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NANOSECOND LASER FLASH PHOTOLYSIS OF 5-HYDROXY-1,4-NAPHTHOQUINONE (JUGLONE)

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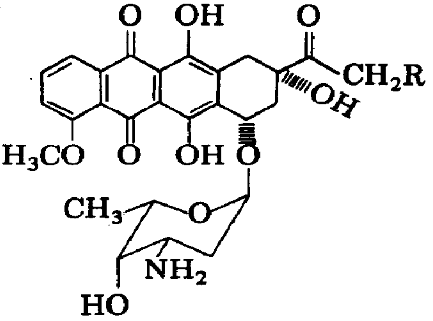
Summary

The triplet properties of juglone, a monohydroxyquinone, were thoroughly investigated in cyclohexane, acetonitrile, methanol and isopropanol, by the technique of nanosecond laser flash photolysis. While the triplets absorb at about 285, 325 and 370 nm, the decay product, which absorbs at about 370 nm, is shown to be a neutral semiquinone free radical of juglone. The extinction coefficient for T–T absorption and the quantum yields of both triplet formation and semiquinone formation are estimated, and all the kinetic parameters associated with the triplet decay are evaluated. The effect of juglone concentration, laser intensity and the presence of triplet scavengers on the triplet properties were studied.

1. Introduction

Hydroxiquinones constitute the basic functional core of first-line quinone antitumor agents such as daunorubicin (Ia) and adriamycin (Ib).



Ia : R ≡ H, daunorubicin
Ib: R ≡ OH, adriamycin

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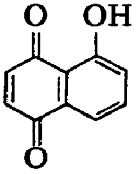
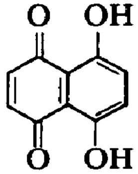
The semiquinone radicals derived from these drugs might be responsible for their antitumor action and the associated toxic effects [1]. Juglone (5-hydroxy-1,4-naphthoquinone) (II), which itself has good antitumor activity [2], is a natural product secreted by black walnut trees (juglans). Although the semiquinone chemistry of juglone [3], naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) (III) [4] and the antitumor drugs [5 - 7] is well established, very little is known about the photochemistry of these compounds [8], and in particular the role of triplet states as possible precursors of the semiquinone free radicals.



II



III

While a considerable amount of data is available on the transients produced by laser flash photolysis of some quinones and phenols [9], no information is available on the properties of transients produced by laser flash photolysis of simple hydroxyquinones such as juglone. We have previously reported [10] the luminescence characteristics of hydroxyquinones in different solvents. We now communicate our data on the triplet state properties of juglone in different solvents as studied by nanosecond laser flash photolysis, and the role of triplets in the production of semiquinone intermediates.

2. Experimental details

Nanosecond laser flash photolysis experiments were performed using a computerized laser kinetic spectrometer (Applied Photophysics Ltd., U.K.); a schematic diagram of the assembly is shown in Fig. 1. The laser excitation pulses were from a KrF excimer laser (248 nm; full width at half-maximum, 12 ns; 100 mJ) from Oxford Lasers (U.K.), and the analysing light, which passed through the first 1 mm of the solution along the laser beam, was from a pulsed 250 W xenon arc lamp (IREM, Italy). Transient absorption was monitored in Suprasil quartz cells of optical path length 1 cm. An *f*/3.4 monochromator (APP Ltd.) with a bandwidth of about 3 nm was used to select the wavelength of the analysing light. The transient absorption was monitored by an IP-28 photomultiplier tube coupled with a Gould Biomation model 4500 digital oscilloscope which was fully interfaced with an LSI-11/23 (DEC, U.S.A.) computer. The latter also controlled the sequence of the experiment through a Biodata microlink interface and the program provided for suitable storage, processing and subsequent plotting of the data on a Hewlett–Packard model HP-7470 digital plotter. Each transient

