

FORMATION OF SEMIQUINONE RADICALS BY ELECTRON TRANSFER FROM OR TO PHOTOEXCITED $\text{Ru}(\text{bpy})_3^{2+}$: AN ELECTRON SPIN RESONANCE STUDY

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Summary

The formation of semiquinone radicals by sensitized photochemical oxidation of hydroquinones or reduction of quinones was studied in the approximate pH range 1 - 8 in aqueous solution. The photosensitizer was the tris-2,2'-bipyridine complex of ruthenium(II).

The paramagnetic species formed after the electron transfer from or to the excited ruthenium complex was studied by electron spin resonance spectroscopy in a flow system.

The varying acidities of the different oxidation states of the quinonic moiety led to coupled proton and electron transfer reactions. Detailed calculations of the pH-dependent redox potentials were carried out, and the results were subsequently used to estimate the rate constants for the electron transfer reactions by Marcus theory.

The agreement between the experiments and the theoretical calculations is fair above a pH of about 3, whereas at low pH deviations occur, probably because the reaction mechanism is more complex. The electron self-exchange rates of quinone and semiquinone can also be determined from the results of the study.

1. Introduction

The unique excited state properties of $\text{Ru}(\text{bpy})_3^{2+}$ have stimulated a large number of investigations into its photochemical reactions. Particularly the bimolecular electron transfer reactions of this complex have been studied in considerable detail (for a recent review see ref. 1). Despite the fact that these reactions are generally one-electron transfers and odd-electron species are thus obtained from diamagnetic substrates, electron spin resonance (ESR) spectroscopy has only been employed in a few cases so far. We have recently shown that a reaction sequence can be studied by ESR spectroscopy

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by illuminating an aqueous solution which contains $\text{Ru}(\text{bpy})_3^{2+}$ or a similar diimine complex, a hydroquinone and a suitable metal ion [2]. This photon-triggered complex formation (PTCF) is initiated by an electron transfer from the hydroquinone H_2Q to the excited state $\text{Ru}(\text{bpy})_3^{2+}$, which is a much stronger one-electron acceptor than the ground state species. It has been shown previously [3] by flash photolytic analysis that $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ can act as an oxidizing agent towards hydroquinones as well as a reducing agent towards quinones. In the studies of PTCF the pH has an important influence because the redox properties of quinones and hydroquinones are strongly pH dependent. We therefore undertook a detailed analysis of the photochemical electron transfer reaction between $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ and quinone or hydroquinone as a function of pH.

In the present paper the radical yields and the linewidths in the reaction systems of $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ with *p*-quinone, *p*-benzohydroquinone and pyrocatechol are reported and discussed.

2. Experimental details

p-Benzohydroquinone and pyrocatechol of the best commercial grade available were used without further purification. *p*-Benzoquinone was sublimed twice under reduced pressure.

The apparatus and procedure were as described in a previous paper [2].

3. Results and discussion

The experimentally determined radical concentrations in the pH range 0 - 8 for the photosensitized generation are given in Figs. 1 and 2 together with calculated values to be discussed below. Above pH 8, spontaneous formation of radicals occurs and photosensitized electron transfer therefore cannot be observed. Although the absolute concentrations are subject to a rather large systematic error, the relative values are highly significant. In all three cases the concentrations pass through a minimum in the medium pH range around 3. At lower and higher pH values the concentrations increase.

It is quite obvious that the pH dependence of the radical concentration results from coupling of proton- and electron-exchange processes, which will now be discussed in some detail.

3.1. Redox potentials

Figures 3 and 4 respectively show the species which are involved and their transformations through proton and electron transfer reactions. Using the parameters given in Tables 1 and 2, it is possible to calculate the standard redox potentials of the para and ortho compounds as a function of pH. The proton transfer characterized by K_{01} can always be neglected in aqueous solution. The calculation procedure [17] is similar to that used by Meisel

