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Quenching of tris(2,2′-bipyridine)chromium(III) and tris(1,10-phenanthroline)chromium(III) excited states by phenols: temperature and pH effect

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Abstract

The quenching rate constant k_q of the excited states $^*Cr(bpy)_3^{3+}$ and $^*Cr(phen)_3^{3+}$ by several substituted phenols was investigated as a function of temperature using the time resolved luminescence quenching technique. The activation parameters showed a pH dependence. The most important contribution to the total activation entropy in basic media was found to be the electrostatic factor. The data obtained from log k_q vs. ΔG^0 plot were analyzed on the basis of the current theories for electron transfer processes. The best fitting analysis in the $\Delta G^{\#}$ vs. ΔG^0 plot yielded reorganization energies of 59 and 55 kcal/mol for the bipyridine and phenanthroline chromium complexes, respectively. The high values of reorganization energies found (λ) were interpreted as a hydrogen bond term contribution (λ_H) to the outer-sphere reorganization energy, λ_o', where $\lambda_o' = \lambda_o + \lambda_H$. The effect of the ionic strength and $[Cl^-]$ on the quenching rate constant for the reaction of $^*Cr(phen)_3^{3+}$ with 2,6-dimethylphenol was investigated. It was found that neither the ionic pair formation nor the $[Cl^-]$ concentration seem to affect the quenching mechanism.

Keywords: Tris(2,2′-bipyridine)chromium(III); Tris(1,10-phenanthroline)chromium(III); Quenching; Phenol

1. Introduction

Electronically excited states that live sufficiently long to be in thermal equilibrium with their surroundings become different entities having chemical and physical properties of their own. The extraordinary redox properties of such entities are currently drawing the attention of many research workers for at least two reasons: (1) they can be used for the conversion of luminous (including solar) energy into chemical energy [1–8] and (2) they allow the checking of the validity of outer-sphere electron-transfer theory over a broad range of free energy changes thus yielding reliable kinetic parameters [9–11]. On the other hand, there is an increasing interest to understand the mechanistic aspects [12,13] and environmental pathways for the photodegradation of phenol and substituted phenols which are mainly used in industry in the production of phenolic pesticides and found in industrial waste water [14,15].

In the present paper, we deal with a systematic reductive quenching study of the luminescent excited state of $Cr(NN)_3^{3+}$ [$^*Cr(bpy)_3^{3+}$ and $^*Cr(phen)_3^{3+}$] by phenols in aqueous solutions at different temperatures and pH in order to help to a better understanding of the reaction mechanism.

2. Experimental

2.1. Materials

Tris(2,2′-bipyridine)chromium(III) and tris(1,10-phenanthroline)chromium(III), as perchlorate salt obtained from previous studies, were synthesized according to the literature [16,17] and were recrystallized at least three times. Phenol (H-), 2,6-dimethylphenol (2,6-diMe-), 4-bromo-2,6-dimethylphenol (4-Br-2,6-diMe-), 4-chloro-3-methylphenol (4-Cl-3-Me-), 4-fluorophenol (4-F-), 2,4-dichlorophenol (2,4-diCl-), 4-chlorophenol (4-Cl-), 4-bromophenol (4-Br-) and 4-iodophenol (4-I-) were purchased from Sigma and purified by vacuum sublimation.

Sodium chloride, sodium acetate, perchloric acid, boric acid, acetic acid and phosphoric acid were used without further purification.

The deionized water used for the preparation of the solutions was obtained with a Milli-Q System Millipore.

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2.2. Apparatus

Fluorescence lifetime measurements were performed with a Nitrogen Laser (Laser Optics, gated at 50 Hz and FWHM of 8 ns at 337 nm) as excitation source. A Thurbly Thandar digital storage adaptor DSA524 working with a PC was employed to monitor the signal collected from a red extended Hamamatsu R928 photomultiplier.

A Shimadzu UV-1601 spectrophotometer was used to measure the absorption spectra. The luminescence was recorded in a 4800C SLM spectrofluorometer.

A careful pH control was achieved with a pH/ISE EA 940 Orion Research pH-meter. Temperature of the solution could be within ±0.2°C over the 3 to 40°C range but it was difficult to set a specific value in advance.

2.3. Procedure

The concentrations of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ were in the range $1.0–2.5\times10^{-4}$ M. The concentration of the phenolic compounds ranged from 1.0×10^{-5} to 1.0×10^{-2} M according to their solubilities in the different media and their efficiency as quenchers. The pH was kept constant (within ±0.02 units) at selected values by using a 2.0×10^{-2} M buffer solution prepared either from AcH/Ac$^-$ or from a Britton–Robinson buffer. The ionic strength was kept at 1.0 M with NaCl. In the presence of phenols, no spectral changes of any sort were observed. The Stern–Volmer plots raised from I_0/I measurements were linear and superimposed quite well with τ_0/τ plots indicating the absence of static quenching over the range of quencher concentrations used, in agreement with the results previously reported [18].

Luminescence lifetime measurements at a particular temperature and pH were carried out with deaerated solutions purged with purified N_2 for at least 30 min immediately prior to measurements; these experiments were performed in the absence and presence of phenolic derivatives. In all cases, fresh solutions were used for each run. Every emission decay recorded corresponded to an average of 16 single decay curves and obeyed a single exponential function for the whole range of temperatures explored.

