

Luminescence quenching of $\text{Cr}(\text{phen})_3^{3+}$ by phenol derivatives

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(Received March 4, 1991; revised July 11, 1991)

Abstract

The luminescence of tris(1,10-phenanthroline) chromium(III) perchlorate quenched by a series of phenols was studied at 22 ± 2 °C in both basic (10^{-5} M NaOH) and acidic (10^{-3} M HClO₄) solutions using 1:1 vol./vol. methanol:water as solvent. Bimolecular rate constants (k_q) were obtained separately from static luminescence intensity and dynamic lifetime measurements and they were coincident. The values were below the diffusional limit in all cases. The results are discussed in terms of the Rehm–Weller–Marcus excited state electron transfer theory. The $RT \ln k'_q$ correlated satisfactorily with the reduction potential of the phenols. The effect of the substituents for the di- or tri-substituted phenols on the k_q value is also discussed.

Introduction

Considerable progress has been made in the photochemistry of transition-metal complexes during the past decade as a result of many works published in this area [1]. Ru(II) and Cr(III) complexes have been extensively used for experiments in photochemical energy storage because their lowest energy excited states are long-lived and capable of a rapid electron-transfer reaction [2–6].

The lowest excited state of chromium(III) complexes consists of two closely spaced emitting states in thermal equilibrium. They apparently have doublet character, and it is customary to apply the ²E assignment to these states [7]. As should be expected from its long lifetime and high reduction potential, the excited state of the chromium(III) complex should easily be reduced by electron donors [5, 6, 8–10]. Plots of $\log k_q$ versus reduction potential of electron donors such as aliphatic and aromatic amines and methoxybenzenes show the expected behavior for electron transfer processes [6]. Transient cations of these quenchers have also been observed in flash photolysis experiments [6].

On the other hand, a number of previous reports have dealt with kinetic and mechanistic aspects of photooxidation of phenol and substituted phenols

sensitized by carbonyl triplets [11] or by the excited state of tris(2,2'-bipyridine) ruthenium(II) (³CT)Ru(bipy)₃²⁺ [12]. We have investigated the photochemistry of polychlorophenols sensitized by Ru(bipy)₃²⁺ and according to the results obtained from emission quenching, laser flash photolysis and continuous photolysis experiments, an electron transfer mechanism is also proposed for the photochemical reaction [13].

We report here a study on the luminescence of $\text{Cr}(\text{phen})_3^{3+}$ (phen = 1,10-phenanthroline) quenched by several substituted phenols that show different redox properties. The results are discussed in terms of the Rehm–Weller's model [14] for charge transfer interaction in the excited state of molecules in a condensed phase.

Experimental

Apparatus

A N₂ laser was used in the majority of the time-resolved experiments. The laser beam was focused on the sample cell (fused silica) of a TRW 31A filter fluorometer equipped with a red extended RCA 4840 photomultiplier. The signal was recorded in a Hewlett Packard HP 54200A digital oscilloscope followed by computer analysis.

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Some front-face excitation time-resolved experiments were carried out using a 130 nf/20 KV capacitor discharged on a Xenon flash lamp. The emitted light was analysed at an angle of 30° from the incident beam and after passing through a 650 nm cut-off filter, it was collected on a Hamamatsu R928 photomultiplier and recorded on a model 206 NICOLET transient recorder. The signal was later transferred to a personal computer for analysis. All data acquisition software was developed in our laboratory.

A Shimadzu UV-140-02 spectrophotometer was used to measure the absorption spectra and a FARRAN Mark I spectrofluorometer to record the luminescence.

Materials

$[\text{Cr}(\text{phen})_3]^{3+}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ was used as previously reported [15] and synthesized according to literature procedures with some minor modifications [16–18]. The solid was purified by at least three recrystallizations from the aqueous solution and further with methanol to obtain yellow crystals.