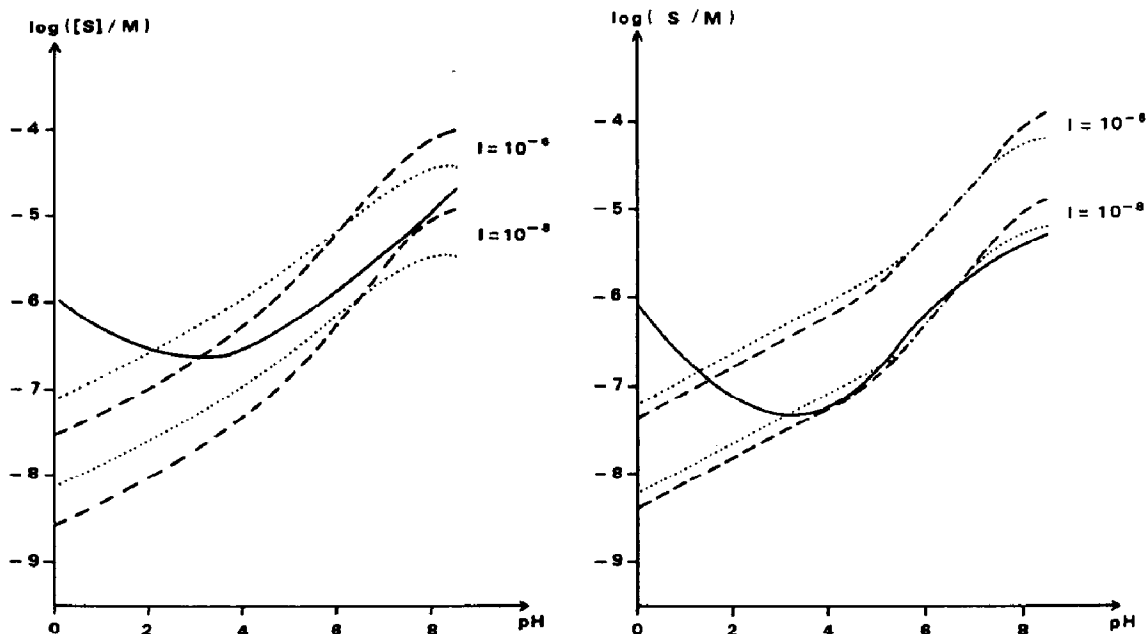


Fig. 1. Semiquinone concentration as a function of pH for *p*-hydroquinone (full line, experimental data; dotted and broken lines, calculated according to Marcus theory (see text)). I (einsteins $\text{s}^{-1} \text{cm}^{-2}$) is the irradiance.

Fig. 2. Semiquinone concentration as a function of pH for pyrocatechol (full line, experimental data; dotted and broken lines, calculated according to Marcus theory (see text)). I (einsteins $\text{s}^{-1} \text{cm}^{-2}$) is the irradiance.

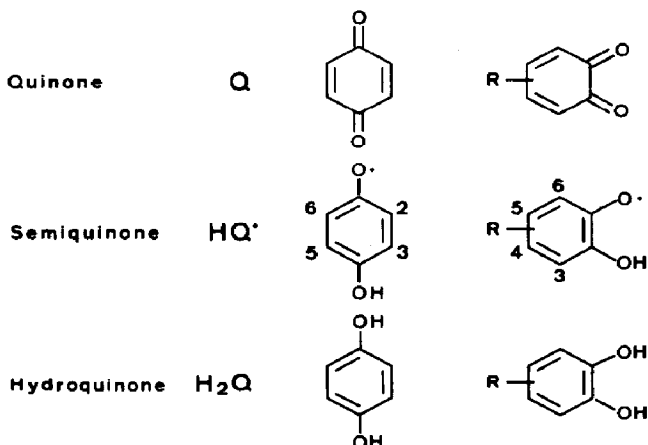


Fig. 3. Structure and abbreviations for the quinone derivatives ($R \equiv H$, pyrocatechol).

and coworkers [18, 19]. E_m^n is the standard redox potential for a given reaction (n) at a given pH (m), with equal amounts of the oxidized and reduced forms. The superscript n refers to the couples quinone/semiquinone ($n = 1$), semiquinone/hydroquinone ($n = 2$) and quinone/hydroquinone ($n = 3$). The results of these calculations are presented in Figs. 5 and 6.