The quenching rate constants (k_q) were obtained from the slope of the Stern–Volmer plots derived from time resolved experiments. At least five different quencher concentrations were used for each rate constant determination.

3. Results and discussion

Solutions of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ are stable at pH < 6. Nevertheless, the ϕ_{rx} (quantum yield of photoaquation of the chromium complex) rises from a negligible value in acid solutions and reaches a plateau between pH 9 and 11 with a yield of ca. 0.1 for the $Cr(bpy)_3^{3+}$ [19] and between pH 9 and 12 with a yield of ca. 0.003 for the $Cr(phen)_3^{3+}$ [20], the latter showing a further increase beyond pH 12; then pH 5 and 10 were chosen to carry out the experiments. At pH 10 not all the phenols are completely dissociated so the observed Stern–Volmer constant ($K_{SV}{}^{obs}$) must be corrected to get the one corresponding to the anionic species $K_{SV}{}^{B}$. From this constant, the true k_q of the phenolic ion ($k_q{}^{B}$) can be obtained. According to the acid–base equilibrium the $K_{SV}{}^{obs}$ can be written as in Eq. (1) [21]

$$K_{SV}^{obs}=K_{SV}^{A}\alpha_0+K_{SV}^{B}\alpha_1 \tag{1}$$

where the superscripts A and B stand for acid and basic media and α_0 and α_1 are the acid association and dissociation coefficients. In as much as $K_{SV}{}^{B}=k_q{}^{B}\tau_0$, a simple rearrangement renders $k_q{}^{B}$

$$k_q^{B}=\frac{K_{SV}^{obs}-K_{SV}^{A}\alpha_0}{\alpha_1\tau_0} \tag{2}$$

Eq. (2) holds if τ_0 does not depend on pH. Since τ_0 shows dependence with pH at low temperatures, while the value in acidic and basic solutions are the same at room temperature, 1 M NaCl solution was added because the presence of Cl$^-$ ion contributes to minimize the pH dependence of τ_0 [22]. Its presence also keeps the ionic strength constant. On the other hand, the set of experiments carried out for a particular quenching could not be reproduced at the same temperature for both pHs. Nevertheless, the good linear Eyring plots obtained at pH 5 allowed an interpolation to be made in order to calculate the acidic rate constant for the temperature at with the basic was measured. In Table 1 can be seen the experimentally obtained $K_{SV}{}^{A}$ and $K_{SV}{}^{obs}$ for phenol and 2,6-dimethylphenol, the thermodynamic parameters for the acidic form as well as the intermediate values that lead to the final quenching rate constant of the anionic form, $k_q{}^{B}$, after inter-

Table 1
Kinetics and thermodynamic parameters for the quenching of $^*Cr(phen)_3^{3+}$ by the anionic form of phenol and 2,6-dimethylphenol after correction for the acid–base equilibrium at pH 10

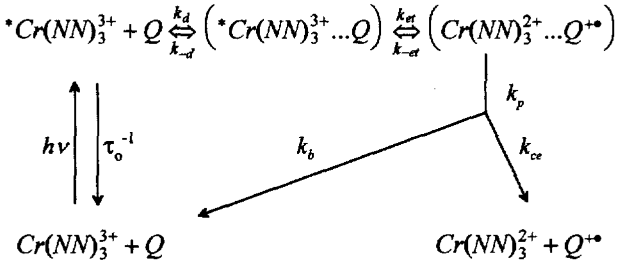
	Phenol	2,6-Dimethylphenol
$K_{SV}{}^{A}(T_1)$ [a]	4.94×10^{3}	8.29×10^{5}
$K_{SV}{}^{obs}(pH=10, T_2)$ [a]	1.39×10^{5}	8.92×10^{4}
$\Delta H^{\#}$	1.81	1.04
$\Delta S^{\#}$	−17.1	−13.9
τ_0	9.67×10^{-5}	9.8×10^{-5}
$k_q{}^{A}$	5.11×10^{7}	8.46×10^{8}
$k_q{}^{A'}(T_1)$ [b]	5.14×10^{7}	9.5×10^{8}
$k_q{}^{A'}(T_2)$ [b]	5.11×10^{7}	9.51×10^{8}
$k_q{}^{A}(T_2)$	5.08×10^{9}	8.48×10^{8}
$K_{SV}{}^{A}(T_2)$	4.9×10^{3}	8.27×10^{4}
$K_{SV}{}^{B}$	2.64×10^{5}	1.13×10^{5}
$k_q{}^{B}$	2.73×10^{9}	1.16×10^{9}
pK_a	10	10.63
$\alpha_o(pH=10)$	0.48	0.79

[a] $T_1=22.2$ and 22.9°C, and $T_2=24.6$ and 24.5°C for phenol and 2,6-dimethylphenol respectively are the temperatures at which acid (T_1) and basic (T_2) experiments were carried out.

