> Reference 68. <sup>h</sup> R. J. Watts and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 3184 (1971). <sup>i</sup> Reference 69. <sup>j</sup> Reference 74. <sup>k</sup> In DMF solution; S. Roffia and M. Ciano, unpublished results.



**Figure 1.** Spectrum of the transient obtained in the flash photolysis of  $\text{Cr}(\text{bpy})_3^{3+}$  in the presence of  $1.0 \times 10^{-2}$  M 1,3,5-trimethoxybenzene (TMB) immediately after the flash. The spectra of  $\text{Cr}(\text{bpy})_3^{3+}$  and  $\text{TMB}^+$  are also shown. The transient was found to disappear by second-order kinetics with  $k = 8.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

**Procedure.** All the experiments were carried out at room temperature ( $\sim 22^\circ \text{C}$ ) in aerated acetonitrile solutions. The TEAP concentration was 0.02 M for the experiments with  $\text{Cr}(\text{bpy})_3^{3+}$  and 0.1 M in all the other cases. The complex concentration was  $5 \times 10^{-5}$  M for  $\text{Cr}(\text{bpy})_3^{3+}$ ,  $6 \times 10^{-5}$  M for  $\text{Ru}(\text{bpy})_3^{2+}$ , and  $3 \times 10^{-4}$  or  $1 \times 10^{-3}$  M for  $\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$ .

For each complex, the quenching of the luminescence emission was measured with at least four different quencher concentrations. In all cases the exciting light was only absorbed ( $\geq 98\%$ ) by the complex.

## Results

In all cases, the absorption spectra of complex-quencher solutions were equal to the sum of the two component spectra with no evidence for ground-state interactions. The lifetime of the emitting excited states of the three complexes under our experimental conditions are shown in Table I together with other spectroscopic and electrochemical data which will be discussed later on. The emission spectra of the complexes were qualitatively unaffected by the quenchers. For each quencher, linear Stern-Volmer plots were obtained from steady-state luminescence measurements. The bimolecular quenching constants were calculated from the Stern-Volmer quenching constants and the lifetimes of the excited states. The values obtained are shown in Table II.

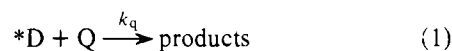
Flash photolysis experiments were performed in order to see whether the quenching process was accompanied by chemical reactions.  $\text{Cr}(\text{bpy})_3^{3+}$  was particularly suitable for this kind of experiment because (1) it does not absorb in the visible region, (2) its excited state lives long enough to allow the use of low quencher concentrations, and (3) the spectrum of its one-electron reduction product,  $\text{Cr}(\text{bpy})_3^{2+}$ , is well known.<sup>60</sup>

With  $\text{Ru}(\text{bpy})_3^{2+}$ , no flash experiment was performed because of difficulties arising from the short excited-state lifetime and the strong visible absorption. With  $\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$ , the flash experiments were made difficult by the short excited-state lifetime and the unavailability of the spectrum of the one-electron reduced product of the complex. In all the systems investigated by flash photolysis, spectral changes were observed. In some cases there was a complete or partial irreversibility. As an example of the spectral changes observed, the transient spectrum obtained for the  $\text{Cr}(\text{bpy})_3^{3+}$ -1,3,5-trimethoxybenzene system is shown in Figure 1.

The nature of the products observed in the various flash experiments is indicated in Table II. A full account of the flash photolysis experiments will be published elsewhere.<sup>61</sup>

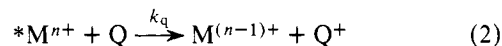
## Discussion

**Quenching Mechanism.** The bimolecular quenching of an excited state molecule in fluid solution

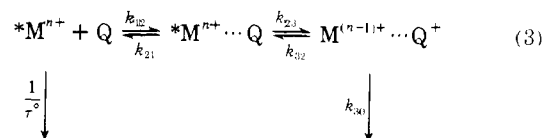


may take place by various mechanisms,<sup>54,62</sup> depending on the properties of the excited state and the quencher. Although the triplet energies of several of the quenchers used in this work are not known, the available data (Tables I and II) indicate that electronic energy transfer is energetically unfavorable for all of the systems examined. Quenching by hydrogen transfer is unlikely even for the amine quenchers because the excited states of our complexes are not expected to exhibit hydrogen abstraction properties; also, no evidence of neutral amine radical ( $\text{R}_2\text{N}\cdot$ )<sup>63</sup> formation has been obtained in the flash experiments. Quenching by electron transfer or charge transfer is expected to imply some relationship between the quenching constant and the redox properties of the quenchers.<sup>16,64</sup> This is indeed the case of our systems, as the  $k_q$  values increase with decreasing oxidation potential of the quencher (Table II).