The phenols, 4-chlorophenol (4-Cl), 3-chlorophenol (3-Cl), 2-chlorophenol (2-Cl), 4-fluorophenol (4-F), 4-bromophenol (4-Br), 4-iodophenol (4-I), 4-aminophenol (4-NH₂), 4-phenylphenol (4-Ph), 2,6-dimethyl-4-bromophenol (2,6-DMe-4Br), 2,6-dichlorophenol (2,6-DCl), 2,5-dichlorophenol (2,5-DCl), 2,4,6-trichlorophenol (2,4,6-TCl), were purchased from Aldrich Co. and purified by vacuum sublimation.

Methanol HPLC grade from Sintorgan was used without purification.

The deionized water used to prepare the solutions was obtained with a Milli Q System Millipore Co.

Procedure

All the samples prepared were aerated solutions between 2 and 5×10^{-4} M in $\text{Cr}(\text{phen})_3^{3+}$. The solvent was 1:1 methanol:H₂O. Basic solutions were 10^{-5} M in NaOH and acidic solutions were 10^{-3} M in HClO₄. In all cases the ionic strength was kept constant by the addition of NaClO₄ so that its concentration reached a value of 10^{-2} M.

Emission quenching

The emission of the lowest lying excited state of tris(1,10-phenanthroline) chromium(III), $(^2\text{E})\text{Cr}(\text{phen})_3^{3+}$, was recorded with and without added quencher. The excitation wavelength was 350 nm and the emission spectra were taken in the 650–750 nm range. All experiments were carried out at a temperature of 22 ± 2 °C.

Results and discussion

The absorption spectra of the quencher + chromium(III) complex solutions were, for every run, equal to the sum of the two component spectra with no deviation that would suggest ground state interactions.

The emission spectrum of the chromium(III) complex was not qualitatively affected by the concentration of the quenchers. The quenching of the luminescence emission was measured with at least five different quencher concentrations. In time resolved experiments, traces were obtained as an average of 16 decay curves. A typical single shot decay curve for the excited state without the addition of quencher and the emission spectra of $(^2\text{E})\text{Cr}(\text{phen})_3^{3+}$ in the presence of quencher are given in Fig. 1. For each one, linear Stern–Volmer plots were obtained from steady-state luminescence intensity (I_0/I) or luminescence lifetime measurements (τ_0/τ). Pretty close values of the Stern–Volmer constants (K_{SV}) were obtained from both measurements.

The bimolecular quenching rate constants (k_q) were calculated from the K_{SV} constants (see Fig. 2) and the lifetime of the excited state in the absence of the quencher, τ_0 (eqn. (1)). The values obtained are shown in Table 1.

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{\text{SV}}[Q] = 1 + k_q\tau_0[Q] \quad (1)$$

The bimolecular quenching of an excited state molecule in a fluid solution (eqn. (2)) may take place through various mechanisms depending on the properties of the excited state and the quencher.



The energy of the triplet state of the quenchers used in this work is not known. The available data for the phenol is 81.7 Kcal/mol [19] and, from the substitution on the rings, one would expect that the energy of triplet states be lower in the substituted phenols and phenolates ions. Whatever the case, the magnitude of the lowering of the triplet state energy is expected to be less than 30 Kcal/mol [12]. Then, the electronic energy transfer is energetically an unfavorable process for all the systems examined because the energy of the (^2E) chromium(III) species (39.3 Kcal/mol) [5] is lower than that for the substituted phenols. Then, the role of the energy transfer in the quenching processes may be considered negligible.

