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Mechanism of oxidation of phenol and 2,6-dimethylphenol in the presence of $Cr(phen)_3{}^{3+}$ excited state: the role of O_2

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Abstract

Phenol and its derivatives react with the excited state of $Cr(phen)_3{}^{3+}$ by electron transfer reaction. The reaction mechanism involves different steps in presence or in absence of O_2. In absence of O_2 and under continuous irradiation of the complex in presence of phenol (Ph) at 366 nm, no products of the oxidation were found. Results in presence of 2,6-dimethylphenol (2,6Me$_2$Ph) indicated that direct oxidation of 2,6Me$_2$Ph by $^*Cr(phen)_3{}^{3+}$ takes place. In presence of O_2 the corresponding benzoquinone was obtained for both phenols. Experiences in deuterated water confirm the intermediacy of O_2 ($^1\Delta_g$). Also, an estimation of $\phi_{so} = 0.035$ (efficiency of $^1O_2$ formation) for $^*Cr(phen)_3{}^{3+}$ is given. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Phenol; $Cr(phen)_3{}^{3+}$

1. Introduction

Phenol and its derivatives are among the major pollutants in the aquatic environment, and there is an increasing interest to understand the mechanistic aspects and environmental pathways for their photodegradation, mainly of those used in the production of phenolic pesticides and found in industrial waste water [1,25].

There are a few works where $Cr(bpy)_3{}^{3+}$ (bpy $=$ $2,2'$-bipyridine) has been used as photosensitizer in the photo-oxidation of phenol in aqueous solution. Kachanova and Koslov [2] studied this reaction without giving information about the photoproducts. Recently, Pizzocaro et al. [3,4] studied the oxidation of phenol photoinduced by $Cr(bpy)_3{}^{3+}$ in aqueous solutions. In absence of O_2, no products of the reaction have been found though in presence of O_2 the only product was benzoquinone (BQ) where a Type II photo-oxidation mechanism (singlet molecular oxygen (O_2 ($^1\Delta_g$)) mediated) takes place [5].

In our laboratory there is a continuous interest in the study of electron transfer reactions involving excited states of transition metal complexes with phenolic derivatives and their characterization in aqueous medium. We have dealt in previous papers [6,7] with photophysics and mechanistic aspects of polypyridine complexes of transition metals in presence of phenols. We report here a study on the direct oxidation of 2,6-dimethylphenol by $^*Cr(phen)_3{}^{3+}$ (phen $=$ 1,10-phenanthroline) and on the role of O_2 in the oxidation of phenols.

2. Experimental

Phenol (Ph), 2,6-dimethylphenol (2,6Me$_2$Ph), benzoquinone (BQ) and 2,6-dimethylbenzoquinone (Me$_2$BQ) were purchased from Sigma (USA). The last was used as received and the others were purified under vacuum sublimation. The $Cr(phen)_3(ClO_4)_3$ was available from previous studies [6,8]. Deionized water used for the preparation of the solutions was obtained with a Milli-Q System Millipore. Fluorescence lifetime measurements were performed with a N_2 Laser system and flash photolysis experiments were carried out with a Nd:YAG (355 nm) pulsed laser system and have been described elsewhere [9,10]. Data were taken using fresh solutions as an average of eight consecutive decays in each case. For continuous photolysis experiments, 366 nm radiation was selected from a 150 W high pressure mercury lamp (OSRAM). The light intensity ($\sim 2.0 \times 10^{15}$ photons cm^{-2} s^{-1}) was measured by ferrioxalate actinometry. HPLC was performed in a KONIC 500G chromatograph using a reverse phase ODS2 column (250 mm $\times$ 4 mm and 5 μm). The eluent was MeOH:H$_2$O 50:50 with 0.5 and 1.0 ml/min flow rates for the experiences performed

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with Ph and 2,6Me$_2$Ph, respectively. A Shimadzu UV-1601 spectrophotometer was used to measure the absorption spectra. Flash and continuous photolysis experiments were carried out at room temperature under high purity N$_2$ bubbling or in air saturated solution that contained 2×10^{-3} M Ac$^-$/HAc buffer (pH = 5) and 1 M NaCl, and were kept constant throughout the experiments.[1] The concentration of Cr(phen)$_3{}^{3+}$ was in the range of 1.0–2.5 × 10^{-4} M while it was 1.0–5.0 × 10^{-4} M for the phenolic compounds.