[b] $k_q{}'$ is the quenching rate constant corrected by diffusional effect (Appendix A).

polation for different temperature and the correction for the acid–base equilibrium. Table 2 includes the calculated diffusional rate constant, k_d, as well as the viscosity (η) and static dielectric (D_s) constants of the solvent at different temperatures (see Appendix A for calculation). The experimental $k_q'^A$ and $k_q'^B$ for the other phenols are given in the supporting information.

The reductive quenching of $^*Cr(phen)_3^{3+}$ complex by phenolic derivatives has been previously established from the linear variation in $RT \ln k_q$ with the redox potentials of the phenolate ions in basic medium in MeOH:H$_2$O 50% (v/v) [18] and it was discussed in terms of the Rehm–Weller mechanism [25,26] as shown in the following scheme:



where k_d is the diffusional forward rate constant that forms the encounter complex between the excited state and the phenol (Q) prior to the electron transfer and k_{-d} its reverse; k_{et} and k_{-et} are the rate constants for electron transfer quenching of the excited state within the encounter complex and the back electron transfer that regenerates the excited state; k_p is the rate constant for the process that leads to net quenching and it is the sum of two competitive processes that include the back electron transfer to give ground state $Cr(NN)_3^{3+}$ (k_b), and the cage escape to give the redox products in solution (k_{ce}).

3.1. Activation parameters

According to Scheme 1 and applying the steady-state approximation, the activation rate constant k_q', $[(1/k_q') = (1/k_q) - (1/k_d)]$, can be written as:

$$k_q' = \frac{k_d}{k_{-d}} k_{et} \left(\frac{k_p}{k_p + k_{-et}} \right) = \frac{k_d}{k_{-d}} k_{et} F \qquad (3)$$

where F is the fraction of net quenching which is close to 1 (see the discussion below) [18].

From the transition state theory, the general expression for the quenching rate constant can be written as:

$$k = \langle \kappa \rangle \frac{k_B T}{h} \exp(-\Delta G^{\#}/RT) \qquad (4)$$

where k_B is the Boltzman constant, h is the Planck constant, κ is the electronic coefficient and $\Delta G^{\#}$ is the free activation energy of the process. The activation parameters (enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$)) were determined from Eyring plots assuming $\kappa = 1$ (adiabatic process) [27].

In Figs. 1 and 2 are shown typical Eyring plots for the reductive quenching of the excited state of the complexes by phenol and 2,6-dimethylphenol and in Tables 3 and 4 are collected the experimental kinetic and thermodynamic parameters obtained for $^*Cr(bpy)_3^{3+}$ and $^*Cr(phen)_3^{3+}$, respectively.

According to the Marcus theory [28–31]:

$$k = Z \exp[-(w_r + \Delta G_\lambda^*)/RT] \qquad (5)$$

and the transition state expression in Eq. (4), the activation free energy and entropy read [32]:

Table 2
Properties of a 1 M NaCl solution at different temperatures and its effect on the diffusional rate constants

Temperature (K)	η [a] (cP×10^3)	D_s [b]	w_p [c] (kcal/mol)	w_r [d] (kcal/mol)	$k_d \times 10^{-9}$ [c] (M^{-1} s^{-1})	$k_d \times 10^{-9}$ [d] (M^{-1} s^{-1})
277	15.2	81.77	0.277	−0.416	4.43	4.92
278	15.2	81.44	0.279	−0.418	4.57	5.08
282	13.5	80.14	0.283	−0.425	5.15	5.72
283	13.1	79.81	0.285	−0.427	5.29	5.88
288	11.4	78.18	0.291	−0.436	6.07	6.74
2911	10.5	77.21	0.294	−0.441	6.55	7.27
295	9.55	75.91	0.299	−0.449	7.22	8.01
300	8.51	74.27	0.305	−0.458	8.09	8.97
301	8.33	73.94	0.307	−0.459	8.26	9.17
304	7.81	72.96	0.309	−0.465	8.79	9.77
305	7.65	72.64	0.311	−0.467	8.99	9.97
308	7.19	71.66	0.315	−0.473	9.54	10.6
311	6.78	70.68	0.319	−0.479	10.1	11.2
312	6.65	70.36	0.321	−0.481	10.3	11.4

[a] Ref. [23].
[b] Ref. [24].
[c] Acid medium.
[d] Basic medium.

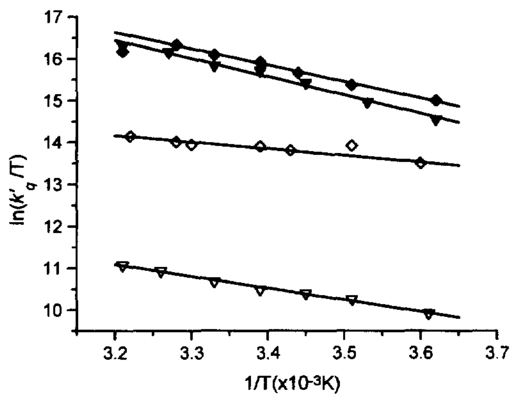


Fig. 1. Temperature dependence of the quenching rate constants for the reductive quenching of $^*Cr(bpy)_3^{3+}$ by phenols in aqueous solution; (H- (▽) acid medium and (▼) basic medium; 2,6-diMe- (◇) acid medium and (◆) basic medium).