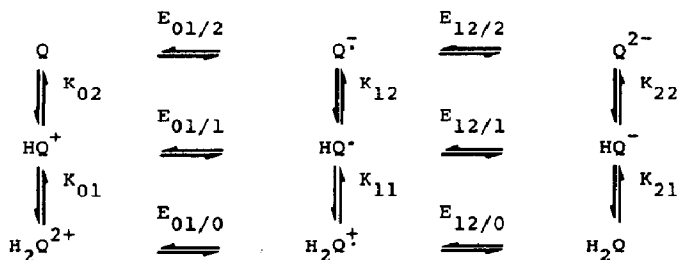


Fig. 4. Equilibria of proton (vertical) and electron (horizontal) transfer reactions for the quinone-semiquinone-hydroquinone system [4].

TABLE 1

Parameters of *p*-hydroquinone used in the calculation of Figs. 1 and 5

Parameter	References
$pK_{02} = -7$	(-7.2 for acetone [5])
$pK_{11} = -0.8$	[6], [7]
$pK_{12} = 3.9$	[8], [9], [10]
$pK_{21} = 9.85$	[10], [11], [12]
$pK_{22} = 11.4$	[10]
$E^\circ(Q/H_2Q) = 0.699$ V	[13]
$E_{12/2} = 0.023$ V	[10]

TABLE 2

Parameters of pyrocatechol used in the calculation of Figs. 2 and 6

Parameter	References
$pK_{02} = -7$	(-7.2 for acetone [5])
$pK_{11} = -1.62$	[7], [6]
$pK_{12} = 5.0$	[8], [10]
$pK_{21} = 9.2$	[14], [15], [10]
$pK_{22} = 12.98$	[14], [15], [10]
$E^\circ(Q/H_2Q) = 0.795$ V	[16], [13]
$E_{12/2} = 0.043$ V	[10]

3.2. Mechanism and rate of reaction

As previously reported [2, 3], semiquinones are produced by electron transfer from $(^3CT)Ru(bpy)_3^{2+}$. In the simplified mechanism given in Fig. 7, the semiquinones are denoted by the letter S, irrespective of the degree of protonation. As mentioned, $(^3CT)Ru(bpy)_3^{2+}$ is reduced in the presence of hydroquinone and is oxidized in the presence of quinone [20].

Below pH 10, the disproportionation reaction of S is exoergic (Figs. 5 and 6) and consequently $k_{-d} < k_d$ (Fig. 7). k_{-d} has therefore been neglected in the calculation. Assuming a steady state concentration for S and

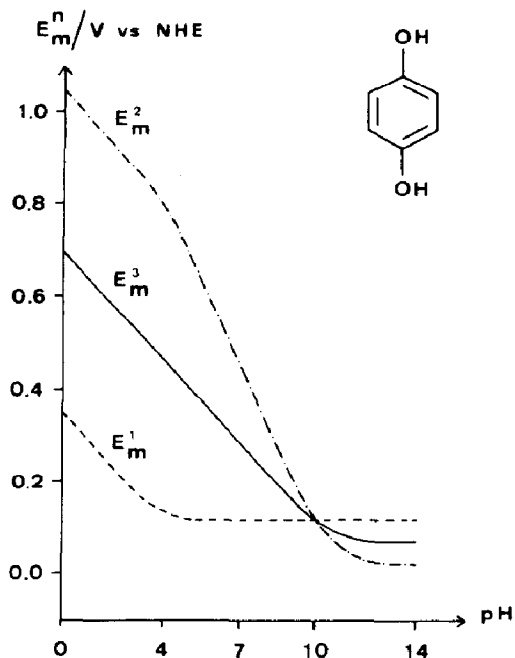


Fig. 5. Standard redox potentials as a function of pH (reduced form, *p*-hydroquinone). E_m^1 , quinone/semiquinone; E_m^2 , semiquinone/hydroquinone; E_m^3 , quinone/hydroquinone.