3. Results and discussion

3.1. Flash photolysis

In order to carry out the flash photolysis experiments, the *Cr(phen)$_3{}^{3+}$ and Cr(phen)$_3{}^{2+}$ (from the reaction of *Cr(phen)$_3{}^{3+}$ with Fe(II)) spectra were taken. Both spectra are in agreement with those previously published [11,12]. These experiments were carried out in presence and in absence of O$_2$ with Ph and 2,6Me$_2$Ph at two different wavelengths, 500 and 690 nm, corresponding to the absorption maximum of *Cr(phen)$_3{}^{3+}$ and Cr(phen)$_3{}^{2+}$ in each case.

The quenching rate constants k_q for Ph and 2,6Me$_2$Ph measured by flash photolysis are fully in accordance with those obtained from flash luminescent experiments [13]. The phenols concentrations were chosen to have a quenching greater than 95%. Since the lifetime of the excited state of Cr(phen)$_3{}^{3+}$ in these conditions is close to 12 μs, the absorption observed at 500 nm and at 50 μs after the excitation pulse should correspond to Cr(phen)$_3{}^{2+}$.

In the experiences with Ph and in absence of O$_2$, absorption at 500 nm was not observed nor at 690 nm, though a slight absorption at 500 and 690 nm was observed at times greater than 50 μs after the flash when 2,6Me$_2$Ph was used. This small but observable absorption indicates the appearance of Cr(phen)$_3{}^{2+}$ (Fig. 1). In aerated solution, absorption was not observed neither for Ph nor for 2,6Me$_2$Ph at the same wavelengths.

3.2. Continuous photolysis

Continuous irradiation of deaereated solution of 2.5×10^{-4} M Cr(phen)$_3{}^{3+}$ yields only the photoaquation product ([Cr(phen)$_2$(H$_2$O)$_2$]$^{3+}$), observed with the appearance of the characteristic absorption band at 500 nm [8]. When 2.0×10^{-4} M Ph was added in absence of O$_2$ the photoaquation absorption band decreased. Furthermore, the chromatographic analysis showed only the peak corresponding to the Ph at retention time $t_R = 9.5$ min. In presence of O$_2$ the chromatograph showed a new peak that grows at $t_R = 6.5$ min identified as BQ by comparison with authentic samples. At the same irradiation time and in experiments with 1.7×10^{-4} M of 2,6Me$_2$Ph in absence of O$_2$, the absorption band of Cr(phen)$_2$(H$_2$O)$_2{}^{3+}$ vanished. From HPLC experiments, two chromatographic peaks were obtained, one of them at $t_R = 9.7$ min belonging to the reactant (2,6Me$_2$Ph) and the other as the only product at $t_R = 4.7$ min area of which increases linearly with photolysis time, after induction time. In presence of O$_2$, only one product is observed but at $t_R = 6.15$ min whose area increases linearly with the irradiation time indicating the formation of a photoproduct different from that obtained in absence of O$_2$ (Fig. 2). This peak was attributed to the Me$_2$BQ by comparison of pure samples and the peaks at $t_R = 4.7$ min belonging to a more polar product than Me$_2$BQ, which could not be identified by mass spectroscopy because of its low concentration. Nevertheless, there is no doubt that it comes from the electron transfer reaction followed by successive oxidative steps [14,15].

The experiments carried out in D$_2$O and in the presence of O$_2$ with 2,6Me$_2$Ph showed an increase of the quantum yield of Me$_2$BQ (Φ_{BQ}) by a factor of ~6.5 (Fig. 2, inset).

3.3. Reaction mechanism

In view of the experimental results, the following mechanism can be proposed:

$$\mathrm{Cr(phen)_3}^{3+} + h\nu \rightarrow {}^*\mathrm{Cr(phen)_3}^{3+} \quad I_a \tag{1}$$

$$^*\mathrm{Cr(phen)_3}^{3+} \rightarrow \mathrm{Cr(phen)_3}^{3+} + h\nu' \quad k_o \tag{2}$$

$$^*\mathrm{Cr(phen)_3}^{3+} + \mathrm{H_2O} \rightarrow \mathrm{Cr(phen)_2(H_2O)_2}^{3+} \quad k_{pa} \tag{3}$$

$$^*\mathrm{Cr(phen)_3}^{3+} + \mathrm{Q} \rightarrow [\mathrm{Cr(phen)_3}^{2+} \cdots \mathrm{Q}^{+\bullet}] \quad k_q \tag{4}$$