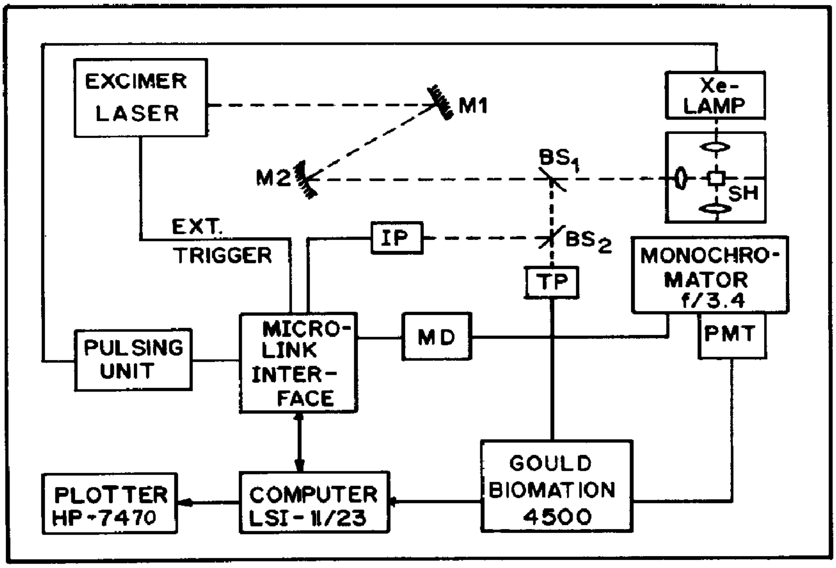


Fig. 1. Schematic diagram of laser kinetic spectrometer: M1, plane mirror; M2, concave mirror; BS1 and BS2, beam splitters; TP, triggering photodiode; IP, integrating photodiode; MD, monochromator drive; SH, sample housing.

signal was stored after averaging over four laser shots. Whenever necessary, the signal displayed on the digital oscilloscope was photographed by a Polaroid camera (Tektronix).

For kinetic analysis and determination of the extinction coefficients and quantum yields, optically thin solutions with OD(248 nm) $\leqslant$ 0.4 were used, whereas for spectral analysis a relatively concentrated solution (OD $\approx$ 0.8) was used. Biphenyl in cyclohexane was chosen [11] as the actinometer for the laser pulse in the sample position. The UV–visible absorption spectra were recorded in a microprocessor-controlled Hitachi model 330 spectrophotometer.

Juglone (Sigma) was crystallized from ethanol, dried and vacuum sublimed immediately before use. β-Carotene (Sigma) and biphenyl (May and Baker, scintillation grade) were used as received. Acetonitrile (Merck), isopropanol (Merck), methanol (Fluka) and cyclohexane (Phillips Petroleum Co., U.S.A.) were all Spectrograde solvents and were used as received. Whenever necessary, solutions were deoxygenated by bubbling high purity nitrogen (IOLAR grade from Indian Oxygen Ltd.) through them for at least 20 min.

3. Results and discussion

3.1. *Transient absorption spectra and decay kinetics*

Figure 2 shows the time-resolved absorption spectra of the transients produced after 248 nm laser excitation of a deaerated solution of about