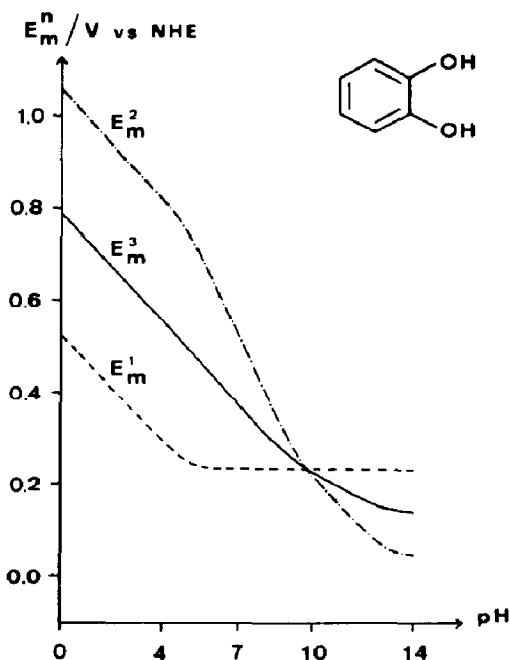


Fig. 6. Standard redox potentials as a function of pH (reduced form, pyrocatechol). E_m^1 , quinone/semiquinone; E_m^2 , semiquinone/hydroquinone; E_m^3 , quinone/hydroquinone.

$(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ and setting $[\text{S}] = [\text{Ru}^+]$ one obtains, for the photochemical reaction in the presence of hydroquinone,

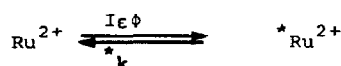
$$[\text{S}] = \left\{ \frac{k_q I \epsilon \phi [\text{Ru}(\text{bpy})_3^{2+}] [\text{H}_2\text{Q}]}{(k_{-\text{H}} + k_d)(k^* + k_q [\text{H}_2\text{Q}])} \right\}^{1/2} \quad (1)$$

where I is the irradiance, ϵ is the extinction coefficient of $\text{Ru}(\text{bpy})_3^{2+}$ ($14\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$), ϕ is the quantum yield for formation of $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ (assumed to be unity), k_q is the quenching constant obtained from Stern–Volmer plots and $k^* = 1/\tau_0$ is the natural decay time of $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ ($1.6 \times 10^{-6} \text{ s}^{-1}$). The remaining parameters are defined in Fig. 7. $k_q < 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for *ortho*- and *para*-hydroquinone. Thus $k_q [\text{H}_2\text{Q}]$ can be neglected ($[\text{H}_2\text{Q}] < 0.1 \text{ M}$).

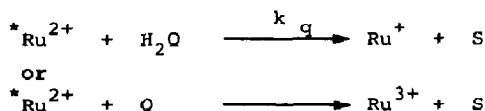
The square root dependence of $[\text{S}]$ on I , $[\text{Ru}(\text{bpy})_3^{2+}]$ and $[\text{H}_2\text{Q}]$ was verified within experimental error in the pH range 4–8. At lower pH the semiquinone concentration is too small to allow any significant correlation. At higher pH the semiquinone is sufficiently stable to appear spontaneously, even without irradiation.

A formula similar to eqn. (1) can be derived for *p*-quinone.

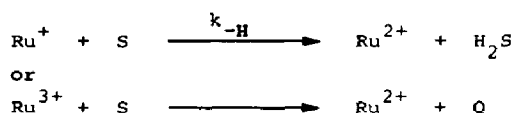
Excitation :



Quenching :



Homogeneous back reaction :



Disproportionation of the semiquinone:

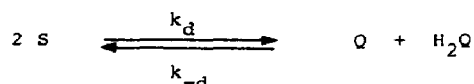


Fig. 7. Simplified reaction scheme (Q, quinone; H₂Q, hydroquinone; S, semiquinone).

3.3. Concentration calculation

Assuming that the electronic properties of the ruthenium complex remain constant between pH 0 and pH 10, the only pH-dependent parameters in eqn. (1) are k_q , k_{-H} and k_d . Their pH dependencies are related to the redox potentials of the semiquinone. We have used simplified Marcus theory to calculate these rate constants as functions of pH.

For a redox reaction



the rate constant k_{12} can be written as [21, 22]:

$$k_{12} = Z \exp\left(-\frac{\Delta G_{12}^\ddagger}{RT}\right) \quad (2)$$

with $Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. The activation energy is given by

$$\Delta G_{12}^\ddagger = \frac{\lambda_o(1 + \Delta G^\circ/\lambda_o)^2}{4} \quad (3)$$

where λ_o is the outer reorganization parameter, calculated according to Kimura *et al.* [22]. The work terms are neglected. ΔG° is the free energy of

the reaction. The latter can be calculated with the redox potentials represented in Figs. 5 and 6 and the values reported by Balzani *et al.* [23] for the $\text{Ru}(\text{bpy})_3^{n+}$ complex.