As is shown in Table II, the products corresponding to the electron transfer quenching, i.e., the one-electron reduction product of the complex and/or the one-electron oxidation product of the quencher, have been observed for each one of the systems which have been studied by flash photolysis. On the other hand, as expected for polar solvents like acetonitrile, no evidence for exciplex emission has been found in our systems. Thus, it seems safe to assume that the only important quenching mechanism in our systems is the electron transfer from the quencher to the excited state:



**Kinetics of Electron Transfer Quenching.** According to Rehm and Weller,<sup>14,16</sup> the electron transfer quenching mechanism can be described by the following reaction scheme:



**Table II.** Bimolecular Quenching Constants and Observed Products

quencher	$E_{1/2}(Q/Q^+)^a$ V	$E_T$ $\mu\text{m}^{-1}$	$\text{Cr}(\text{bpy})_3^{3+}$		$\text{Ru}(\text{bpy})_3^{2+}$		$\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$	
			$k_q$ $\text{M}^{-1}\text{s}^{-1}$	observed products <sup>b</sup>	$k_q$ $\text{M}^{-1}\text{s}^{-1}$	observed products <sup>b</sup>	$k_q$ $\text{M}^{-1}\text{s}^{-1}$	observed products <sup>b</sup>
4-aminodiphenylamine	0.27 <sup>c</sup>		$9.4 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$	$6.7 \times 10^9$			
<i>N,N,N',N'</i> -tetramethylbenzidine	0.32 <sup>c</sup>	2.18 <sup>d</sup>	$1.1 \times 10^{10}$	$\text{M}^{(n-1)+}, \text{Q}^+$	$7.4 \times 10^9$		$8.1 \times 10^9$	$\text{Q}^+$
<i>N,N'</i> -diphenyl- <i>p</i> -phenylenediamine	0.35 <sup>c</sup>		$7.2 \times 10^9$	<i>e</i>	$5.8 \times 10^9$		$9.4 \times 10^9$	
benzidine	0.46 <sup>c</sup>		$8.7 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$	$4.5 \times 10^9$		$9.1 \times 10^9$	
phenothiazine	0.53 <sup>c,f</sup>	2.14 <sup>g</sup>			$4.1 \times 10^9$			
$\alpha$ -naphthylamine	0.54 <sup>c</sup>	1.90 <sup>h</sup>	$7.2 \times 10^9$	<i>e</i>				
$\beta$ -naphthylamine	0.64 <sup>c</sup>	2.09 <sup>h</sup>	$8.2 \times 10^9$					
<i>N,N</i> -dimethyl- <i>p</i> -toluidine	0.65 <sup>c</sup>				$1.1 \times 10^9$			
<i>N,N</i> -diethylaniline	0.76 <sup>i</sup>		$6.4 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$	$1.5 \times 10^8$		$9.1 \times 10^9$	$\text{Q}^+$
<i>N,N</i> -dimethylaniline	0.78 <sup>i</sup>				$6.5 \times 10^{7m}$		$1.0 \times 10^{10}$	
diphenylamine	0.83 <sup>c</sup>	2.52 <sup>h</sup>	$9.1 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$			$6.8 \times 10^9$	$\text{Q}^+$
triphenylamine	0.86 <sup>c</sup>	2.45 <sup>h</sup>	$7.3 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$			$6.5 \times 10^9$	
tributylamine	0.92 <sup>c,j</sup>		$6.9 \times 10^8$	$\text{M}^{(n-1)+}, -$			$2.3 \times 10^9$	
triethylamine	0.96 <sup>c,j</sup>		$7.4 \times 10^8$	$\text{M}^{(n-1)+}, -$			$1.4 \times 10^9$	
<i>N,N</i> -dimethylbenzylamine	1.01 <sup>c,j</sup>		$2.5 \times 10^8$	$\text{M}^{(n-1)+}, -$			$4.1 \times 10^8$	
<i>N</i> -methylaniline	1.03 <sup>i</sup>		$1.1 \times 10^{10}$	$\text{M}^{(n-1)+}, \text{Q}^+$			$5.8 \times 10^9$	
dicyclohexylamine	1.12 <sup>c,j</sup>		$2.0 \times 10^8$	$\text{M}^{(n-1)+}, -$			$8.9 \times 10^8$	
1,2,4-trimethoxybenzene	1.12 <sup>c</sup>	<i>k</i>	$2.8 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$			$5.5 \times 10^9$	$\text{Q}^+$
dibutylamine	1.17 <sup>c,j</sup>		$1.6 \times 10^8$	$\text{M}^{(n-1)+}, -$			$7.0 \times 10^8$	
dipropylamine	1.22 <sup>c,j</sup>		$1.5 \times 10^8$	$\text{M}^{(n-1)+}, -$			$6.4 \times 10^8$	
aniline	1.28 <sup>i</sup>	2.68 <sup>h</sup>	$9.9 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$			$7.7 \times 10^9$	
diethylamine	1.30 <sup>c,j</sup>		$8.9 \times 10^7$	$\text{M}^{(n-1)+}, -$			$4.1 \times 10^8$	
1,4-dimethoxybenzene	1.34 <sup>c</sup>	<i>k</i>	$1.1 \times 10^9$	$\text{M}^{(n-1)+}, \text{Q}^+$			$2.4 \times 10^9$	
dibenzylamine	1.38 <sup>c,j</sup>		$1.0 \times 10^7$	$\text{M}^{(n-1)+}, -$			$4.6 \times 10^7$	
1,2,3-trimethoxybenzene	1.42 <sup>c</sup>	<i>k</i>	$4.3 \times 10^7$	$\text{M}^{(n-1)+}, \text{Q}^+$			$6.4 \times 10^7$	
1,2-dimethoxybenzene	1.45 <sup>c</sup>	<i>k</i>	$2.4 \times 10^8$	$\text{M}^{(n-1)+}, \text{Q}^+$			$4.8 \times 10^7$	
<i>tert</i> -butylamine	1.45 <sup>i</sup>		$1.4 \times 10^7$	$\text{M}^{(n-1)+}, -$			$2.0 \times 10^6$	
1,3,5-trimethoxybenzene	1.49 <sup>c</sup>	<i>k</i>	$1.9 \times 10^7$	$\text{M}^{(n-1)+}, \text{Q}^+$				