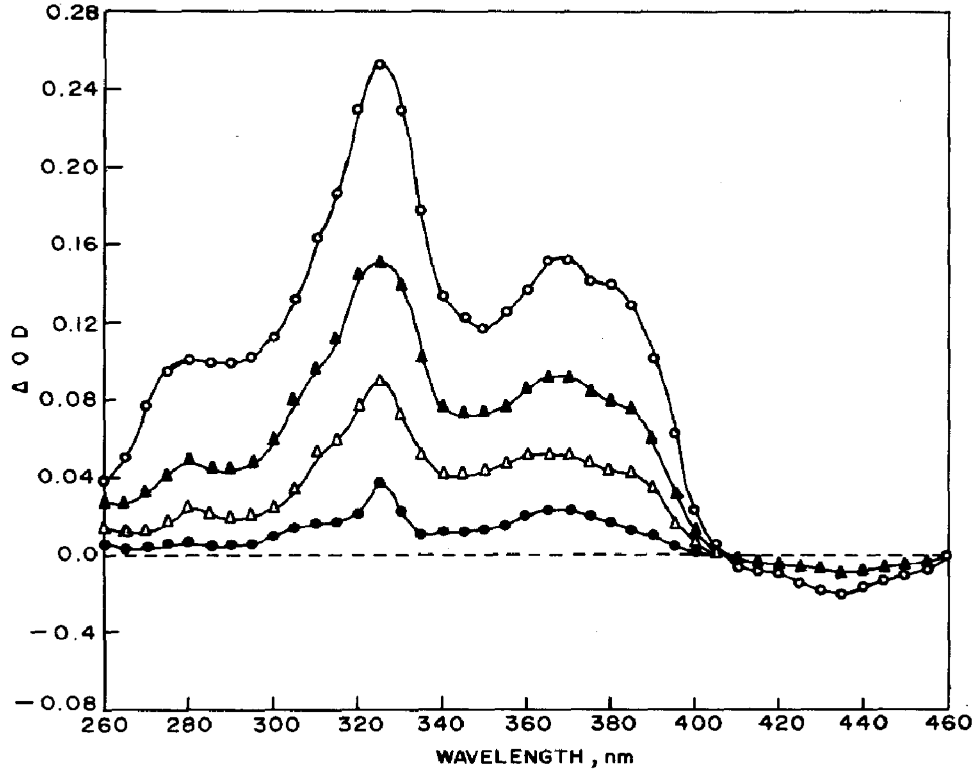


Fig. 2. Time-resolved T–T absorption spectra of juglone in cyclohexane (deaerated) 100 ns (—○—), 400 ns (—▲—), 800 ns (—△—) and 1.8 μs (—●—) after the laser flash.

10^{-5} mol dm^{-3} juglone in cyclohexane. The spectra show three peaks at about 280, 325 and 367 nm and a shoulder at about 380 nm. At each wavelength the absorption of the transient decays by first-order kinetics with a rate constant of $(1.35 \pm 0.05) \times 10^6$ s^{-1}. The permanent bleaching of the parent quinone absorption is insignificant, as is evident from the oscilloscope traces shown in Figs. 3(a) and 3(b). The complete spectra might thus be attributed to T–T absorption from the excited triplet level of juglone at about 288 kJ mol^{-1} [10]. Air saturation of the solution leads to an enhanced first-order decay rate for the transient absorption, with a rate constant of $(4.1 \pm 0.2) \times 10^6$ s^{-1}, indicating that the triplet probably reacts with oxygen.

In acetonitrile, a solvent lacking labile hydrogen atoms, the spectral characteristics of the transient species produced after the laser flash are quite similar to those in cyclohexane. But in the case of methanol and isopropanol, which are solvents with labile hydrogen atoms, the behaviour of the transients is more complex, as shown in the oscilloscope traces in Figs. 3(b), 3(d) and 4. Figure 5 shows the time-resolved spectra of the transient species produced in methanol. Immediately after the laser flash, the absorption maxima are similar to those in cyclohexane or acetonitrile. But after about 2.4 μs the absorption maximum at 325 nm vanishes completely, whereas the transient species still present in the solution has absorption

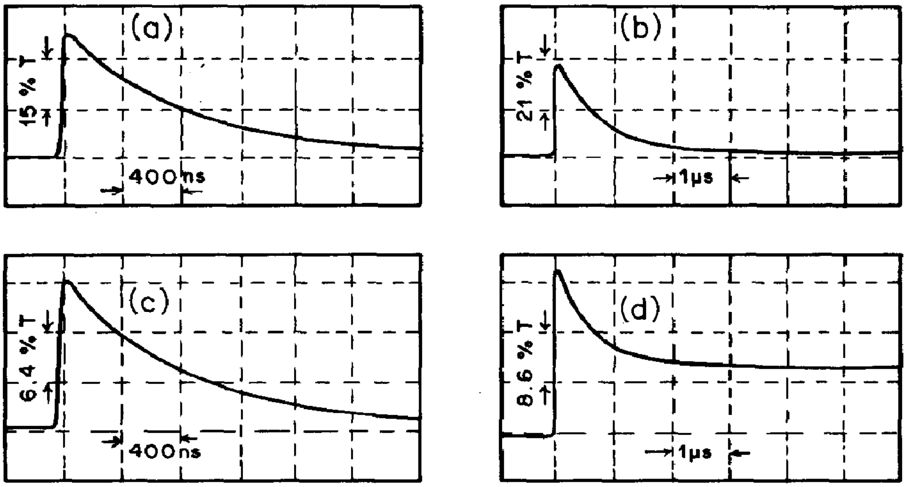


Fig. 3. Oscilloscope traces of transient absorption due to laser flash photolysis of juglone: (a) cyclohexane, 325 nm; (b) methanol, 325 nm; (c) cyclohexane, 370 nm; (d) methanol, 370 nm.