$$[\mathrm{Cr(phen)_3}^{2+} \cdots \mathrm{Q}^{+\bullet}] \rightarrow \mathrm{Cr(phen)_3}^{2+} + \mathrm{Q}^{+\bullet} \quad k_{ce} \tag{5}$$

$$[\mathrm{Cr(phen)_3}^{2+} \cdots \mathrm{Q}^{+\bullet}] \rightarrow \mathrm{Cr(phen)_3}^{3+} + \mathrm{Q} \quad k_{bet} \tag{6}$$

$$^*\mathrm{Cr(phen)_3}^{3+} + \mathrm{O_2} \rightarrow \mathrm{Cr(phen)_3}^{3+} + {}^1\mathrm{O_2} \quad k_q^{\mathrm{O_2}} \tag{7}$$

$$\mathrm{Q}^{+\bullet} + \mathrm{Q}^{+\bullet} \rightarrow \mathrm{I} \quad k_I \tag{8}$$

$$\mathrm{I} + {}^*\mathrm{Cr(phen)_3}^{3+} \rightarrow \mathrm{Products} \quad k_P \tag{9}$$

$$^1\mathrm{O_2} + \mathrm{Q} \rightarrow \mathrm{BQ} \quad k_{BQ} \tag{10}$$

$$^1\mathrm{O_2} \rightarrow \mathrm{O_2} \quad k_o^{\mathrm{O_2}} \tag{11}$$

$$\mathrm{Q}^{+\bullet} + \mathrm{O_2} \rightarrow \mathrm{BQ} \quad k_{BQ}^{\mathrm{O_2}} \tag{12}$$

In absence of O$_2$ and after excitation of the ground state (Eq. (1)), the luminescent Cr(phen)$_3{}^{3+}$ excited state decays via a radiative process (Eq. (2)), or via a reactive process which renders the photoaquation product [Cr(phen)$_2$(H$_2$O)$_2$]$^{3+}$ (Eq. (3)). The quenching process (Eq. (4)) competes with the photoaquation. Table 1 shows the known rate constant values that are involved in the proposed mechanism. The ratio of the rates for competitive processes is $v_q^Q/v_{pa} \cong 3$ and $v_q^Q/v_{pa} \cong 50$ for Ph and

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[1] Although the formation of ion-pairing at high Cl$^-$ concentration affects the species lifetime, the quenching rate constant of *Cr(phen)$_3{}^{3+}$ by phenols was not affected as shown previously [14].