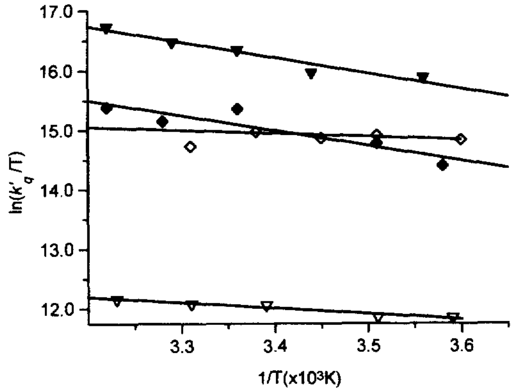


Fig. 2. Temperature dependence of the quenching rate constants for the reductive quenching of $^*Cr(phen)_3^{3+}$ by phenols in aqueous solution; (H- (▽) acid medium and (▼) basic medium; 2,6-diMe- (◇) acid medium and (◆) basic medium).

$$\Delta G^{\#} = -RT\ln\left(\frac{hZ}{k_B T}\right) + \Delta G_\lambda^* + w_r \qquad (6)$$

$$= \Delta G^{\#}_{trans} + \Delta G_\lambda^* + w_r$$

$$\Delta S^{\#} = \Delta S^{\#}_{trans} + \Delta S^{\#}_\lambda + \Delta S^{\#}_{w_r} \qquad (7)$$

where Z and w_r are the collision frequency and the work term, respectively. The term $\Delta G_{trans}^{\#} = -RT\ \ln[(hZ)/(k_BT)]$ takes into account the loss of the rotational and vibrational degrees of freedom upon formation of the activated complex, and ΔG_λ^* is associated to the change in the free energy, ΔG^0, given for the overall reaction by Eq. (8) [28–31]:

$$\Delta G_\lambda^* = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \qquad (8)$$

where λ is the sum of the inner and outer sphere reorganization energies $\lambda = \lambda_i + \lambda_o$. The ΔG^0 values shown in Tables 3 and 4 were calculated from the reduction potentials of the species involved given in Table 5 (see Appendix B).

The reorganization energy estimated by the best fitting of the data using Eqs. (6) and (8) are shown in Figs. 3 and 4 for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, respectively. The λ values obtained were 59 ± 1 kcal/mol$^+$ and of 55 ± 1 kcal/mol using Z values of 5.11×10^{11} and 5.05×10^{11} M^{-1} s^{-1}, respectively [36].

From Tables 3 and 4 can be observed that both values $\Delta H^{\#}$ and $\Delta S^{\#}$, rise as the pH increases. As in the case of $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ depend not only upon a work term, ($\Delta H^{\#}_{w_r}$ and $\Delta S^{\#}_{w_r}$), but on a term that is a function of λ and ΔG^0, ($\Delta H_\lambda^{\#}$ and $\Delta S_\lambda^{\#}$). It should be noted that, for both complexes, neither $\Delta H^{\#}$ nor $\Delta S^{\#}$ show any observable trend with ΔG^0, although the theory predicts an increase of $\Delta H^{\#}$ and a decrease of $\Delta S^{\#}$ as ΔG^0 increase [36,37].

From the experimental data can be seen that larger values of $\Delta H^{\#}$ are compensated with larger values of $\Delta S^{\#}$ and vice versa. This fact results in values of $\Delta G^{\#}$ that are in agreement with the trend shown by other systems, which has been attributed to specific effects of the solvent [27,38]. We failed to observe any dependence of $\Delta S^{\#}$ on ΔG^0 over the range of ΔG^0 but a significant change in $\Delta S^{\#}$ was noticed in going from acid to basic medium, that is, the term $\Delta S^{\#}_{w_r}$ seems to be the most important contribution to the total $\Delta S^{\#}$. This could be explained in terms of the increase of the phenol electrostatic charge in basic medium.

Table 3
Rate constant and activation parameters for the reductive quenching of $^*Cr(bpy)_3^{3+}$ by the phenols in aqueous solution at 298 K

