Triplet state and semiquinone free radical of 5-methoxyquinizarin: A laser flash photolysis and pulse radiolysis study

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The triplet(T) state properties like T-T absorption spectra, quantum yield, energy level and decay kinetics of 5-methoxyquinizarin (5-methoxy-1,4-dihydroxy-9,10-anthraquinone; MQZ) have been investigated in cyclohexane, acetonitrile and isopropyl alcohol using nanosecond laser flash photolysis technique. In isopropyl alcohol, a neutral semiquinone radical is also formed which has been characterised by comparing the long lived transient spectra with the MQZ-semiquinone spectra obtained by pulse radiolysis of MQZ in the same solvent. A relatively small amount of a long lived transient formed in cyclohexane and acetonitrile, along with the triplet state of MQZ, could not be characterised unambiguously, but has been attributed to the semiquinone radical of MQZ, produced by the reaction of the excited states of the quinone with the solvent. The quantum yield of the semiquinone radical in isopropyl alcohol is considerably higher than the triplet quantum yield, showing that both the excited singlet and the triplet states of the quinone probably react with the solvent molecules to form the semiquinone radical. The photophysical properties of the triplet and the semiquinone radical of MQZ have been compared with those of simple 1,4-disubstituted anthraquinones.

Amino and hydroxy substituted 9,10-anthraquinones have long been used as dispersed dyes for colouring synthetic polymer materials. It has been observed that the light fastness of these anthraquinonoid dyes is often hampered by catalytic fading when applied as mixtures. Among several mechanisms suggested for photobleaching, the most popular is the formation of intermediate singlet molecular oxygen by reactions of the triplet states of the anthraquinonoid dyes with ground state triplet oxygen. Hence the ability of bleaching is related to the quantum efficiencies of formation of the triplet states (φ₁), which depends upon the nature and position of the substituents in the basic anthraquinone moiety. Triplet states of quinones and their derivatives are well known to form semiquinone radicals by abstracting hydrogen atoms from hydrogen donating solvents. The anthrasemiquinone radicals are also involved in the photosensitized degradation of textile materials dyed with anthraquinonoid dyes. The photochemistry of quinones also plays an important role in a number of biological processes, e.g., the initiation of biological electron transport through light absorption by the quinones.

The triplet state and the semiquinone characteristics of 1,4-amino and hydroxy disubstituted anthraquinones are already reported. In the present work the triplet state and the semiquinone characteristics of MQZ, a 5-methoxy derivative of 1,4-dihydroxy-9,10-anthraquinone, were investigated in different solvents like cyclohexane, acetonitrile and isopropyl alcohol to understand the effect of the additional methoxy group on the excited state characteristics of the substituted quinones.

Materials and Methods

Pure MQZ was kindly donated by Dr J M Bruce of Manchester University, U.K., and was used without further purification. All solvents were of spectroscopic grade from Spectrochem (India) and used without further purification. Anthracene, biphenyl and fluorenone (scintillation grade from J.T. Baker Chemical Co., USA) and perylene (Aldrich) were used as received. All solutions were deoxygenated by bubbling oxygen-free nitrogen (IOLAR grade from Indian Oxygen Ltd.) for about 15 min, using a proper solvent trap prior to the solution.

Ground state absorption spectra were recorded with a Shimadzu UV-160 A spectrophotometer. Nanosecond flash photolysis experiments were carried out using the laser kinetic spectrometer model K 347 (Applied Photophysics, U.K.), the details of which have been described earlier. Pulse radiolysis experiments were conducted with a 7 MeV linear electron accelerator (Ray Technology, U.K.). The details of the pulse radiolysis set up have been described elsewhere.
Results and Discussions

Transient absorption spectra and decay kinetics

Time-resolved difference [(transient)-(parent)] absorption spectra produced by KrF excimer laser (248 nm) excitation of MQZ in cyclohexane and isopropyl alcohol are shown in Figs 1 and 2 respectively. In acetonitrile, the time-resolved spectra were qualitatively identical to those in cyclohexane.

The time-resolved spectra in cyclohexane (Fig.1) and acetonitrile indicate that in both the solvents at least two different transients were produced. The optical density values of the long-lived transients were, however, very small in comparison to those of the short-lived transients. The decay of the short-lived transients followed a first order kinetics and the transients have been characterised as the triplet states of MQZ by the usual oxygen quenching and the triplet-triplet (T-T) energy transfer method. The first order decay rate constants \(k_T\) of the triplets are given in Table 1.