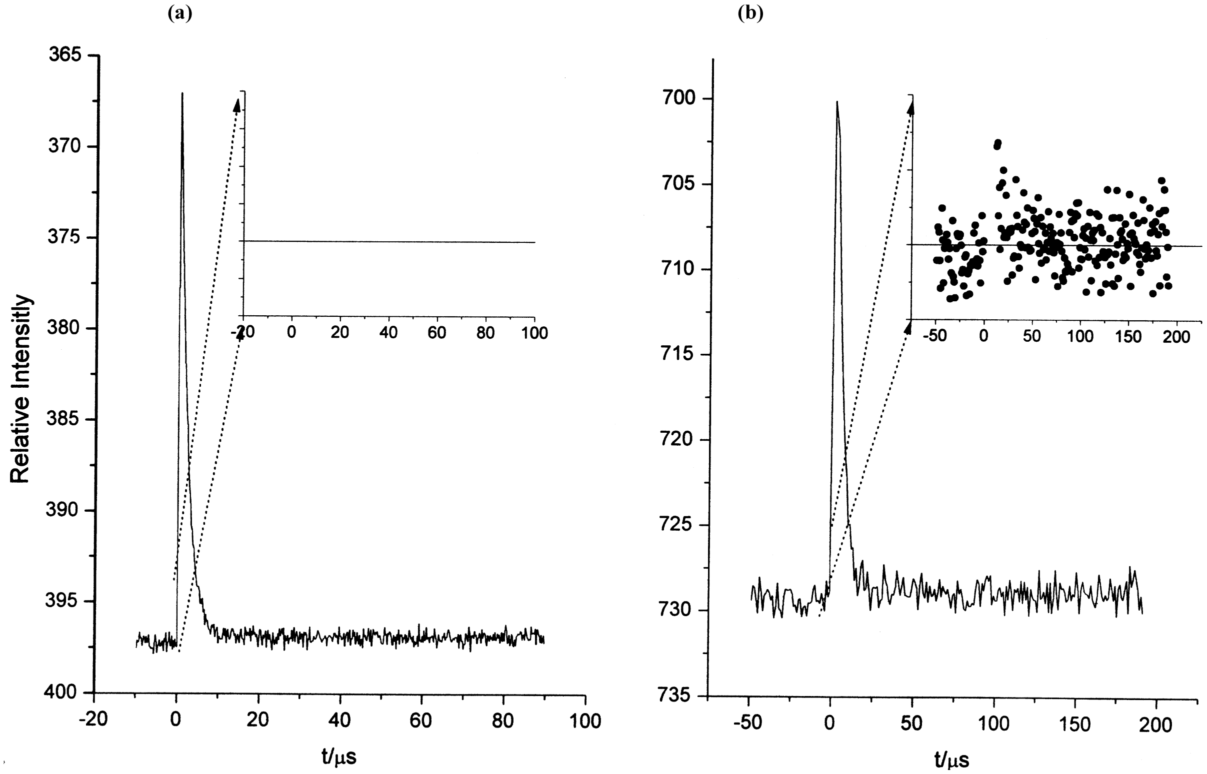

Fig. 1. Data from pulsed flash photolysis experiments for 1.17 × 10^{-4} M of $Cr(phen)_3^{3+}$ with 8.2 × 10^{-5} M of $2,6Me_2Ph$: (a) absence of O_2 and (b) air saturated solution.

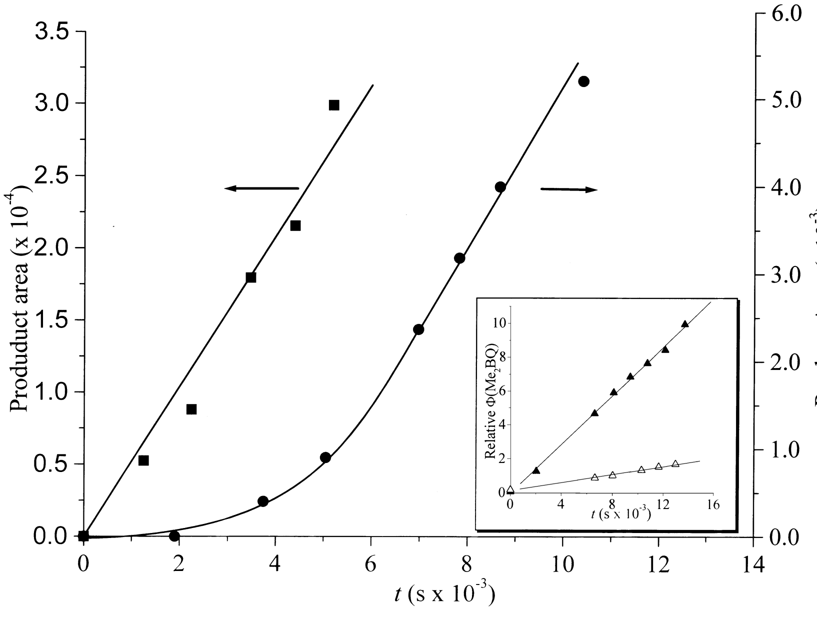

Fig. 2. Plot of product area vs. photolysis time at 1.5 × 10^{-4} M of $Cr(phen)_3^{3+}$ with 1.7 × 10^{-4} M of $2,6Me_2Ph$ of (●) air free and (■) air saturated solution. The inset shows a plot of relative quantum yield ($\Phi(Me_2BQ)$) vs. photolysis time for the irradiation of 2.5 × 10^{-4} M of $Cr(phen)_3^{3+}$ with 1.7 × 10^{-4} M of $2,6Me_2Ph$ aerated solutions in H_2O (△) and D_2O (▲).

Table 1
Standard and half-wave reduction potential (vs. NHE) and rate constants for the steps involved in the proposed mechanism

	$Cr(phen)_3^{3+}$	Ph	2,6Me_2Ph	O_2
E^0 (V vs. NHE)	1.42[a]	0.910[b], 1.2[b]	0.704[b]	
k_o (s^{-1})	5.0×10^{3}[c]			
k_{pa} ($s^{-1}\,M^{-1}$)	0.8×10^{2}[a]			
k_q ($s^{-1}\,M^{-1}$)		5.1×10^{7}[d]	9.5×10^{8}[d]	5.0×10^{7}[e]
k_{BQ} ($s^{-1}\,M^{-1}$)		0.26×10^{7}[f]	$\sim2\times10^{7}$[f]	

[a] Standard reduction potential of the $Cr(phen)_3^{3+}$ excited state, M.A. Jamieson, et al. Coord. Chem. Rev. 39 (1981) 121.