$Cr(bpy)_3^{3+}$

Phenol	pH = 5					pH = basic				
	$k_q' \times 10^{-7}$ (M^{-1} s^{-1})	ΔG^0 (kcal/mol)	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (eu)	$\Delta G^{\#}$ (kcal/mol)	$k_q' \times 10^{-9}$ (M^{-1} s^{-1})	ΔG^0 (kcal/mol)	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (eu)	$\Delta G^{\#}$ (kcal/mol)
(1) H-	1.27 ± 0.06	−23.4	5.6 ± 0.2	−7.3 ± 0.2	7.76 ± 0.25	2.06 ± 0.12	−30.1	8.6 ± 0.4	12.9 ± 0.3	4.7 ± 0.4
(3) 4-Cl-	2.8 ± 0.2	−22.9	1.6 ± 0.1	−18.9 ± 0.3	7.3 ± 0.1	3.6 ± 0.1	−28.9	7.9 ± 0.3	11.9 ± 0.2	4.4 ± 0.4
(4) 4-I-	14.5 ± 0.9	−26.01	3.1 ± 0.2	−10.9 ± 0.2	6.3 ± 0.2	3.6 ± 0.2	−31.9	7.2 ± 0.3	9.3 ± 0.2	4.5 ± 0.3
(5) 4-Br-	2.79 ± 0.18		6.4 ± 0.4	−2.9 ± 0.1	7.3 ± 0.4	2.8 ± 0.1		7.5 ± 0.4	9.8 ± 0.2	4.6 ± 0.4
(6) 2,4-diCl-	2.3 ± 0.1	−20.9	10.7 ± 0.7	11.1 ± 0.4	7.4 ± 0.7	7.2 ± 0.3	−24.8	5.6 ± 0.2	5.3 ± 0.1	4.1 ± 0.2
(7) 2,6-diMe-	33.2 ± 2.9	−27.1	3.1 ± 0.3	−8.9 ± 0.3	5.8 ± 0.3	2.74 ± 0.09	−33.8	7.8 ± 0.2	10.6 ± 0.1	4.6 ± 0.3
(8) 4-Br-2,6-diMe-	68 ± 9	−28.9	1.8 ± 0.2	−12.1 ± 0.3	5.4 ± 0.3	1.8 ± 0.2	−35.1	3.6 ± 0.3	−4.2 ± 0.1	4.8 ± 0.3
(9) 4-Cl-3-Me-	10.3 ± 0.6		2.3 ± 0.1	−13.9 ± 0.2	6.5 ± 0.1	2.3 ± 0.1		8.3 ± 0.5	12.1 ± 0.3	4.7 ± 0.5

Table 4
Rate constant and activation parameters for the reductive quenching of $^*Cr(phen)_3^{3+}$ by the phenols in aqueous solution at 298 K

$Cr(phen)_3^{3+}$

Phenol	pH = 5					pH = basic				
	$k_q' \times 10^{-7}$ ($M^{-1} s^{-1}$)	ΔG^0 (kcal/mol)	$\Delta H^\#$ (kcal/mol)	$\Delta S^\#$ (eu)	$\Delta G^\#$ (kcal/mol)	$k_q' \times 10^9$ ($M^{-1} s^{-1}$)	ΔG^0 (kcal/mol)	$\Delta H^\#$ (kcal/mol)	$\Delta S^\#$ (eu)	$\Delta G^\#$ (kcal/mol)
(1) H-	5.1 ± 0.7	−22.7	1.8 ± 0.2	−17.1 ± 0.5	6.9 ± 0.4	3.6 ± 0.6	−29.5	5.6 ± 0.8	4.1 ± 0.1	4.3 ± 0.8
(2) 4-F-	8.9 ± 4.5		0.8 ± 0.3	−19 ± 1	6.6 ± 0.7	3.4 ± 0.5		14.8 ± 2.3	34.9 ± 3.0	4.5 ± 3.0
(3) 4-Cl-	5.8 ± 0.5	−22.3	2.9 ± 0.2	−13.2 ± 0.3	6.8 ± 0.4	11.3 ± 2	28.3	12.7 ± 1.5	30.4 ± 1.7	3.6 ± 1.9
(4) 4-I-	73 ± 11	−25.3	4.1 ± 0.6	−4.1 ± 0.2	5.4 ± 0.6	5.1 ± 0.3	−31.2	5.6 ± 0.3	4.9 ± 0.1	4.2 ± 0.3
(5) 4-Br-	40 ± 1		19.9 ± 0.8	47 ± 1	5.8 ± 1.1	4.9 ± 0.6		10.4 ± 1.1	20.7 ± 0.9	4.2 ± 1.3
(6) 2,4-diCl-	10.8 ± 2.3	−20.3	14.1 ± 2.8	25.2 ± 3.3	6.5 ± 3.3	9.3 ± 0.8	−24.3	7.4 ± 0.8	12.1 ± 0.8	3.8 ± 0.9
(7) 2,6-diMe-	94.8 ± 51	−26.5	1.1 ± 0.5	−13.9 ± 0.8	5.2 ± 0.8	1.0 ± 0.5	−34	4.8 ± 1.0	−1.01 ± 0.09	5.2 ± 1.1
(8) 4-Br-2,6-diMe-	202 ± 18	−28.3	3.1 ± 0.2	8.6 ± 0.1	5.7 ± 0.2	3.7 ± 0.1	−34.4	8.4 ± 0.3	10.3 ± 0.1	5.3 ± 0.4

Table 5

(a) Half wave potentials for phenol and its derivatives at both pHs

Phenol	pH = 5	pH = basic
	$E_{1/2}$[a] (V vs. EHN)	$E_{1/2}$ (V vs. EHN)
H-	0.43	0.14
4-Cl-	0.45	0.19
2,4-DiCl-	0.53	0.37
4-I-	0.31	0.06
2,6-diMe-	0.23	−0.03
4-Br-2,6-diMe-[b]	0.18	−0.07

(b) Standard redox potentials of the complexes

Complex	Redox potentials (V vs. EHN)[c] 3+*/2+
$Cr(phen)_3^{3+}$	1.42
$Cr(bpy)_3^{3+}$	1.44

[a] Data for pH = 5 were taken from Refs. [33,34].
[b] E^0 estimated from Marcus theory with polypiridyl complexes.
[c] Data taken from Ref. [35].