In isopropyl alcohol also, the time-resolved transient absorption spectra clearly revealed the presence of two transient species following the laser excitation. Moreover, the optical density of the long-lived transient was comparatively higher, at least in some wavelength ranges. The short-lived transient in isopropyl alcohol was characterised as the triplet state of the quinones by the usual techniques. The first order decay rate constant \(k_T\) of the triplet could be determined accurately only at selective wavelength where the overlapping of the spectra of the shorter-lived triplet and longer-lived transient was minimum. The \(k_T\) values thus determined at suitable wavelengths are given in Table 1.

The short lifetimes \(=1/k_T\) of the triplet states \((\sim 6 \mu s)\) in all the three solvents may be due to the involvement of excited state intramolecular proton

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\phi_T)</th>
<th>(\epsilon_T(\lambda, \text{nm})) ((10^4 \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}))</th>
<th>(k_T) ((10^4 \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>0.17±0.03</td>
<td>1.6±0.2(320)</td>
<td>1.8±0.2</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.24±0.04</td>
<td>0.7±0.2(600)</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.12±0.03</td>
<td>2.2±0.4(320)</td>
<td>2.5±0.3</td>
</tr>
</tbody>
</table>

Table 1—Photophysical characteristics of the triplet state and the semiquinone radical of MQZ in different solvents

(a) Triplet Characteristics:

(b) Semiquinone Characteristics:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\phi_{OH^-})</th>
<th>(\epsilon_{OH^-}(\lambda, \text{nm})) ((10^3 \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}))</th>
<th>(2k_{OH^-}) ((10^4 \text{mol}^{-1}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl alcohol</td>
<td>0.20±0.03</td>
<td>4.4±0.3(600)</td>
<td>6.6±0.3</td>
</tr>
</tbody>
</table>
transfer (ESIPT\textsuperscript{13–16}), a likely process as the two hydroxy groups in MQZ are intramolecularly hydrogen-bonded to the two quinonoid oxygens. It was, however, difficult to obtain any direct evidence of ESIPT process in the T\textsubscript{1} state, since the ESIPT is a much faster process than the triplet decay rate. Considering that the ESIPT process is occurring, the triplet state structure of MQZ is most likely to be a rapid equilibrium one of the two proton transferred forms (Scheme 1).

![Scheme 1](image)

A careful investigation of the time-resolved spectra of the transients produced in all the three solvents, especially in isopropyl alcohol, revealed that the longer-lived transients were also present immediately after the laser excitation. The longer-lived transient spectra obtained in isopropyl alcohol were qualitatively identical to the absorption spectra of the neutral semiquinone radical of MQZ, obtained by pulse radiolysis study in pure isopropyl alcohol, in the wavelength range 340–760 nm. The difference absorption spectrum of the semiquinone radical produced by pulse radiolysis of MQZ in isopropyl alcohol is shown in Fig. 3. Hence the longer-lived transient produced in isopropyl alcohol by laser flash photolysis was characterised as the neutral semiquinone radical, probably formed by both the triplet (\textsuperscript{3}Q\textsubscript{1}) and the excited singlet (\textsuperscript{1}Q\textsubscript{1}) states of the quinones abstracting a hydrogen atom from the solvent\textsuperscript{5–7,10}.

\[
\text{\textsuperscript{3}Q\textsubscript{1} (\textsuperscript{3}Q\textsubscript{1}) + (CH\textsubscript{3})\textsubscript{2}CHOH \rightarrow QH \textsuperscript{+} + (CH\textsubscript{3})\textsubscript{2}COH} 
\]

... (1)

The isopropyl ketyl radicals (CH\textsubscript{3})\textsubscript{2}COH] thus formed in reaction 1 could also react with the ground state quinones (\textsuperscript{1}Q\textsubscript{0}) to produce more semiquinone radicals\textsuperscript{5–10}.

\[
\text{\textsuperscript{1}Q\textsubscript{0} + (CH\textsubscript{3})\textsubscript{2}COH \rightarrow QH + (CH\textsubscript{3})\textsubscript{2}CO} 
\]

... (2)

However, unlike juglone (5-hydroxy-1,4-naphthoquinone)\textsuperscript{10} and 1,4-disubstituted-9,10-anthraquinones\textsuperscript{5} the reaction 2 was not clearly indicated in the kinetic spectrophotometric traces for MQZ.