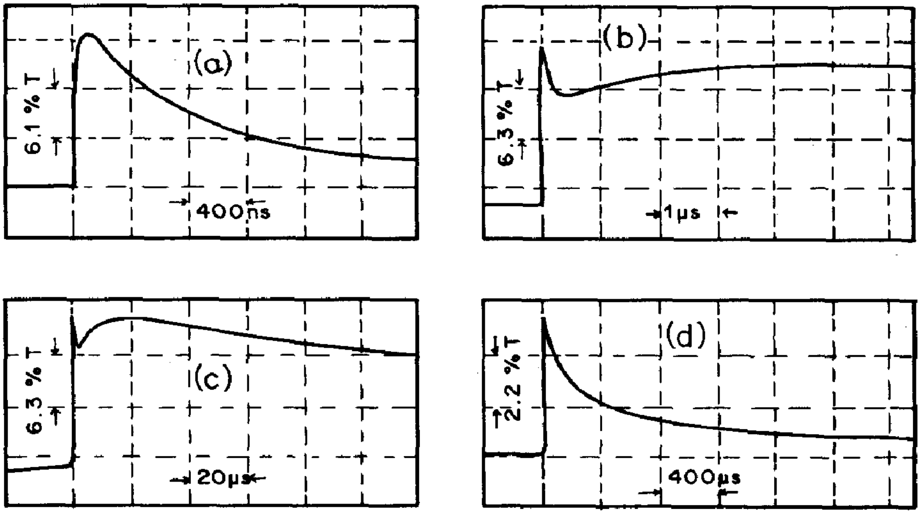


Fig. 4. Oscilloscope traces of transient absorption due to laser flash photolysis of juglone in isopropanol. Wavelength: (a) 330 nm; (b), (c) and (d), 370 nm.

peaks at about 285 nm and 365 nm. The transient decay curve at 325 nm (Fig. 3(b)) follows first-order kinetics with a rate constant of $(1.6 \pm 0.1) \times 10^6\ s^{-1}$, resulting in some residual absorption even at 2.4 μs after the laser flash. The residual absorption at 370 nm in methanol (Fig. 3(d)) is very significant. The transient decay curves at 280 and 370 nm show that the absorption decays by at least two processes, the rate of decay of the faster process following first-order kinetics with a rate constant equal to that at 325 nm, while the very slow process follows second-order kinetics with a rate constant of $(4.0 \pm 0.5) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. Although the absorption at 285 nm is only half that at 325 nm, the former does not decay completely while the latter does after 2.4 μs. Similarly, although the hump at 380 nm vanishes completely after 2.4 μs, the peak at about 370 nm remains significant. These observations indicate that the transient absorption with absorption maxima at 280 nm (sh), 325 nm, 365 nm and 380 nm (sh) observed 100 ns after the laser flash are identical in behaviour with those in cyclohexane or acetonitrile and may provisionally be attributed to T–T absorption, whereas the transient absorption maxima at 365 nm and 285 nm observed 2.4 μs after the laser flash may be assigned to the absorption of semiquinone free radical produced by the interaction of triplet with the solvent.

In isopropanol, a solvent in which the hydrogen atoms are more labile than in methanol, abstraction of a hydrogen atom by the reaction

$$^3\text{JH} + (\text{CH}_3)_2\text{CHOH} \longrightarrow \text{JH}_2^{\bullet} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} \qquad (1)$$

should be more facile and result in a better yield of juglone semiquinone free radical ($\text{JH}_2^{\bullet}$). ^{3}JH represents the lowest triplet state of juglone. Reaction (1) can then be followed by the reaction

$$\text{JH} + (\text{CH}_3)_2\dot{\text{C}}\text{OH} \longrightarrow \text{JH}_2^{\bullet} + (\text{CH}_3)_2\text{CO} \qquad (2)$$

to give a higher yield of the semiquinone. The kinetics thus become complex. The oscilloscope traces (Fig. 4) are too complex to allow any meaningful or accurate kinetic parameter to be determined, except at 330 nm (Fig. 4(a)), the analysis of which gives first-order kinetics with a decay rate constant of $(2 \pm 0.2) \times 10^6\ \text{s}^{-1}$.