3.2. Cl^- ion effect

The reactant ions are ion-paired with the dominant counter ions under the conditions of the experiments. Using the Fouss's expression [5] the equilibria constants for the ionic-pair formation (K_{ip}) between the complex and Cl^- is ~6 M^{-1} at both pHs whereas that corresponding to phenolate ions and Na^+ is 0.5 M^{-1} in 1 M of NaCl.

No changes were observed in k_q when the concentration of Cl^- was varied up to 1 M of NaCl in the quenching reaction of the $^*Cr(phen)_3^{3+}$ by 2,6-dimethylphenol at both pHs. The overall quenching rate constant of the reaction can be made up by two contributions according to the Olson–Simmonson treatment as shown in Eq. (9) [39]:

$$k_q = \frac{k_{nip}}{1+K_{ip}[X^-]} + \frac{k_{ip}K_{ip}[X^-]}{1+K_{ip}[X^-]} \qquad (9)$$

where the first term takes account of the contribution to the quenching of the species that are not ion-paired (k_{nip}) and the second term takes account for the contribution to the quenching of the species that are ion-paired (k_{ip}). Taking for

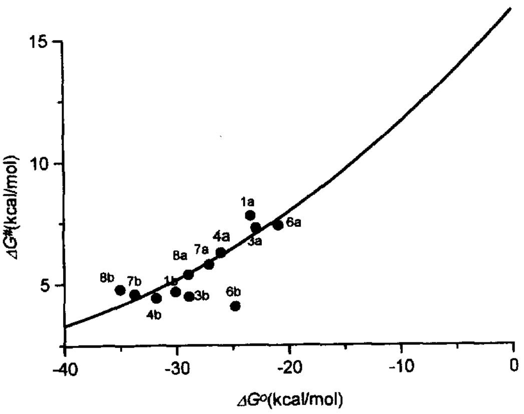


Fig. 3. Free energy relationship of the activation free energy of the reductive quenching of $^*Cr(bpy)_3^{3+}$ by phenols in aqueous solution. The numbering corresponds to the phenols listed in Table 3; (a) and (b) refer to acid and basic media, respectively.

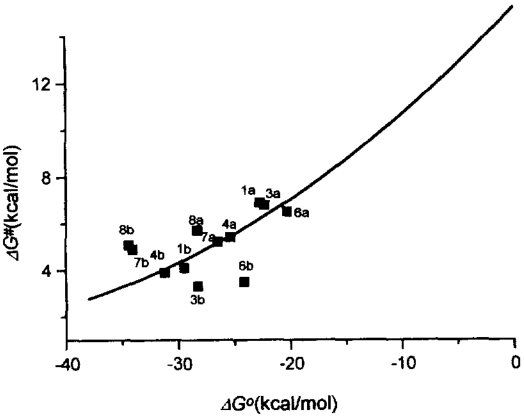


Fig. 4. Free energy relationship of the activation free energy of the reductive quenching of $^*Cr(phen)_3^{3+}$ by phenols in aqueous solution. The numbering corresponds to the phenols listed in Table 4; (a) and (b) refer to acid and basic media, respectively.

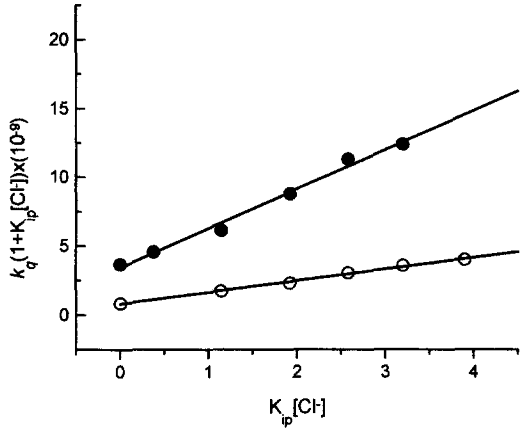


Fig. 5. Effect of the ion pairing on the k_q for the reductive quenching of $^*Cr(phen)_3^{3+}$ by 2,6-diMe- at 22.0°C with NaCl; (●) pH = 10.0 and (○) pH = 5.0.

K_{ip} the above values, a plot of $k_q(1+K_{ip}[X^-])$ vs. $K_{ip}[X^-]$ allows to obtain k_{nip} and k_{ip} from the ordinate and the slope, respectively (Fig. 5). In the present case the values for k_{nip} and k_{ip} are 8×10^8 M^{-1} s^{-1} and 8×10^8 M^{-1} s^{-1} at pH 5 and 3×10^9 M^{-1} s^{-1} and 3×10^9 M^{-1} s^{-1} at pH 10. In view of these results, it can be concluded that neither the ionic pair formation nor the Cl^- concentration affect significantly the quenching mechanism.