The curves in Figs. 1 and 2 were calculated with $[\text{Ru}^{2+}] = 10^{-3} \text{ M}$ and $[\text{H}_2\text{Q}] = 10^{-2} \text{ M}$ and neglecting $k_q[\text{H}_2\text{Q}]$.

The irradiance cannot be determined with a high degree of accuracy in the flow system. We have estimated I to be in the range $10^{-8} - 10^{-6}$ einsteins $\text{s}^{-1} \text{ cm}^{-2}$. The values of $\log[S]$ obtained by these calculations are represented by broken lines in Figs. 1 and 2. Equation (2) predicts $k_{12} = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ for $\Delta G_{12}^\ddagger = 0$. It is possible to include in the calculation a diffusion limit with $k_{12} < 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In this case the calculated concentrations are different and the $\log[S]$ are represented by dotted lines. The experimentally estimated concentration is represented by a full line. At pH 4 - 10 there is fairly good agreement between the calculated and the experimental curves. The uncertainties in the measurements of $[S]$ do not allow a better correlation to be obtained.

At lower pH the observed concentrations cannot be reproduced very well by the calculations. Figure 8 shows that k_{-H} is in the Marcus inverted region, particularly at low pH. Marcus theory then predicts low values for k_{-H} . This would qualitatively explain an increase in $[S]$ at low pH. The experimentally observed increase is, however, even larger than that predicted

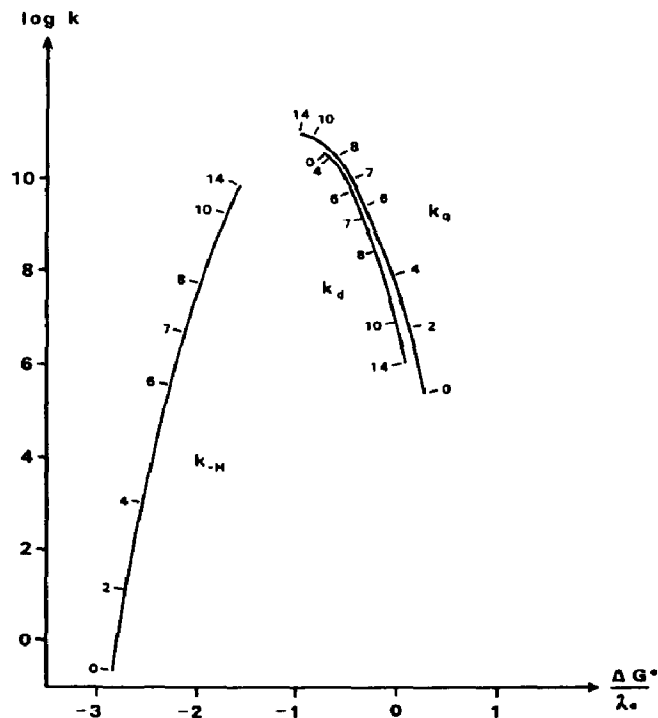


Fig. 8. Calculated rate constants (Fig. 7, *p*-hydroquinone) as a function of pH (0 - 14). $\lambda_0 = 79.5 \text{ kJ mol}^{-1}$ for k_q and k_{-H} ; $\lambda_0 = 94.2 \text{ kJ mol}^{-1}$ for k_d .

by the theoretical calculations, because k_a (eqn. (1)) increases at the same time that k_{-H} decreases (Fig. 8).

With *p*-quinone as the quencher, the rate constants calculated using Marcus theory are near the diffusion-controlled limit over the whole pH range, with the exception of k_a which is identical with that represented in Fig. 8. Since the experimental dependence is analogous to the curve determined for the hydroquinones it is not predicted by the calculations. The failure of the Marcus calculations to explain the increase in [S] at low pH for the hydroquinones could be due to intermediate steps in the reaction mechanism being neglected. It may well be possible that protons are exchanged on the successor complex $Ru^+ \dots H_2Q^+$ before it dissociates (Fig. 9). At low pH, k_a will, in this case, increase more rapidly than k_b because of electrostatic repulsion. The total concentration of semiquinone will therefore increase as the pH decreases.