<sup>a</sup> Half-wave oxidation potential in acetonitrile solution vs. SCE, unless other wise indicated. <sup>b</sup>  $\text{M}^{(n-1)+}$  is the one-electron reduction product of the complex.  $\text{Q}^+$  is the one-electron oxidation product radical cation of the quencher. The products have been identified by comparison with published spectra of identical or similar compounds. For  $\text{M}^{(n-1)+}$  see ref 60. Spectra of  $\text{Q}^+$  species are reported by ref 22, 33, 37, and 63; T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966); A. Ronlán, J. Coleman, O. Hammerich, and U. D. Parker, *J. Am. Chem. Soc.*, **96**, 845 (1974); P. O'Neill, S. Steenken, and G. Schulte-Frohlinde, *J. Phys. Chem.*, **79**, 2773 (1975). <sup>c</sup> C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Non-aqueous Systems", Marcel Dekker, New York, N.Y., 1970. <sup>d</sup> S. A. Alkaitis and M. Graetzel, *J. Am. Chem. Soc.*, **98**, 3549 (1976). <sup>e</sup> The observed spectral changes, although compatible with the presence of  $\text{M}^{(n-1)+}$ , could not be analyzed because the spectrum of  $\text{Q}^+$  is unknown. <sup>f</sup> Obtained from half-wave oxidation potential vs.  $\text{Ag}/\text{Ag}^+$  0.01 M by adding 0.26 V. <sup>g</sup> S. A. Alkaitis, M. Graetzel, and A. Henglein, *Berg. Bunsenges. Phys. Chem.*, **79**, 541 (1975). <sup>h</sup> C. A. Parker, "Photoluminescence of Solutions", Elsevier, Amsterdam, 1968. <sup>i</sup> Reference 33. <sup>j</sup> Obtained from half-wave oxidation potential vs.  $\text{Ag}/\text{Ag}^+$  0.1 M by adding 0.30 V. <sup>k</sup>  $E_T = 2.62 \mu\text{m}^{-1}$  for anisole. <sup>l</sup> R. O. Loufty and R. O. Loufty, *Can. J. Chem.*, **50**, 4052 (1972). <sup>m</sup> To be compared with the value of  $7.1 \times 10^7 \text{M}^{-1} \text{s}^{-1}$  reported by C. P. Anderson, D. J. Salmon, T. J. Meyer, and R. C. Young, *J. Am. Chem. Soc.*, **99**, 1980 (1977).