3.3. Mechanism of reductive quenching

The reductive quenching of $Cr(NN)_3^{3+}$ by amine sulfides and phenols has been studied by several authors [40,41,18,13]. From an analysis of the kinetic reactions involved, Bock et al. [42] have demonstrated that the reductive quenching of $Ru(NN)_3^{2+}$ by aromatic amines can be ultimately expressed by Eq. (10)

$$RT\ln k_q' = RT\ln k_q'(0) - \frac{\Delta G^0}{2}\left(1+\frac{\Delta G^0}{2\lambda}\right) \tag{10}$$

where the assumption that $k_p \gg k_{-et}$, that is $F=1$, has been already taken into account and $k_q'(0)$ is a characteristic constant for a given family of structurally similar quenchers.

When $\Delta G^0 \ll 2\lambda$, the theory predicts a straight line with a slope of -0.5 when representing RT ln k_q' vs. ΔG^0. This condition does not hold in our system; nevertheless, we were able to get good non-linear fittings to Eq. (10) for λ values of 59 and 55 kcal/mol for the $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, respectively, as can be seen in Fig. 6, still with the assumption that the quenching process dominates. Also the dependence of k_q' with temperature provides useful information. An increase in k_q' with increasing temperature involves a positive $\Delta H^{\#}$ and as long as the trend is not reverted in the whole range of temperatures studied, one can assume that the back electron transfer to the excited state (k_{-et}) is not an important step in the time regime studied [43]. The present results do show such a temperature dependence (see Figs. 1 and 2 and Tables 3 and 4). In view of these observations, we conclude that the reductive quenching of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ by the phenols proceeds via the mechanism shown in the scheme and that back electron transfer to regenerate the excited state (k_{-et}) is negligible in the microsecond scale, and therefore the activation parameters determined from k_q' represent those for the electron transfer process.

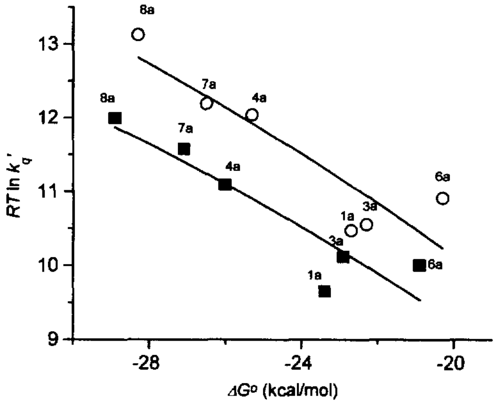


Fig. 6. RT ln k_q' vs. ΔG^0 for the reductive quenching of $^*Cr(bpy)_3^{3+}$ (■) and $^*Cr(phen)_3^{3+}$ (○) by phenols in aqueous solution. The numbering corresponds to the phenols listed in Table 4; (a) refers to acid medium.

A brief comment about the steps following the quenching process follows. Pizzocaro et al. [44] have reported that the escape cage yield η_{ce}, $[\eta_{ce}=(k_{ce})/(k_{ce}+k_b)]$ for $Cr(bpy)_3^{3+}$ with phenol in absence of O_2 would be too small ($\ll 1$). That is, k_b would be large and/or k_{ce} would be abnormally small for the chromium systems. We tried to look for the characteristic transient absorption band of $Cr(phen)_3^{2+}$ at 690 nm in order to have an estimation of k_{ce}. The results proved to be negative, indicating that k_{ce} is in fact negligible in accordance with the observation of Ref. [44] for the $Cr(bpy)_3^{3+}$ system.

3.4. Outer-sphere reorganization energy

The outer-sphere reorganization energy (λ_o) can be estimated using the hard spheres model coupled to a dielectric continuum model for the solvent:

$$\lambda_0 = (\Delta e)^2\left[\frac{1}{2r_R}+\frac{1}{2r_Q}-\frac{1}{d}\right]\left[\frac{1}{D_{op}}-\frac{1}{D_s}\right] \tag{11}$$

where r_R is the radius of the complex, r_Q is the average radius of the quencher and $d=r_R+r_Q$, Δe is the number of electrons transferred, D_{op} and D_s are the optical and static dielectric constants of the medium, respectively. Using $r_R=7.1$ Å and $r_Q=3.8$ Å [42], Eq. (11) yields a value of 20 kcal/mol for λ_o of both complexes. In contrast, higher values of λ^{exp} have been obtained in the present work. Similar behaviors have been found in other systems. In the quenching of the excited state of $Cr(NN)_3^{3+}$ by sulfides in acetonitrile, Gnanaraj et al. [41] found $\Delta\lambda$, $(\lambda^{exp}-\lambda_o)$, of 5 and 8 kcal/mol for $Cr(bpy)_3^{3+}$ and attributed this difference to λ_i. In the quenching of $(^3CT)Ru(bpy)_3^{2+}$ by primary (PA), secondary (SA) and tertiary (TA) aromatic amines in acetonitrile, Kitamura et al. [43] found that $\Delta\lambda$ were equal for PA and SA, the value being around 10 kcal/mol and 6 kcal/mol for TA. They assumed that this difference was due to the more relevant solvent reorganization around the amine group than either around the aromatic group or the whole molecule. In the present study, the difference is 39 and 35 kcal/mol for $Cr(bpy)_3^{3+}$ and for $Cr(phen)_3^{3+}$, respectively, but at variance with Gnanaraj data, we found a greater value of $\Delta\lambda$ for $Cr(bpy)_3^{3+}$. The difference in $\Delta\lambda$ is too large to be attributed only to inner sphere effects as done in Ref. [41] indicating that other factors should have to be taken into account.