A careful analysis of the time-resolved spectra (Fig. 6) of the transients shows that the spectrum monitored 100 ns after the laser flash are very similar to those in other solvents, but that a longer-lived transient is gradually formed in place of the short-lived transient. The longer-lived transient has a main absorption peak at about 370 nm with a weak absorption at 285 nm. The overall spectral behaviour is very similar to that in methanol. However, the kinetics of the decay of the longer-lived species can only be analysed at the very long time base of 20 μs division^{-1}, where the decay is somewhat simpler. Second-order kinetics, with a rate constant of $(5.9 \pm 0.5) \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ is observed. The slow growth (Figs. 4(b) and 4(c)) between about 1.5 μs and 20 μs cannot be analysed properly.

3.2. Assignment of transient absorption

Sensitization of the triplet state of β-carotene through energy transfer [12] was used to confirm that juglone triplets are generated in solution. In the absence of juglone, no β-carotene T–T absorption could be observed at 520 nm. However, on addition of 10^{-5} mol dm^{-3} juglone to a solution of 10^{-5} mol dm^{-3} β-carotene in cyclohexane, an intense absorption characteristic of T–T absorption of β-carotene developed after the laser flash. The initial absorption produced by laser flash photolysis of juglone must therefore be due to T–T absorption. The results in other solvents were comparable. However, owing to a very large energy difference between the

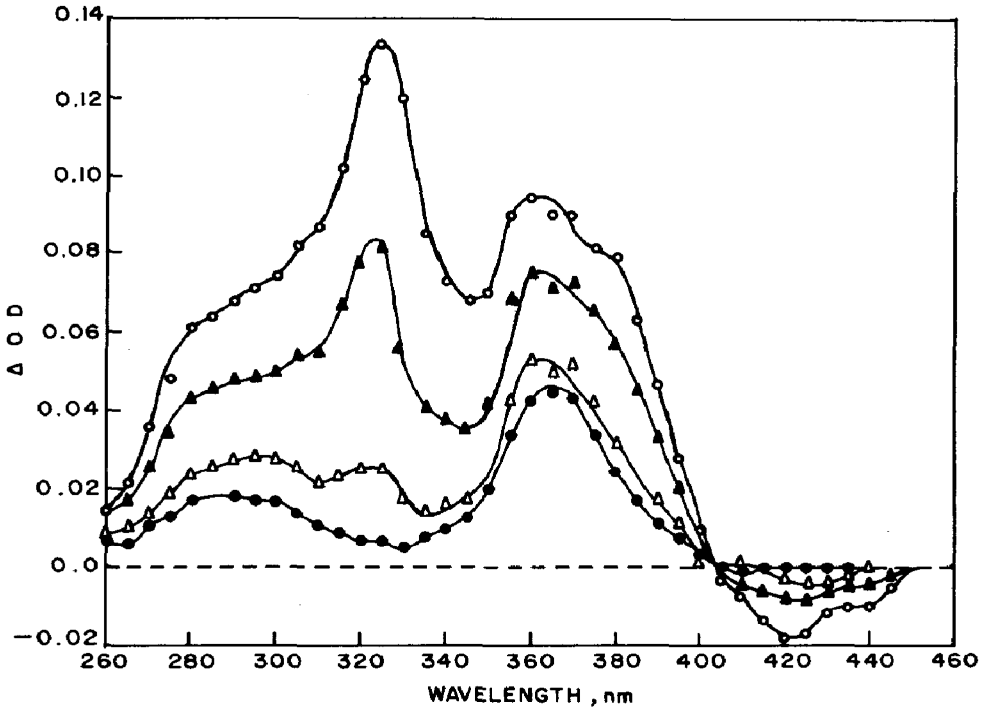


Fig. 5. Time-resolved spectra of the transients formed by laser flash photolysis of juglone in methanol 100 ns (—○—), 400 ns (—▲—), 1.2 μs (—△—) and 3.6 μs (—●—) after the laser flash.