[b] Reduction potential for the deprotonated phenoxyl radical estimated from J.C. Suatoni, R.E. Snyder, R.O. Clark, Anal. Chem. 33 (1961) 1894; K. Miedlar, P.K. Das, J. Am. Chem. Soc. 104 (1982) 7462, and correlate with that of J. Lind; X. Shen, T.E. Eriksen, G. Merënyi, J. Am. Chem. Soc. 112 (1990) 479. 1.2 V is a more recently taken value from J. Phys. Chem. B 103 (1999) 6653.

[c] In N_2 purged solution, 1 M NaCl and $\sim 1.25 \times 10^{-4}$ M of complex.

[d] D. Pagliero, G.A. Argüello, E.H. Staricco, J. Photochem. Photobiol. A 115 (1998) 199.

[e] Taken from B. Brunschwig, N. Sutin, J. Am. Chem. Soc. 100 (1978) 7568.

[f] Approximation of the value for 2,6Me2Ph in basic medium taken from N.A. García, J. Photochem. Photobiol. B 22 (1994) 185.

2,6Me_2Ph, respectively. This fact is in accordance with changes observed in the UV–Vis spectra at 500 nm. After quenching, the germinate redox pair inside the solvent cage can escape to yield the redox product into the bulk solution (Eq. (5)) in competition with back electron transfer (Eq. (6)). The quantum yield $\phi_{et} = \eta_q\eta_{ce}$[2] ($\eta_q$ and η_{ce} are the efficiencies of quenching and cage escape, respectively) could not be evaluated and consequently η_{ce}. Flash photolysis experiments in presence of Ph show that no redox product is present, indicating that back electron transfer should prevail over the cage escape; then, η_{ce} should be $\sim$0 ($k_{bet} \gg k_{ce}$).

On the other hand, when 2,6Me_2Ph was used as quencher, the small change in the optical density (ΔOD) observed at 500 nm and 50 μs after the pulse would indicate that $\eta_{ce} \neq 0$ so it should lead to the direct oxidation of the quencher to yield the *ortho–ortho*-dimethyl phenoxyl radical ($Q^{\bullet+}$), although k_{bet} still predominates over k_{ce}. Furthermore, the formation of the $Q^{\bullet+}$ radicals via electron transfer quenching of $^*Cr(phen)_3^{3+}$ in absence of oxygen is expected to lead to the generation of dimer species via bimolecular combination reaction. Experiments by pulse radiolysis have demonstrated that Ph radicals react in a second order manner ($2k \sim 10^9\,M^{-1}\,s^{-1}$) to yield dimers as main products [16,17]. Since the *ortho* positions are blocked, the only recombination possible should be the *para–para* to render an intermediate (I) (Eq. (8)) prior to the formation of the dimer Q_2. HPLC experiments with pure dimer confirmed its absence as product indicating that a more complex mechanism is involved. The excited state of the $Cr(phen)_3^{3+}$ has a reduction potential $^*E^0 = 1.42$ V vs. NHE, which could be large enough to oxidize I to give another stable product. Then, the observed induction time in the generation of product (Fig. 2) would indicate that it was not formed in a primary process but through successive stages that would involve that intermediate.

In presence of O_2, $^*Cr(phen)_3^{3+}$ is quenched by phenols and by O_2 via an energy transfer process to form $^1O_2$ (Eq. (7)) (see Table 1) [18]. The fact that, under continuous irradiation, the only products found were the corresponding benzoquinones suggests the participation of O_2 ($^1\Delta_g$) as intermediate of the reaction. The singlet oxygen mediated photodegradation of phenols indicated that the main degradation products of phenols in presence of $^1O_2$ is the corresponding benzoquinone (Eq. (10)) [3,4,19,20]. Furthermore, the phenolic radical could be formed from Eqs. (4) and (5), leading to the formation of benzoquinone as the main product in presence of O_2, Eq. (12) [21], indicating a competitive process between Eqs. (4) and (5) with Eq. (7) to yield Me_2BQ. The fact that η_q of 2,6Me_2Ph and quenching efficiency by O_2, η'_q ($\eta'_q = k_q[O_2]/(k_o + k_q[Q] + k_q^{O_2}[O_2])$) are 0.07 and 0.93, respectively, using $[2,6Me_2Ph] = 1.7 \times 10^{-4}$ M, and that no absorption was observed in flash photolysis experiments, would indicate once again an η_{ce} value too low for the $^*Cr(phen)_3^{3+}$–2, 6Me_2Ph couple.

