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Oxidative Quenching of *Rubipy_3^{2+} by *ortho-* and *para*-Quinones in Aprotic Media

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Both *para-* and *ortho*-quinones are able to oxidize transition metal complexes when thermodynamic requirements are met [1–4], these reactions being of great biological and catalytical importance [4–8]. However, the elucidation of the kinetics and mechanism of the quinone redox reactions presents a challenging problem as there are several possible types of the interaction between the metal complexes and quinones, each one leading to different types of products. Both *o-* and *p*-quinones are able to participate in one- or formally two-electron processes producing, in aprotic media, semiquinone radical-anions or dianions respectively. These reduced forms may be either direct products of the redox processes, or they may be ligated to the oxidized central metal atom depending on various properties of the particular system [3].

Until now the redox reactions of metal complexes with *ortho-* and *para*-quinones were always treated as two distinct types of redox processes. However, as was shown recently [3], essentially identical mechanisms operate in the 'inner-sphere' one-electron oxidation of coordinatively unsaturated transition metal complexes by both *ortho-* and *para*-quinones, in spite of sterically different pathways available for the mutual approach of the metal complex and the quinone, as well as different coordinative properties of the two quinone isomers.

In order to compare the redox behaviour of *ortho-* and *para*-quinones in a typical 'outer-sphere' redox process involving coordinatively saturated complex, we performed the study of the luminiscence quenching of electronically excited *Rubipy_3^{2+} by a series of *o-* and *p*-quinones in aprotic media.

Experimental

All quinones were obtained from Fluka, with the exception of 2,6-di-tert-butyl-*p*-benzoquinone (Aldrich). All *p*-quinones and the 9,10-phenanthrenequinone were purified by vacuum sublimation whereas other *o*-quinones were used as obtained. $\text{Rubipy}_3\text{Cl}_2\cdot n\text{H}_2\text{O}$ was obtained from Carlo Erba. All experiments were carried out in air-saturated N,N'-dimethylformamide (DMF), Merck-Uvasol. The luminiscence quenching was studied with a Perkin-Elmer MPF 3 Spectrofluorometer using 90° and 60°-cell geometry for the quenching by *p-* and *o*-quinones, respectively. Lifetime and transient absorption measurements were performed on a laser flash-photolysis apparatus using a Lambda-Physics N_2-laser. All measurements in the presence of quinones were complicated by strong quinone absorption at the laser excitation wavelength (337 nm). The lifetime of the excited *Rubipy_3^{2+} in the absence of the quinones was checked in each solution of $\text{Rubipy}_3\text{Cl}_2$ used, and was found to be on average 196 ns.

Results and Discussion

All quinones quench the Rubipy_3^{2+} luminiscence with nearly diffusion-controlled rate constants which were evaluated from Stern-Volmer (SV) plots of the luminiscence intensity quenching (Table I). All SV plots were exactly linear up to rather high quenching values ($I^0/I > 4$), proving that no static quenching is present. Chemical quenching may also be excluded, as no permanent photochemical change occurs in the reaction mixture after prolonged irradiation at 436 nm except for slow photochemical reactions of some quinones with DMF, which take also place in the absence of Rubipy_3^{2+}.

TABLE I. Rate Constants of the *Rubipy_3^{2+} Quenching by Quinones.

Quinone	$k_q \times 10^{-9}$ [a]	${}^1E_{1/2}$ [b]
p-chloranil	6.89	+0.05
p-benzoquinone	6.32	−0.455
p-toluquinone	5.05	−0.505
p-naphtoquinone	4.36	−0.635
2,6-di-Bu^t-1,4-benzoquinone	2.24	−0.64
p-duroquinone	2.36	−0.765
o-chloranil	7.17	+0.155
3,5-di-Bu^t-1,2-benzoquinone	3.36	−0.49
o-naphtoquinone	5.11	−0.50
o-phenanthrenequinone	4.10	−0.59

[a] Rate constant in $\text{mol}^{-1}\ \text{l}\ \text{s}^{-1}$. [b] First half-wave reduction potential (V) measured in 10^{-1} mol l^{-1} solutions of Bu_4NClO_4 in DMF *vs.* SCE.

Weak transient absorption at 420 nm was observed in the case of the quenching by *p*-duroquinone, which

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is the only quinone suitable for laser flash photolysis due to its low partial absorption at the excitation wavelength of 337 nm. This transient was tentatively attributed to a *p*-durosemiquinone radical, as no other solution component absorbs strongly in this wavelength region. Any detailed analysis was made impossible by Rubipy_3^{2+} bleaching occurring at the same wavelength; nevertheless, this transient absorption may be considered as evidence in favour of the electron-transfer mechanism of the quenching process.