Quenching by electron transfer or charge transfer is expected to imply some relationship between the

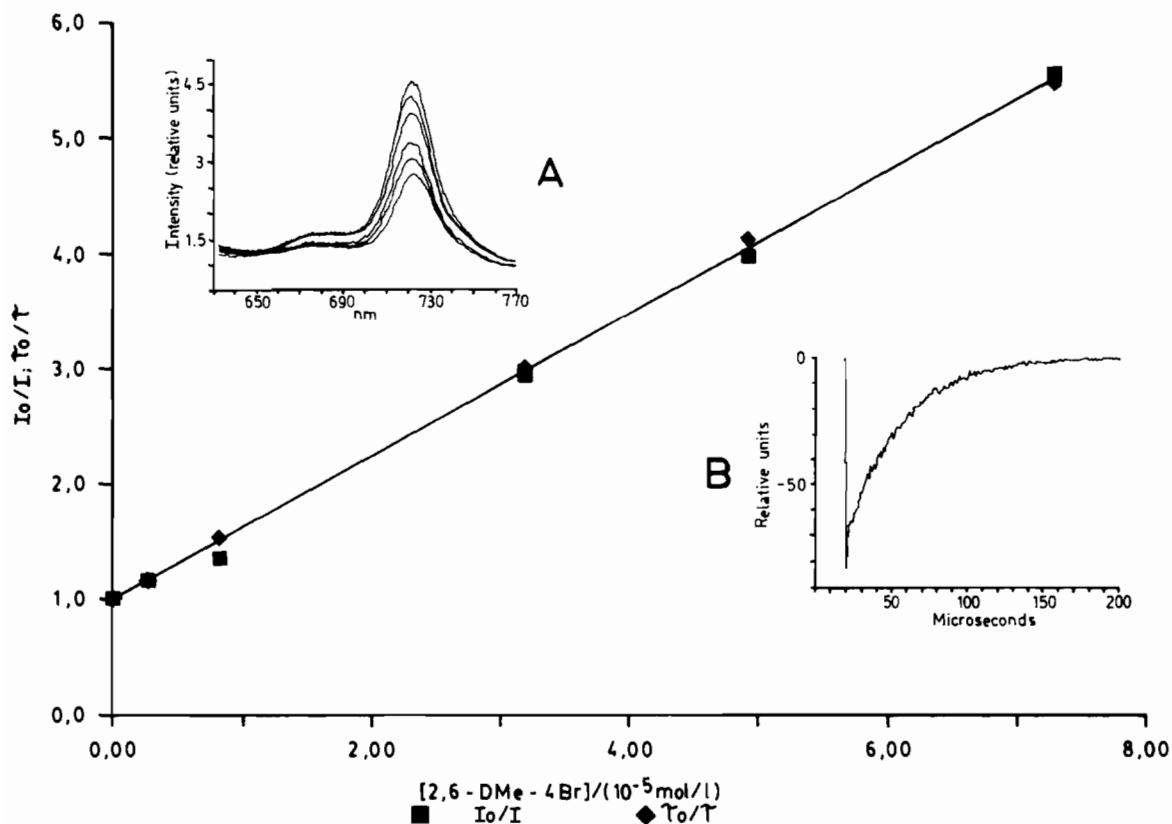


Fig. 1. Stern-Volmer plot comparing data from I_0/I and τ_0/τ from the quenching of $(^2E)\text{Cr}(\text{phen})_3^{3+}$ by 2,4-DMe-4Br. Inset A: emission spectra of $\text{Cr}(\text{phen})_3^{3+}$ 2.4×10^{-4} M in the presence of 2,5-DCl in concentrations ranging from 0 – 10^{-3} M in 1:1 MeOH:H₂O solutions, pH=9 and $\mu=1.0 \times 10^{-2}$ M. Inset B: single shot decay of $(^2E)\text{Cr}(\text{phen})_3^{3+}$ (2.4×10^{-4} M in 1:1 MeOH:H₂O, pH=9 and $\mu=1.0 \times 10^{-2}$ M aerated solution).