The long-lived transient absorption spectra in cyclohexane and acetonitrile were so weak that it was difficult to characterise the species. However, comparing the difference absorption spectrum of this transient (Fig.1) with the corresponding spectrum in isopropyl alcohol (Fig.2) and also comparing similar results obtained for 1,4-amino and hydroxy disubstituted 9,10-anthraquinones\textsuperscript{5}, it can be stated that the long-lived transient produced in these two solvents is the reduced semiquinone radical of MQZ. The latter is formed probably by a hydrogen abstraction reaction similar to reaction 1. The S\textsubscript{1} state of the quinone probably reacts with the solvent molecules of cyclohexane and acetonitrile, which are not normally hydrogen donating solvents.

The semiquinone radicals produced in isopropyl alcohol decayed by a second-order process, attributed to their disproportionation into the parent quinone (\textsuperscript{1}Q\textsubscript{0}) and the fully reduced hydroquinone (QH\textsubscript{2}).

\[
2QH \rightarrow \text{\textsuperscript{1}Q\textsubscript{0} + QH\textsubscript{2}} 
\]

... (3)

The second-order decay rate constants of the semiquinone radicals (2k\textsubscript{QH}) determined by pulse radiolysis in isopropyl alcohol, are given in Table 2.

**Triplet energy levels**

The energy of the first triplet state (\textit{E}\textsubscript{T}) of MQZ in cyclohexane was determined by triplet-triplet energy transfer method\textsuperscript{17}. T-T energy transfer was observed from anthracene (\textit{E}\textsubscript{T} = 176 kJ mol\textsuperscript{-1}) to MQZ, while T-T energy transfer occurred from the latter to perylene (\textit{E}\textsubscript{T} = 151 kJ mol\textsuperscript{-1}). The triplet energy of MQZ was thus estimated to be in the range of 151–176 kJ mol\textsuperscript{-1}. It must be mentioned here that the triplet energy of MQZ is in the same range as those of 1,4-, 1,5- and 1,8- amino and hydroxy disubstituted anthraquinones\textsuperscript{5,18}. Thus, the additional methoxy group does not have any significant effect on the triplet state energies of the substituted anthraquinones.

**Extinction coefficient (\textit{e}\textsubscript{T}) and corrected spectra**

Extinction coefficient for T-T absorption (\textit{e}\textsubscript{T}) was determined by energy transfer method\textsuperscript{19}, using XeF
excimer laser (351 nm) as the excitation source, as MQZ has negligible absorption at this wavelength. The composition of the solution was maintained in such a way that at least 90% of the excitation laser light was absorbed by the donor, thus minimising the formation of the acceptor triplet by direct excitation. For cyclohexane and isopropyl alcohol, anthracene triplet \( \epsilon_{T} = 6.47 \times 10^{4} \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1} \) in cyclohexane at 422.5 nm, and \( \epsilon_{T} = 6.35 \times 10^{4} \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1} \) in ethyl alcohol at 420 nm was taken to be 5.1 under our experimental condition. Therefore, the extinction coefficient \( \epsilon_{T} \) at any particular wavelength \( \lambda \) was calculated as, 

\[
\epsilon_{T} = \epsilon_{S} + \Delta \text{OD}_{T}/[Q_{1}]
\]  

where \( \epsilon_{S} \) is the extinction coefficient of the ground state absorption and \( \Delta \text{OD}_{T} \) is the observed [(triplet) - (quione)] difference in optical density at the wavelength of interest and \( [Q_{1}] \) is the concentration of the triplet formed, estimated using the experimentally determined \( \epsilon_{T} \) and the difference in optical density at that particular wavelength. Hence the true or absolute T-T absorption spectra were determined by applying Eq.4 to the difference absorption spectra of the triplets in cyclohexane and acetonitrile and they are presented in Fig. 4. It was not possible to determine the true T-T absorption spectra in isopropyl alcohol due to the fact that the difference absorption spectra obtained immediately after the laser pulse could not be assigned to pure triplet but a combination of the triplet and the semiquinone radical formed from the singlet and triplet states, since an appreciable amount of the radical is also formed immediately after the laser pulse, was indicated by the time-resolved spectra and also by the kinetic traces (Fig. 4).

Extinction coefficients for the semiquinone radical absorption (\( \epsilon_{QH} \)) in isopropyl alcohol were determined using pulse radiolysis method. The G-value for semiquinone radical formation (\( G_{QH} \)) was taken to be 5.1 under our experimental condition. Therefore, the extinction coefficient \( \epsilon_{QH} \) at any particular wavelength \( \lambda \) was calculated as, 

\[
\epsilon_{QH} = \epsilon_{S} + \frac{\Delta \text{OD}_{OH} \times \epsilon_{QH} \times G_{QH}}{\text{OD}_{QH} \times G_{QH}} \tag{5}
\]