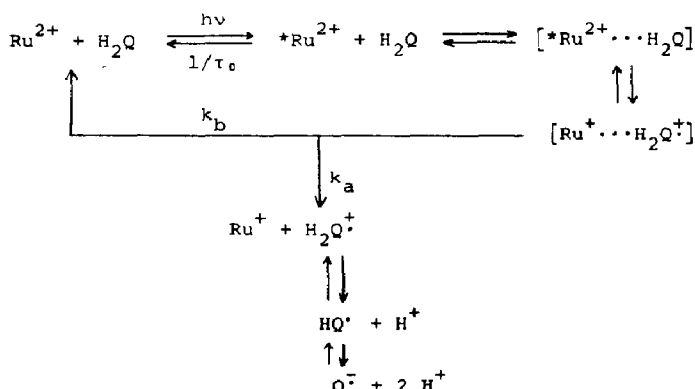
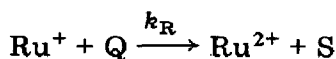


Fig. 9. Photochemical reactions of $Ru(bpy)_3^{2+}$ (Ru^{2+}) with hydroquinones (H_2Q).

Another possibility would be a mechanism in which the homogeneous back reaction (k_{-H} , Fig. 7) is replaced by a fast reaction [3] between Ru^+ and Q (formed by disproportionation):



We then have a completely reversible cycle with the reaction constants $I\epsilon\phi$, k^* , k_q , k_d and k_R . Assuming a steady state for [$(^3CT)Ru(bpy)_3^{2+}$], [S] and [Ru^+] the following expression is obtained:

$$[S] = \left\{ \frac{2k_q I\epsilon\phi [Ru^{2+}] [H_2Q]}{k_d(k^* + k_q[H_2Q])} \right\}^{1/2} \quad (4)$$

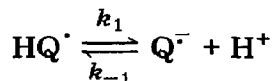
This formula gives results similar to those presented in Figs. 1 and 2 (formula (1)) and it cannot, therefore, explain the increase in [S] at low pH either.

4. Conclusions of the model calculations for coupled proton- and electron-exchange reactions

Calculations based on the Marcus model yield results in reasonable agreement with experiment in the high to medium pH range. They do not predict the experimentally observed increase in the radical concentration in the low pH range. The most questionable point in the kinetic calculation is the use of S instead of the detailed protonated forms of the semiquinone. This simplified formalism is correct only if the following two conditions are fulfilled: (i) the proton exchange reactions are always faster than the considered redox reaction; (ii) the electron transfer always proceeds through the same semiquinonic form.

These conditions are, indeed, probably fulfilled at $\text{pH} > \text{pK}(\text{HQ}^\cdot)$ (i.e. $\text{pH} > 4.5$) where essentially Q^\cdot and H_2Q ($\text{pH} < 9$) are present.

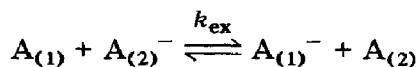
At lower pH these conditions do not apply. For instance, Smith and Carrington [9] have estimated the rates k_1 and k_{-1} of proton transfer:



$k_1 = 8 \times 10^6 \text{ s}^{-1}$ for *p*-hydroquinone and $k_1 = 3.2 \times 10^8 \text{ s}^{-1}$ for pyrocatechol; $k_{-1} = 4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for *p*-hydroquinone and $k_{-1} = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for pyrocatechol. It might be necessary to consider a more detailed mechanism which takes into account these rates of proton exchange. Unfortunately the available kinetic data are not well established, as pointed out by Loth *et al.* [24].

4.1. Electron exchange reactions

The linewidth of an ESR spectrum is, in certain cases, directly determined by an electron exchange process:



The linewidth ΔH_{pp} is given by

$$\Delta H_{\text{pp}} = \Delta H_{\text{pp}}^\circ + \frac{2}{\gamma_e 3^{1/2}} k_{\text{ex}} [\text{A}] \quad (5)$$

where $\Delta H_{\text{pp}}^\circ$ is the natural linewidth in the absence of the diamagnetic form, γ_e is the electron gyromagnetic ratio and k_{ex} is the rate constant of the self-exchange process [25]. ΔH_{pp} is the peak-to-peak width of the first derivative ESR spectrum, and the factor $2/3^{1/2}$ arises from the assumption of a Lorentzian lineshape [25].

We have measured the linewidth ΔH_{pp} of the central line of the ESR spectrum of *p*-benzosemiquinone at various pH values and at different concentrations of *p*-hydroquinone or *p*-quinone.