where all possible reactions by which the  $\text{M}^{(n-1)+} \dots \text{Q}^+$  "radical pair" can disappear are included in  $k_{30}$ .<sup>65</sup> Using the Stern-Volmer relationship and steady-state approximations, Rehm and Weller<sup>14,16</sup> obtained the following equation for the observed bimolecular quenching constant,  $k_q$ :

$$k_q = \frac{k_{12}}{1 + \frac{k_{12}}{\Delta V k_{30}} \left[ \exp\left(\frac{\Delta G_{23}^\ddagger}{RT}\right) + \exp\left(\frac{\Delta G_{23}}{RT}\right) \right]} \quad (4)$$

where  $\Delta G_{23}$  and  $\Delta G_{23}^\ddagger$  are the free-energy difference and the free energy of activation between encounter complex and ion pair, and  $\Delta V = k_{12}/k_{21}$  is the encounter volume. Equation 4 reduces to eq 5 when  $\Delta G_{23}$  becomes large and negative and to eq 6 when  $\Delta G_{23}$  becomes large and positive:

$$k_q = \frac{k_{12} \Delta V k_{30}}{\Delta V k_{30} + k_{12} \exp(\Delta G_{23}^\ddagger/RT)} \quad (5)$$

$$k_q = \frac{\Delta V k_{30}}{2} \exp(-\Delta G_{23}/RT) \quad (6)$$

According to Rehm and Weller,<sup>14,16</sup> the free energy of activation for an electron-transfer reaction,  $\Delta G^\ddagger$ , is related to the overall free-energy change,  $\Delta G$ , by eq 7:

$$\Delta G^\ddagger = \frac{\Delta G}{2} + \sqrt{\left(\frac{\Delta G}{2}\right)^2 + (\Delta G^\ddagger(0))^2} \quad (7)$$

where  $\Delta G^\ddagger(0)$  is the free energy of activation for  $\Delta G = 0$ . If eq 7 holds, eq 5 can be further reduced to

$$k_q^{\text{max}} = \frac{k_{12} \Delta V k_{30}}{\Delta V k_{30} + k_{12}} \quad (8)$$

On the other hand,  $\Delta G_{23}$  can be written in terms of redox potentials as

$$\Delta G_{23} = -E_{1/2}(*\text{M}^{n+}/\text{M}^{(n-1)+}) + E_{1/2}(\text{Q}/\text{Q}^+) + w_p - w_r \quad (9)$$

where  $w_p$  and  $w_r$  represent the work required to bring the products ( $\text{M}^{(n-1)+}$  and  $\text{Q}^+$ ) and the reactants ( $\text{M}^{n+}$  and  $\text{Q}$ ) together at the separation distance of the encounter complex. For our systems,  $w_r$  is always negligible because  $\text{Q}$  is an uncharged species, and  $w_p$  can also be neglected because it is  $\leq 0.05$  eV in the most unfavorable case ( $\text{Cr}(\text{bpy})_3^{3+}$ ). According to this treatment,  $\log k_q$  vs.  $E_{1/2}(\text{Q}/\text{Q}^+)$  is expected (1) to show a region of linear increase at high  $E_{1/2}$  values, with slope  $-1/2.3RT$  (eq 7), and (2) to reach a plateau at low  $E_{1/2}$  (eq 8). The plots of Figures 2-4 show that our systems fit, at

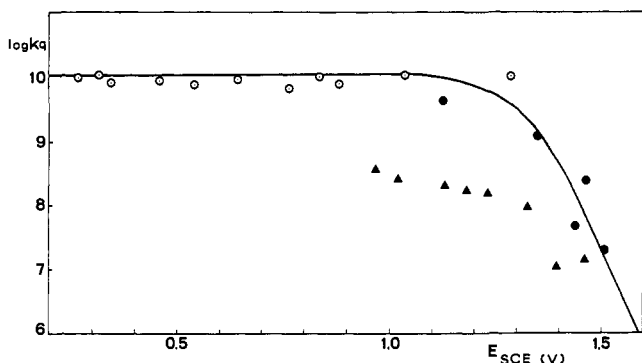


Figure 2. Plot of the logarithm of the rate constant vs.  $E_{1/2}(Q/Q^+)$  for the quenching of  $\text{Cr}(\text{bpy})_3^{3+}$  by aromatic amines (O), methoxybenzenes (●), and aliphatic amines (▲).