Our experiments carried out in D_2O confirm the intermediacy of O_2 ($^1\Delta_g$) via Type II mechanism. The deactivation rate constant of the singlet oxygen ($k_o^{O_2}$) in H_2O and D_2O can be expressed as a function of the molar fraction of D_2O (χ_{D_2O}) as $k_o^{O_2}$ (μs^{-1}) $= 0.248 - 0.23\chi_{D_2O}$ [22]. In net water the lifetime of $^1O_2$ ($\tau_\Delta = 1/k_o^{O_2}$) is $\tau_\Delta = 4\,\mu s$ and in 95% of D_2O (used in these experiments) is $\tau_\Delta = 33\,\mu s$. These values show that $^1O_2$ lives 8.2 times in D_2O than in H_2O in agreement with the 6.5 factor in the Φ_{BQ} obtained experimentally in D_2O.

3.4. Quantum yields analysis

The quantum yields (Φ) of reactants disappearance and the Φ of products formation in presence of O_2 are shown in Table 2. It can be seen in the table that the Φ of products formation for Ph and 2,6Me_2Ph are almost the same. On account of the mechanism proposed, one can write

$$\Phi_{BQ} = \eta'_q\phi_{so}\eta_{so}\eta_{rx} \tag{13}$$

Table 2
Quantum yields of the reaction in absence and presence of O_2 ($\Phi \times 10^4$)

	$^*Cr(phen)_3^{3+}$	Ph	2,6Me_2Ph
$\Phi(O_2)$[a]		<7	<7
$\Phi(N_2)$[a]		0	<20
$\Phi_{BQ}(O_2)$[b]		0.35	0.44
Φ(pa)	5	–	–

[a] Quantum yield of reactant disappearance.

[b] Quantum yield of product appearance.

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[2] The efficiency of quenching is given by $\eta_q = k_q[Q]/(k_o + k_q[Q] + k_q^{O_2}[O_2])$ and the efficiency of cage escape (η_{ce}) is $\eta_{ce} = k_{ce}/(k_{bet} + k_{ce})$, where the rate constants are those defined in the mechanism.

where η'_{q} is the quenching efficiency by O_2, ϕ_{so} the yield of $^1O_2$ formation from the complex in Eq. (7), η_{so} the reaction efficiency of Ph with $^1O_2$ ($\eta_{\mathrm{so}} = k_{\mathrm{BQ}}[\mathrm{Q}]/k_{\mathrm{BQ}}[\mathrm{Q}] + k_{\mathrm{o}}^{\mathrm{O}_2}$) and η_{rx} the formation efficiency of BQ (η_{rx} includes several steps to reach the final product).

Knowing the value of k_{BQ} (Table 2) and the concentration of O_2 for air saturated solutions ($[\mathrm{O}_2] = 2.5 \times 10^{-4}\,\mathrm{M}$) in presence of $3.5 \times 10^{-4}\,\mathrm{M}$ of Ph and $1.7 \times 10^{-4}\,\mathrm{M}$ of 2,6$\mathrm{Me_2}$Ph, we found that the efficiency values for Ph are $\eta'_{\mathrm{q}} = 0.5$, $\eta_{\mathrm{so}} = 0.0018$ and for 2,6$\mathrm{Me_2}$Ph $\eta'_{\mathrm{q}} = 0.07$, $\eta_{\mathrm{so}} \approx 0.004$;[3] for Ph is $\eta'_{\mathrm{q}}\eta_{\mathrm{so}} = 9 \times 10^{-4}$ and for 2,6$\mathrm{Me_2}$Ph is $\cong 3 \times 10^{-4}$. In as much as ϕ_{so} and η_{rx} remain equal for both phenols, the Φ_{BQ} for the two phenols should be close to each other (see Eq. (1)) as we found experimentally (see Table 2). These results also confirm the proposed mechanism.

The ϕ_{so} for polypyridine Cr(III) complexes is still unknown in the literature. It can be estimated ϕ_{so} from our experimental results of $\mathrm{Cr(phen)_3}^{3+}$ with Ph, since the BQ is formed only via Eq. (10) ($\eta_{\mathrm{ce}} = 0$). Using $\eta_{\mathrm{rx}} = 1$ [4], a value of $\phi_{\mathrm{so}} = 0.035$ can be estimated. This value is lower than that for polypyridine Ru(II) complexes (0.5–1) [23] and for Cr(III)-triazacyclononane thiocyanato complex (≈0.5) [24].

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[3] See footnote f of Table 1.