The electron-transfer quenching mechanism (eqn. 1, Q denotes both *o*- and *p*-quinones):

$$^*\text{Rubipy}_3^{2+} + \text{Q} \xrightarrow[k_q]{} \text{Rubipy}_3^{3+} + \text{Q}^{\overline{\cdot}} \qquad (1)$$

and is strongly evidenced by the correlation of the quenching rate constant, log k_q, with the values of the first quinone reduction potentials, $^1E_{1/2}$ (Fig. 1)*.

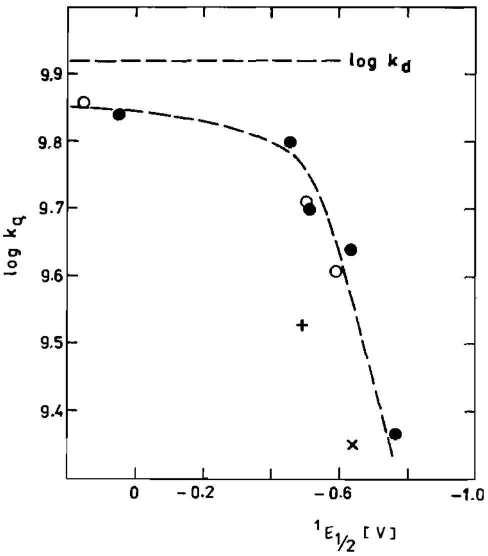

Fig. 1. Correlation of the quenching rate constant, log k_q, of $^*\text{Rubipy}_3^{2+}$ quenching with the first quinone reduction potential. ○: *o*-quinones; ●: *p*-quinones; +: 3,5-di-Bu^t-*o*-quinone; x: 2,6-di-Bu^t-*p*-quinone.

The values of log k_q asymptotically approach the diffusion-controlled limit (log k_d = 9.92 l mol^{-1} s^{-1} in DMF at 25 °C) as the thermodynamic oxidizing power of the quinone increases, *i.e.* as the reaction (1) becomes more exoergonic. This behaviour is exactly that expected [9, 10] for the *oxidative quenching* of $^*\text{Rubipy}_3^{2+}$ by quinones according to eqn. 1. Moreover, the oxidative quenching of $^*\text{Rubipy}_3^{2+}$ by *p*-benzoquinone has been recently proved to take place in aqueous media [2].

As no permanent photochemical change is present and Rubipy_3^{2+} bleaching observed in some cases is rather fast, the quenching by eqn. 1 should be followed by a fast back reaction (2):

$$\text{Rubipy}_3^{3+} + \text{Q}^{\overline{\cdot}} \longrightarrow \text{Rubipy}_3^{2+} + \text{Q} \qquad (2)$$

The rate constants of the oxidative-quenching of $^*\text{Rubipy}_3^{2+}$ by quinones (eqn. 1) follow the same dependence upon $^1E_{1/2}$ for both *ortho*- and *para*-quinones (Fig. 1), proving that the quinone isomers react with $^*\text{Rubipy}_3^{2+}$ via the same mechanism, the Marcus reorganizational energy and the degree of adiabacity (the pre-exponential factor) being approximately the same. It may thus be assumed that the same type of orbital interaction operates regardless of the *o*- and *p*-character of the quinone. The oxidation of excited $^*\text{Rubipy}_3^{2+}$ by both *o*- and *p*-quinones may be best regarded as an outer sphere redox process taking place presumably via weak interaction between the singly occupied π^*-bipy orbital of the MLCT-excited $^*\text{Rubipy}_3^{2+}$ and π^*-orbitals (LUMO) of the quinones.

Interestingly, di-tert.Butyl derivatives of both *ortho*- and *para*-quinones quench $^*\text{Rubipy}_3^{2+}$ more slowly than might be expected based on their $^1E_{1/2}$ values. This is presumably due to the bulky Bu^t groups preventing close mutual approach of the reactants thereby decreasing the adiabaticity of the reaction. The ability of the quinone for the plane-to-plane approach with the bipy-ligands in the $^*\text{Rubipy}_3^{2+}$ complex thus seems to be more important in determining the redox-orbital interaction [12] between the reactants than does the sterical accessibility of the quinone oxygen atoms.

Both *ortho*- and *para*-quinones are equally good oxidative agents, even for coordinatively-saturated transition metal complexes reacting via an outer-sphere mechanism. Both quinone isomers are thus able to play an important role as redox catalysts which may be coupled with the proton-transfer reactions or, in the case of *o*-quinones, with great ability of *o*-semiquinone radicals and dianions to chelate both transition [4] and non-transition [13] metal ions.

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*These half-wave potentials may be regarded as standard electrode potentials $^1E°$, as they correspond to electrochemically fully reversible processes.

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