where \( \Delta \text{OD}_{OH} \) is the observed semiquinone-quione difference in optical density at wavelength \( \lambda \), \( \text{OD}_{QH} \) is the optical density of (SCN)\(_{2}^{2-} \) radicals at 500 nm formed in air-saturated thiocyanate dosimeter solution under an isodose condition, \( \epsilon_{QH} \) is the extinction coefficient for the (SCN)\(_{2}^{2-} \) radical absorption at 500 nm, taken to be 7.1 \times 10^{3} \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1} \) and \( G_{QH} \) is the G-value for semiquinone radical formation, taken to be 2.9 molecules (100 eV)\(^{-1}\). The true absorption spectra of semiquinone radicals were determined by two methods. First, from the difference absorption spectra obtained by pulse radiolysis, applying Eq.5 to correct them. The corrected absorption spectra of the semiquinone radicals of MQZ in isopropyl alcohol thus obtained from pulse radiolysis experiment are shown in Fig. 5. In the second method, the extinction coefficient values of the semiquinone radical at a
suitable wavelength (in the range 600-700 nm, where the parent quinone does not absorb), obtained from pulse radiolysis data, were used to correct the difference absorption spectra of the semiquinone obtained by laser flash photolysis (18 μs after the laser flash, Fig. 2), using an equation similar to Eq. 4. The corrected semiquinone absorption spectrum thus obtained from flash photolysis experiment is also presented in Fig. 5. Comparison of the true semiquinone spectra obtained by the above two methods shows that the peak positions and shapes of the spectra are in good agreement. The little differences in the absolute extinction coefficient values in the wavelength region 380 nm-500 nm may be due to the uncertainty of getting correct values of the extinction coefficient in this wavelength region of high ground state depletion and/or due to the formation of some permanent products in either of the two techniques.

Quantum yields of triplets and semiquinone radicals

From the known extinction coefficients for T-T and semiquinone radical absorption, it had been possible to determine the singlet to triplet crossing efficiency or triplet quantum yield (φ_T) and the quantum yield of semiquinone radical formation (φ_QH) by the comparative method. For determination of φ_T and φ_QH, the quantum yield of biphenyl triplet in cyclohexane was used as the reference (φ_T = 0.84 and ε_T = 4.28 × 10^4 dm^3mol⁻¹cm⁻¹ at 361.5 nm). For φ_T determination the difference in optical density (ΔOD_T), obtained immediately after the laser pulse, was taken at a wavelength where the overlapping of the short-lived triplet absorption was minimum. Also, for both the cases, the wavelengths chosen were such that the absorption coefficients of the ground state quinones were either negligible or zero. The values of φ_T and φ_QH thus obtained are given in Table 1.

Quantum yield of triplet formation for MQZ is somewhat higher than that of 1,4-amino and hydroxy disubstituted anthraquinones. This may be due to the fact that the introduction of the methoxy group in one benzenoid ring of the quinone perturbs the intra-molecular hydrogen bonded structure of the parent 1,4-dihydroxy-9,10-anthraquinone and thus increases its quinone character and consequently the triplet quantum yield.

It is very interesting to note that in the isopropyl alcohol solution the φ_QH values are significantly higher than the φ_T values. Hence, it is evident that the triplet state was not the only precursor for the semiquinone radical formation. The semiquinone radicals also may have been formed by the reaction of the excited singlet states of the quinones with the solvents, as was also evident from the time-resolved transient absorption spectra. Formation of the semiquinone radicals by the reaction of isopropyl ketyl radicals with the ground state quinones (reaction 2), may also contribute to the higher φ_QH values.

The present studies thus indicate that in hydrogen atom donating solvents like isopropyl alcohol, the semiquinone free radicals are formed quite substantially over and above the usual triplet state of the quinone due to the H-abstraction by the latter from the solvent. The singlet excited state of the quinone is also involved as the precursor of the semiquinone radicals in such solvents. A quantitative estimation of the contribution of the excited singlet states to the semiquinone formation has, however, not been possible in the present experimental conditions as the other channels (e.g. reaction of the triplets with the solvent molecules (Eq. 1) and the reaction of CH₃COHCH₃ radical with the parent quinone (Eq. 2)) of semiquinone formation are not quantitatively separable. In cyclohexane and acetonitrile, a long lived transient is also formed along with the usual triplet state, attributed to be the semiquinone radical of MQZ.

The energy of the lowest triplet state of MQZ is seen to be comparable to those of the 1,4-amino and hydroxy disubstituted 9,10-anthraquinones. The triplet quantum yield of MQZ is, however, relatively higher than those of the latter anthraquinone derivatives.
References