If Q (Q, *p*-quinone) reacts with $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ in an oxidative quenching reaction, an ESR spectrum of the semiquinoid form is obtained

whose linewidth depends on the concentration of the quencher at $\text{pH} > 5$. In this pH range Q^- is not protonated ($\text{p}K_a^{\text{HQ}^-} = 3.9$) and the line broadening can therefore be interpreted as being due to self-exchange:



On fitting the observed line broadening to eqn. (5), a value $k_{\text{ex}} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is obtained for the self-exchange rate constant, which is in close agreement with that determined by Miller and Adams [26] in dimethylformamide ($k_{\text{ex}} = 3.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). At lower pH the linewidth becomes independent of the concentration of the quencher Q, because the latter is immediately protonated after the electron transfer has taken place. The exchange reaction



is strongly endoergic and is thus not observable. If H_2Q (*p*-hydroquinone) is used as a reductive quencher, the linewidth is independent of the quencher concentration at $\text{pH} > 5$ (Fig. 10). This is in agreement with the observations for the oxidative quenching because a very fast deprotonation of the product takes place, leaving in solution the pair $\text{Q}^-/\text{H}_2\text{Q}$ for which the exchange reaction



is, again, very unfavourable. In an intermediate pH range from about 3 to 5, the linewidth depends on the pH but not on the quencher concentration. This is due to proton exchange reactions [9]. The electron transfer pair $\text{HQ}^-/\text{H}_2\text{Q}$ again shows no observable electron exchange. At pH values below about 3, the linewidth becomes strongly dependent on the quencher concentration. Now, electron self-exchange can take place according to the reaction

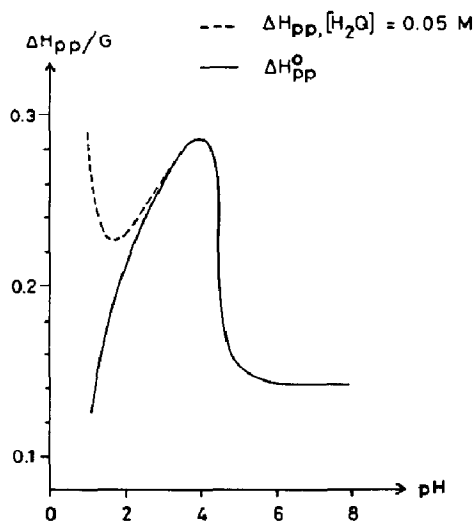


Fig. 10. Width of the centre line of the ESR spectrum of *p*-benzosemiquinone as a function of pH ($[\text{Ru}(\text{bpy})_2^{2+}] = 10^{-3} \text{ mol l}^{-1}$).



because $\text{H}_2\text{Q}^{\ddagger}$ which is formed in the quenching reaction is present in a sufficiently high equilibrium concentration ($\text{p}K_{\text{a}}^{\text{H}_2\text{Q}^{\ddagger}} = -0.8$). From the observed line broadening (Fig. 10) as a function of quencher concentration, a self-exchange rate constant $k^{\text{H}_2\text{Q}^{\ddagger}/\text{H}_2\text{Q}} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated using the equation

$$\Delta H_{\text{pp}}(\text{pH}) = \Delta H_{\text{pp}}^{\circ}(\text{pH}) + \frac{2}{\gamma_e 3^{1/2}} k_{\text{ex}} \frac{[\text{H}^+][\text{H}_2\text{Q}]}{K_{\text{a}}^{\text{H}_2\text{Q}^{\ddagger}}} \quad (10)$$

at each pH value. The self-exchange in the pair $\text{H}_2\text{Q}^{\ddagger}/\text{H}_2\text{Q}$ is one order of magnitude faster than in the pair $\text{Q}/\text{Q}^{\ddagger}$, and approaches the diffusion-controlled limit in the former. This may be due to the possibility of a hydrogen-bridged transition state being formed in the pair $\text{H}_2\text{Q}^{\ddagger}/\text{H}_2\text{Q}$.

The photosensitized generation of radicals by electron transfer reactions from excited state (^3CT) $\text{Ru}(\text{bpy})_3^{2+}$ or from similar complexes may be studied conveniently by ESR spectroscopy, because light in the visible energy range can be used for the generation of such radicals. Investigation of other systems is in progress in this laboratory.

Acknowledgments

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