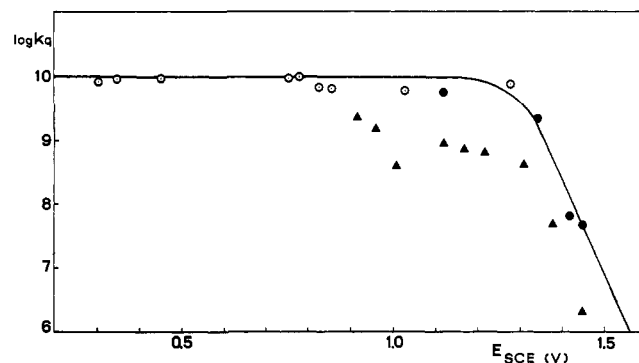


Figure 4. Plot of the logarithm of the rate constant vs.  $E_{1/2}(Q/Q^+)$  for the quenching of  $\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$  by aromatic amines (O), methoxybenzenes (●), and aliphatic amines (▲).

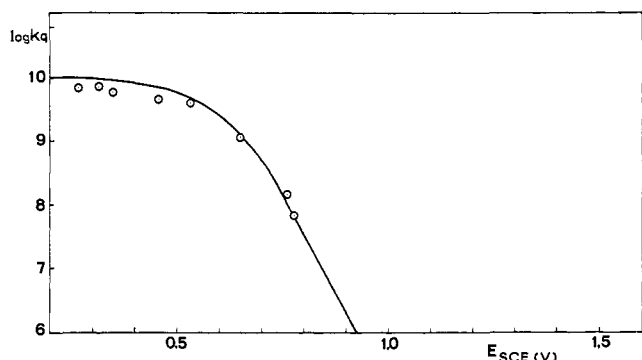


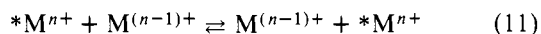
Figure 3. Plot of the logarithm of the rate constant vs.  $E_{1/2}(Q/Q^+)$  for the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by aromatic amines.

least qualitatively, these theoretical expectations. For aromatic amines and methoxybenzenes as quenchers, the best fits are obtained with  $k_{12} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta V k_{30} = 8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ , and assuming the following values for  $\Delta G^\ddagger(0)$  and  $E_{1/2}(*M^{n+}/M^{(n-1)+})$ :  $\sim 3 \text{ kcal/mol}$  and  $\sim +1.3 \text{ V}$  for  $\text{Cr}(\text{bpy})_3^{3+}$ ,  $\sim 4 \text{ kcal/mol}$  and  $\sim +0.7 \text{ V}$  for  $\text{Ru}(\text{bpy})_3^{2+}$ , and  $\sim 2 \text{ kcal/mol}$  and  $\sim +1.25 \text{ V}$  for  $\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$ . The uncertainty in the  $E_{1/2}$  values can be estimated as  $\pm 0.15 \text{ V}$ . The "theoretical" values (Table I) that can be obtained from

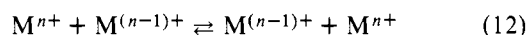
$$E_{1/2}(*M^{n+}/M^{(n-1)+}) = \Delta E_{0,0} + E_{1/2}(M^{n+}/M^{(n-1)+}) \quad (10)$$

i.e., assuming that all the spectroscopic energy of the excited state can be used as free energy in the redox process, are also affected by considerable experimental errors.<sup>66</sup> Within these limitations, the kinetically estimated values are in reasonable agreement with the "theoretical" ones.