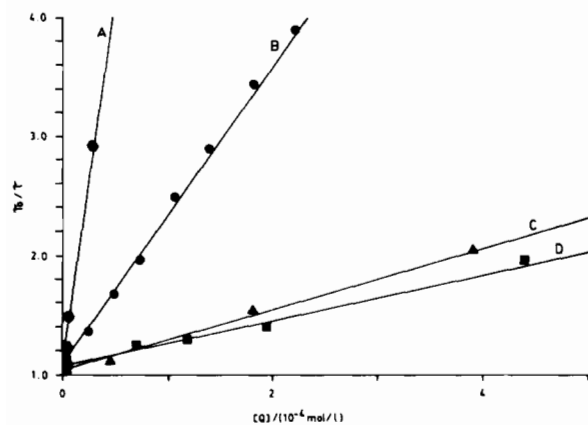


Fig. 2. Stern-Volmer plots for the quenching of $(^2E)\text{Cr}(\text{phen})_3^{3+}$ by (a) 2,6-DM-4Br; (b) 2,4,6-TCl; (c) 4-F and (d) 2-Cl.

redox properties of the quenchers and the quenching constant [20].

The products that correspond to the electron transfer quenching process, the one-electron oxidation product of the quencher and/or the one-electron reduction product of the complex, have been

observed for other systems of chromium(III) complexes [6, 10, 21] which have been studied by flash photolysis.

On the other hand, strong support in favor of a reductive electron-transfer reaction is given by the formation of $\text{Ru}(\text{bpy})_3^{2+}$ in the study of the luminescence quenching of $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ by phenol and substituted phenols [12, 13].

It should be noticed that the $(^2E)\text{Cr}(\text{phen})_3^{3+}$ species has a reduction potential (versus NHE) in water of 1.42 V [5] so this is a more powerful oxidizing agent than the ground state species. It should also be noted here that $(^2E)\text{Cr}(\text{phen})_3^{3+}$ is a more powerful oxidizing agent than $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ (the corresponding reduction potential versus NHE in water is 0.84 V [22]). Then, it is possible to assume that the only important quenching mechanism for the deactivation of the luminescent state of $\text{Cr}(\text{phen})_3^{3+}$ is the electron transfer from the quencher to the excited state of the chromium(III) complex.

Clear evidence for a reductive electron-transfer quenching mechanism, at least for the systems in

TABLE 1. Rate constants for the quenching of $(^2E)Cr(phen)_3^{3+}$ by substituted phenols at 22 ± 2 °C^a

Phenol	k_q (M ⁻¹ s ⁻¹)	k'_q ^b (M ⁻¹ s ⁻¹)	$E_{1/2}$ ^{c,d} (V)	pKs ^f
4-NH ₂	7.6×10^9	1.7×10^{10}	0.256	10.9
4-Ph	2.1×10^9	2.5×10^9	0.335	10.1
2,6-DMe-4Br	1.6×10^9 2.7×10^8 ^e	1.8×10^9		
2,6-DCI	1.1×10^9	1.2×10^9		
4-I	4.5×10^8	4.7×10^8	0.36 ^g	9.9
2,4,6-TCl	3.1×10^8	3.2×10^8		
4-Br	1.3×10^8 1.0×10^8 ^e	1.3×10^8		10.0
4-Cl	5.7×10^7 2.4×10^7 ^e	5.7×10^7	0.455	10.0
4-F	5.6×10^7	5.7×10^7		10.6
2-Cl	3.7×10^7	3.7×10^7	0.439	9.1
2,5-DCI	1.4×10^7	1.4×10^7	0.548	8.1
3-Cl	1.0×10^7	1.0×10^7	0.538	9.7

^a1:1 MeOH:H₂O, $\mu = 1.0 \times 10^{-2}$ M and pH=9. ^bFrom eqn. (3). ^cTaken as reduction potential for the Q⁺/Q couples vs. SCE. ^d $E_{1/2}$ for substituted phenols in 1:1 methanol:water at pH 9 can be estimated from the data for phenols at pH 5.6 in 1:1 i-propanol:water [23]*. ^epH=3. ^fTaken from tables for aqueous solutions [26] and corrected*. ^gFrom ref. 12 and corrected.