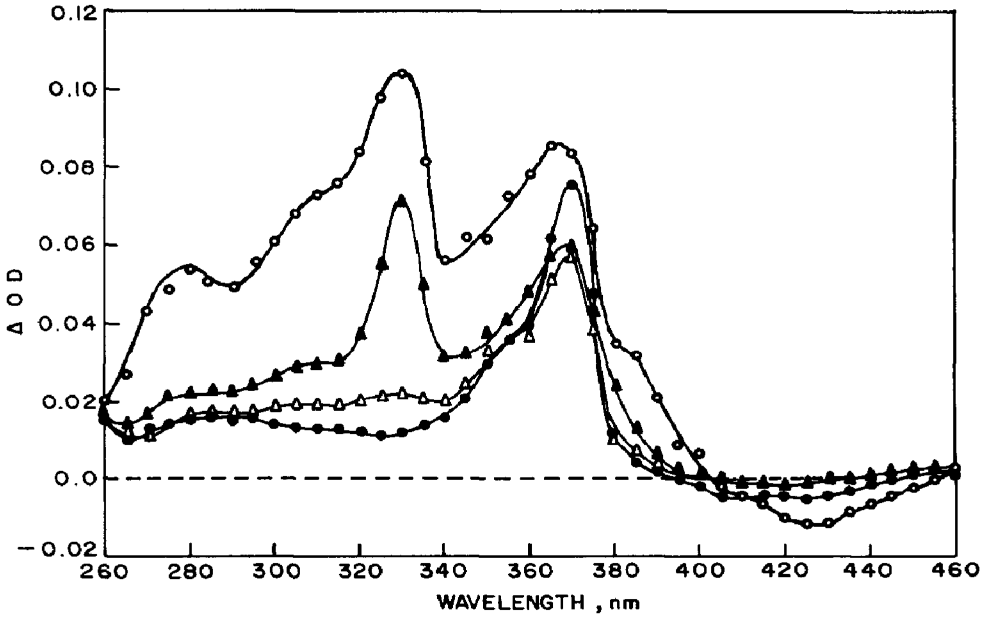


Fig. 6. Time-resolved spectra of the transients produced by laser flash photolysis of juglone in isopropanol 100 ns (—○—), 1 μs (—▲—), 2 μs (—△—) and 9 μs (—●—) after the laser flash.

juglone triplet level (about 280 - 290 kJ mol^{-1} depending on the solvent) [10] and that of β-carotene (about 75 kJ mol^{-1}) [13], the energy transfer rate was very low. In an aerated solution of juglone, the rate of disappearance of the transient at 325 nm became very fast, indicating again that a triplet state was involved.

Figures 3 and 4 clearly indicate that the triplet decay is complete after a few microseconds in all four solvents. It is well known that in solvents such as cyclohexane and acetonitrile which do not offer an abstractable hydrogen atom only triplet states are formed, but that in polar solvents such as alcohols which have abstractable hydrogen atoms the triplets may react with the solvent to give semiquinone radical [13], following the sequence of reactions:

$$^1JH_0 \xrightarrow{h\nu} {}^1JH^* \xrightarrow{k_{isc}} {}^3JH \tag{3}$$

$$^3JH \xrightarrow{k_4} {}^1JH_0 \tag{4}$$

$$^3JH + SH \xrightarrow{k_5} JH_2^{\cdot} + S^{\cdot} \tag{5}$$

$$2JH_2^{\cdot} \xrightarrow{2k_6} JH_3 + {}^1JH_0 \tag{6}$$

where $^1JH_0$ is the ground state of juglone, $JH_2^{\cdot}$ the semiquinone free radical, JH_3 the juglone hydroquinone and SH the solvent. The longer-lived transient in alcohol is thus most probably the juglone semiquinone free radical. This is in agreement with the pulse radiolysis results for juglone in aqueous solution [3], where the semiquinone absorbs at 370 nm, with negligible absorption at 325 nm. The decay of 370 nm absorption in aerated alcoholic juglone solutions became slower, indicating slow attainment of an equilibrium of the type

$$JH_2^{\cdot} + O_2 \rightleftharpoons {}^1JH_0 + HO_2^{\cdot} \tag{7}$$

3.3. *Extinction coefficient of juglone triplet*

The extinction coefficient for the T–T absorption of juglone in cyclohexane was determined using the method of energy transfer [14], from juglone triplet as donor to β-carotene triplet as acceptor ($\epsilon_T = 2.4 \times 10^5$ dm^3 mol^{-1} cm^{-1}, $k_T = 1.8 \times 10^5$ s^{-1}). Necessary corrections were introduced for the decay of acceptor triplets after they had been formed and ^3JH decay by means other than energy transfer [14]. The extinction coefficient was first determined at 280 nm, since the parent absorption is negligible at this wavelength, thus avoiding the need for any correction for the depletion of the ground state of juglone. The extinction coefficients at other wavelengths were determined after proper correction for the depletion of the ground state absorption.