The  $\Delta G^\ddagger(0)$  values obtained by the best fitting procedure are relatively small. As the contribution of the quencher,  $\Delta G^\ddagger(Q, Q^+)$ , to the intrinsic barrier of the cross electron transfer reaction 2 is about  $3 \text{ kcal/mol}$ ,<sup>70</sup> the intrinsic barrier  $\Delta G^\ddagger(*M^{n+}, M^{(n-1)+})$  for the excited state self-exchange reaction



has to be lower than  $5 \text{ kcal/mol}$ , i.e., comparable to that obtained for the ground-state self-exchange reaction<sup>51,52</sup>



This indicates that the ground and excited state of these complexes are quite similar in size and shape, as expected on the basis of the small values of the Stokes shifts.<sup>60,71-73</sup>

If eq 7 of the above kinetic treatment is replaced by the Marcus equation

$$\Delta G^\ddagger = \Delta G^\ddagger(0) \left( 1 + \frac{\Delta G}{4\Delta G^\ddagger(0)} \right)^2 \quad (13)$$

a plot of  $\log k_{23}$  vs.  $\Delta G$  for constant reorganization energy should be parabolic.<sup>6</sup> This implies that, when  $-\Delta G$  is larger than  $2[\Delta G^\ddagger(*M^{n+}, M^{(n-1)+}) + \Delta G^\ddagger(Q, Q^+)]$ , the quenching constant  $k_q$  should decrease as the free-energy change becomes more favorable ("inverted" or "abnormal" region).<sup>8-11,51</sup> When both the reactants are in their ground state  $\Delta G$  is usually not large enough to allow the exploration of the inverted region. Rehm and Weller<sup>14,16</sup> in their electron transfer quenching of aromatic hydrocarbon fluorescence did not find any evidence of decrease of the rate constant up to  $\Delta G = -62 \text{ kcal/mol}$ , although the inverted region was expected at  $\sim -10 \text{ kcal/mol}$ . More recently, Creutz and Sutin<sup>51</sup> have reported evidence for "vestiges" of the inverted region for the electron transfer quenching of  $*\text{Ru}(\text{bpy})_3^{2+}$  and  $*\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$  by  $\text{Cr}(\text{bpy})_3^{3+}$ ,  $\text{Os}(\text{bpy})_3^{3+}$ ,  $\text{Ru}(\text{bpy})_3^{3+}$ , and  $\text{Ru}(\text{Me}_2\text{bpy})_3^{3+}$ . In our systems, for the quenching of  $*\text{Cr}(\text{bpy})_3^{3+}$  and  $*\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$  the onset of the inverted region would be expected at  $-12$  and  $-8 \text{ kcal/mol}$ , respectively. Figures 2 and 4, however, show that there is no evidence of  $k_q$  decrease up to  $E_{1/2}$  values that correspond to  $\Delta G = -23 \text{ kcal/mol}$  for  $\text{Cr}(\text{bpy})_3^{3+}$  and  $-21 \text{ kcal/mol}$  for  $\text{Ir}(\text{Me}_2\text{phen})_2\text{Cl}_2^+$ . Our results seem thus to be in disagreement with the conventional Marcus theory. Following Rehm and Weller,<sup>16</sup> a possible explanation for this disagreement could be that electronically excited  $M^{(n-1)+}$  and/or  $Q^+$  may be initially formed in the electron transfer process, thus decreasing the  $\Delta G_{23}$  value relative to the calculated one. This may be true for at least some of the systems studied (e.g.,  $\text{Cr}(\text{bpy})_3^{3+}$  and aromatic amines) in which  $M^{(n-1)+}$  and  $Q^+$  are likely to have low-lying electronically excited states. On the other hand, theoretical approaches not involving the intermediacy of electronically excited states have recently been proposed<sup>8-11</sup> in order to account for the observed lack of the "Marcus inverted region".

Finally, it is clear from Figures 2 and 4 that aliphatic amines do not lie on the same curve as aromatic amines and methoxybenzenes. This is not surprising for three reasons: (1) the oxidation of aliphatic amines is an irreversible process, so that the  $E_{1/2}$  values may not represent thermodynamic quantities; (2) the reorganization energy is expected to be higher for aliphatic than for aromatic amines; the electron to be transferred is, in fact, much more localized in the case of the aliphatic amines, which implies a more extended geometrical change upon oxidation; (3) owing to the greater localization, steric factors will slow down the reaction rate of the aliphatic amines. Slower electron transfer quenching by aliphatic amines compared to aromatic amines has also been observed for triplet methylene blue.<sup>36</sup>

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