*The following set of equations was used. The expression used to calculate $E_{1/2}$ at the working pH is the following [24]:

$$E_{1/2} = C + 0.059 \log \left(\frac{K_a + [H^+]}{K_a} \right)$$

where K_a is the acidic dissociation constant for phenol estimated from the variation of the dielectric constant when changing from water to 1:1 methanol:water according to the following expression [25]:

$$pK_a = pK_a + 229 \left(\frac{1}{D_{\text{solvent}}} - \frac{1}{D_{\text{H}_2\text{O}}} \right)$$

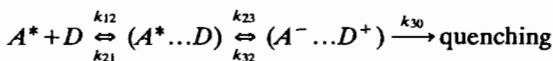
which the half-wave potential ($E_{1/2}$) of substituted phenols are known, comes from the decrease of the rate constant with the increase of $E_{1/2}$ calculated at pH 9 as shown in Table 1.

The effect of pH on $E_{1/2}$ for the phenol or substituted phenols increases on going from acidic to basic solutions where oxidation is favored [27]. Taking into account this effect, it is then conceivable to observe a lower value of k_q or k'_q in acidic medium (see Table 1).

Furthermore, if the trend to oxidation of the phenolate ion is associated with its basic character, a correlation between k_q and pKs should become apparent. The trend of k_q to increase with the increase of the pKs of the phenol derivatives, as expected,

is shown in Table 1. However, this correlation does not hold for 3-Cl and 4-F.

The half-wave potentials given in Table 1 can be taken as a measure of the reduction potential of the quencher in 1:1 methanol:water. Accordingly, the results can be treated by the Rehm–Weller kinetic scheme [14]:



Before interpreting the quenching data, it is necessary to make corrections for diffusional effects using eqn. (3).

$$\frac{1}{k_q} = \frac{1}{k'_q} + \frac{1}{k_d} \quad (3)$$

where k_d is the diffusion-controlled rate constant, k_q is the measured uncorrected quenching rate constant and k'_q represents the true activation-controlled quenching rate constant. According to the kinetic scheme, this rate constant can be written as:

$$k'_q = K_{12} k_{23} F \quad (4)$$

where K_{12} is the equilibrium constant for the formation of the cage encounter complex and $F = k_{30}/(k_{30} + k_{32})$ is the fraction of electron transfer quenching events which lead to net quenching.

Using the Marcus–Hush theory to express the free energy of activation for the electron transfer process in the association complex ($^* \Delta G_{23}$), one can obtain (for details see ref. 28) eqn. (5) in the limit of $k_{30} \gg k_{32}$ ($F \sim 1$) and $\Delta G_{23} \ll 2\lambda$ (the rearrangement energy involved in the electron transfer process):

$$RT \ln k'_q = RT \ln k'_q(0) - \frac{\Delta G_{23}}{2} \quad (5)$$

where $k'_q(0)$ is a constant for a series of structurally and electronically related quenchers and ΔG_{23} is the Gibbs energy change involved in the electron transfer process which is given by eqn. (6):

$$\Delta G_{23} = -(E_{A^*/A^-} - E_{D^+/D}) + w_p - w_r \quad (6)$$

where w_r and w_p are the Coulombic energy associated with bringing together of the reactants and products in order to form the association complex and the ionic pair and E_{A^*/A^-} and $E_{D^+/D}$ are the thermodynamical reduction potential for $(^2E)Cr(phen)_3^{3+}/Cr(phen)_3^{2+}$ and Q^+/Q , respectively.

Equation (5) predicts a linear dependence of $RT \ln k'_q$ versus ΔG_{23} . Likewise, through eqn. (6) linear dependence is found with the reduction potential of the quencher.