Two possible interpretations to account for this difference are: (1) The effective ionic radii should be shorter than the calculated ones using a space-filling model and this could be due to the interligand pockets, which could allow a closer approximation of the quencher [45]. Even the use of a radius value 30% smaller than that calculated by the space-filling model or the use of different radii for each complex and each phenol, provide λ_o values which do not support the difference found in $\Delta\lambda$. (2) The continuum dielectric model used by Marcus does not take into account other interactions which may come from the solute–solvent and solvent–solvent interactions. For example, the effect of the hydrogen bond is equivalent to an increase of the polarity of the solvent which would be equivalent to an increase of D_s. As the hydrogen bond also increases the polarizability of the solvent, this is equivalent to an increase of the refraction index (n; $D_{op}=n^2$). In such a case, it is necessary to introduce an additional term in the reorganization energy that accounts for the breaking of hydrogen bonds between the molecules of the electroactive solvents and solutes along with the energy required to rearrange the solvent in the vicinity of the electroactive species. We can thus consider the reorganization energy $\lambda=\lambda_i+\lambda_o'$ with $\lambda_o'=\lambda_o+\lambda_H$, where λ_H is the term that accounts for the contribution of the hydrogen bonding [46].

On account of the preceding interpretation, the excess of reorganization energy obtained experimentally ($\Delta\lambda$, 39 and 35 kcal/mol) could be due, in part, to the fact that the solvent is highly polar and structurally linked by hydrogen bonds. This overall effect decreases as the solvent looses its hydrogen bond linked structure and is not present in aprotic solvents [47]. The study of the solvent effect is currently underway. When changing the solvent from water to mixtures of water/organic there is evidence that supports the above conclusion. In fact, the quenching rate constant of $^*Cr(phen)_3^{3+}$ with 2,6-dimethylphenol is dependent on the molar fraction of the organic (X_{org}) solvent. It also depends on the nature of the organic solvent. Thus, k_q increases reaching a maximum at $X_{org}=0.2$, 0.1, and 0.05 for methanol, ethanol, and propanol, respectively. This can be interpreted in terms of the breakage of the H_2O structure, that is, the longer the hydrocarbon chain the smaller the molar fraction needed to reach an equivalent effect [Bierbrauer, unpublished results].

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Appendix A

A.1. Diffusional constant

The value of the diffusional constant at different temperatures can be estimated from the equation

$$k_d=\frac{2RT}{3000\eta}\left[2+\frac{r_Q}{r_R}+\frac{r_R}{r_Q}\right]\frac{1}{a\int_a^{\infty} r^{-2}\exp[w(r,\mu)/RT]\mathrm{d}r}$$

where r_Q and r_R are the radii of the quencher and the complex with $r_Q=3.8$ A and $r_R=7.1$, respectively. $a=r_Q+r_R$, r is the distance separating the two reactants, η is the viscosity of the medium and $w(r,\mu)$ is the work term, where μ is the ionic strength. The η values were obtained from the data in Handbook of Chemistry and Physics [23].

A.2. Coulombic work

The term of the Coulombic work was calculated from the following equation which includes corrections due to effects of the ionic strength of the Debye–Hückel:

$$w(r,\mu)=$$

$$\frac{Z_A Z_B e^2}{2D_S r}\left(\frac{\exp(\kappa\sigma_Q\sqrt{\mu})}{1+\kappa\sigma_Q\sqrt{\mu}}+\frac{\exp(\kappa\sigma_R\sqrt{\mu})}{1+\kappa\sigma_R\sqrt{\mu}}\right)\exp(-\kappa r\sqrt{\mu})$$

where κ^{-1} is the Debye radii

$$\kappa=\left(\frac{8\pi N^2e^2}{1000D_S RT}\right)^{1/2}$$

where Z_R and Z_Q are the charges of the reagents, r is the meeting distance, N_0 is the Avogadro number, μ is the ionic strength, e is the unit electron charge and D_S is the static dielectric constant of the solvent and σ_R or σ_Q is the radius of R or Q plus that of the dominant counter ion in the ionic atmosphere.

The D_S data of a 1 M NaCl solution were interpolated at different temperatures from data [24] fitted from an equation of the type of:

$$\frac{\ln D_S}{\ln T}=-0.368\ln T+2.856$$

Appendix B

The ΔG^0 values were calculated from the reduction potentials of the species involved according to:

$$\Delta G^0[nF(E_{(D^+/D)}-E_{(A^*/A^-)})+w_r-w_p]$$

where $E_{(D^+/D)}$ and $E_{(A^*/A)}$ are reduction potentials of phenols and the excited state of the complexes, F is the Faraday constant and w_r and w_p are the work terms of the reactives and products, respectively.

They were used as half wave potentials in order to obtain ΔG^0 because the standard reduction potentials are not available from bibliography due to the irreversibility of the redox couple. The half wave potentials were taken from the bibliography available [33,34].

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