A plot of $RT \ln k'_q$ versus $E_{1/2}$ shows a linear dependence with a slope of approximately -0.6 in reasonable agreement with eqn. (5) (Fig. 3). Besides,

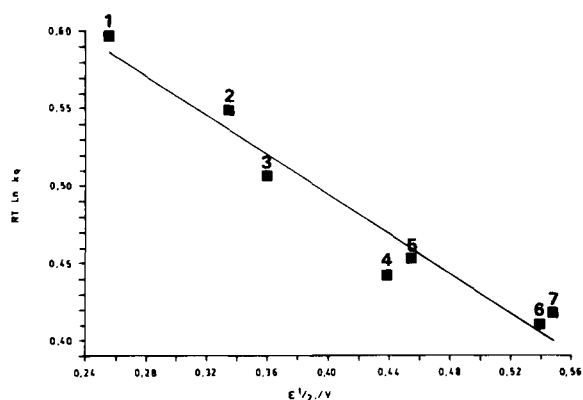


Fig. 3. Plot of $RT \ln k_q$ vs. $E_{1/2}$ for the quenching of $(^2E)Cr(phen)_3^{3+}$ by substituted phenols: 1, 4-NH₂; 2, 4-Ph; 3, 4-I; 4, 2-Cl; 5, 4-Cl; 6, 3-Cl; 7, 2,5-DCl.

the k_q value for 4-NH₂ is close to the diffusion controlled rate in 50% vol./vol. aqueous methanol solution ($k_d = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [29]; a value of 1.1 mm has been taken for the distance of closest approach of ions ($r_A + r_B$)).

Only a simple correlation between the activation-controlled quenching rate constant and the driving force is shown in Fig. 3 because the potentials used do not represent a thermodynamical value. Taking into account the reduction potential for phenol in ACN [30], the phenolic derivatives seem to be less reductive than was estimated in this work, and consequently, the electron transfer reaction would be much less exergonic than the value inferred from Table 1. (c. $\Delta G_{23} > -1 \text{ eV}$). In this context, it is not possible to obtain either an accurate value of $RT \ln k_q(0)$ or the energy barrier to electron transfer arising from reorganization of inner and outer coordination spheres.

It has been shown [23] that the metachloro substituted compound is the most difficult to oxidize within the monochloro substituted phenols. Then, should the effect of each individual substituent be additive, a decrease of the k_q value for 2,5-DCl with respect to the k_q value for 2-Cl is expected from a *meta*-substitution in the *ortho*-chloro compound (Table 1).

In contrast, the *ortho-para* directing groups increase the electron density at the carbon atom to which the hydroxyl group is attached making it easier to oxidize. This effect can be seen as an increment of k_q in the 2,6-DMe-4-Br compound with respect to 4-Br and in 2,4,6-TCl with respect to 4-Cl (Table 1).

It is well known that in the halogen substituted phenols, the electron density of the hydroxylic group decreases as the electronegativity of the halogen increases with respect to that of the parent. It should also be noted that this effect is minimized in 2,4,6-

TCl according to the symmetrical distribution of the substituents. Therefore, an increment in the electronic density would favor oxidation and we should observe an increase in the k_q' values when 2,6-DCl is compared with 2,4,6-TCl. In the same way, a diminution in the electronic density over the hydroxylic group and therefore in the k_q values should be expected if 4-Cl is compared with the trichlorosubstituted compound (Table 1).

A similar effect could be observed among the *p*-halogen substituted phenols. The electron transfer rate constant should increase when the electron withdrawing character of the halogen decreases. An examination of the data in Table 1 shows that $k_q^F < k_q^{Cl} < k_q^{Br} < k_q^I$. A similar effect has also been observed in the photoreduction of $Ru(bipy)_3^{2+}$ by phenols and phenolate ions [12].

Acknowledgements

The authors wish to thank the Consejo Nacional de Investigaciones Cientificas y Tecnicas de Argentina (CONICET) and the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR) for financial support.

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