Once the extinction coefficient of juglone triplets in cyclohexane is known, it is possible to estimate the extinction coefficient in the other three solvents by assuming [14] that the oscillator strength f is independent of solvent. However, this assumption may not be completely valid for solvents such as methanol and isopropanol, whose interaction with the triplets is stronger than in the case of cyclohexane and acetonitrile. The oscillator strength for T–T absorption of juglone in cyclohexane over the wavelength range 270 - 350 nm (where ground state absorption is negligible) was calculated from the expression

$$f = \frac{4.39 \times 10^{-9}}{n} \int \epsilon(\bar{\nu})\, \mathrm{d}\bar{\nu}$$

$$= \frac{4.39 \times 10^{-9}}{n} \frac{1}{C_{\mathrm{T}}} \int \mathrm{OD}(\bar{\nu})\, \mathrm{d}\bar{\nu} \qquad (8)$$

Using $\epsilon_{\mathrm{T}}(280\ \mathrm{nm}) = 2.34 \times 10^4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$ and $\epsilon_{\mathrm{T}}(325\ \mathrm{nm}) = 5.7 \times 10^4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$, f was calculated to be 0.11.

The areas under the absorption spectra of juglone triplet in cyclohexane, acetonitrile, methanol and isopropanol were compared such that OD(juglone) was equal at the excitation wavelength and the laser energy was equal for each solution. All the extinction coefficients thus calculated are given in Table 1. Using the extinction coefficients determined and the ground state singlet–singlet absorption coefficient [10], the T–T absorption spectra taken in the solvents cyclohexane and methanol were corrected for depletion of the ground state; the corrected spectra are shown in Fig. 7.

3.4. *Triplet quantum yields*

It has been shown previously [10] that the triplet quantum yield of juglone is small, resulting in very weak phosphorescence. If the extinction coefficients of the triplet in different solvents were known, the S–T crossover efficiency or triplet quantum yield ϕ_{T} could be estimated by using the comparative method [11], which involves using the expression

$$\phi_{\mathrm{T}}{}^{\mathrm{J}} = \phi_{\mathrm{T}}{}^{\mathrm{R}} \frac{\mathrm{OD}_{\mathrm{T}}{}^{\mathrm{J}}}{\mathrm{OD}_{\mathrm{T}}{}^{\mathrm{R}}} \frac{\epsilon_{\mathrm{T}}{}^{\mathrm{R}}}{\epsilon_{\mathrm{T}}{}^{\mathrm{J}}} \qquad (9)$$

where the superscripts J and R refer respectively to juglone and biphenyl, the latter being a reference compound whose quantum yield and extinction coefficient in cyclohexane are known [11]: $\epsilon_{\mathrm{T}}(361\ \mathrm{nm}) = 4.28 \times 10^4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$ and $\phi_{\mathrm{T}} = 0.84$. Optically thin ($\mathrm{OD} \leqslant 0.4$) solutions of juglone and biphenyl, with identical values of OD at 248 nm (the exciting wavelength) were irradiated separately and the number of triplets formed were determined and then used in eqn. (9) to find ϕ_{T}. The values thus calculated are given in Table 1.

TABLE 1

Photophysical parameters for the triplet state of juglone

Solvent	(ϵ_T^{λ} ± 0.05) × 10^{-4} (dm^3 mol^{-1} cm^{-1})			ϕ_T	k_T^{b} × 10^{-6} (s^{-1})	k_O × 10^{-6} (s^{-1})	k_{TT} × 10^{-10} (mol dm^{-3} s^{-1})
	280 nm	*325 nm*	*370 nm*[a]				
Cyclohexane	2,34	5.70	3.05	0.24 ± 0.02	1.35 ± 0.05	4.1 ± 0.2	1.5 ± 0.5
Acetonitrile	2.00	4.89	—	0.22 ± 0.02	1.30 ± 0.05	4.2 ± 0.2	2.5 ± 0.5
Methanol	1.96	5.06	2.98	0.21 ± 0.02	1.65 ± 0.1	6.9 ± 0.3	—
Isopropanol	1.92	3.62	—	0.18 ± 0.02	2.00 ± 0.2	—	—

[a] Corrected for depletion of singlet ground state.

[b] Intercept of the straight line obtained from the plot of k_T(obs) *vs.* [^{3}JH]$_0$.

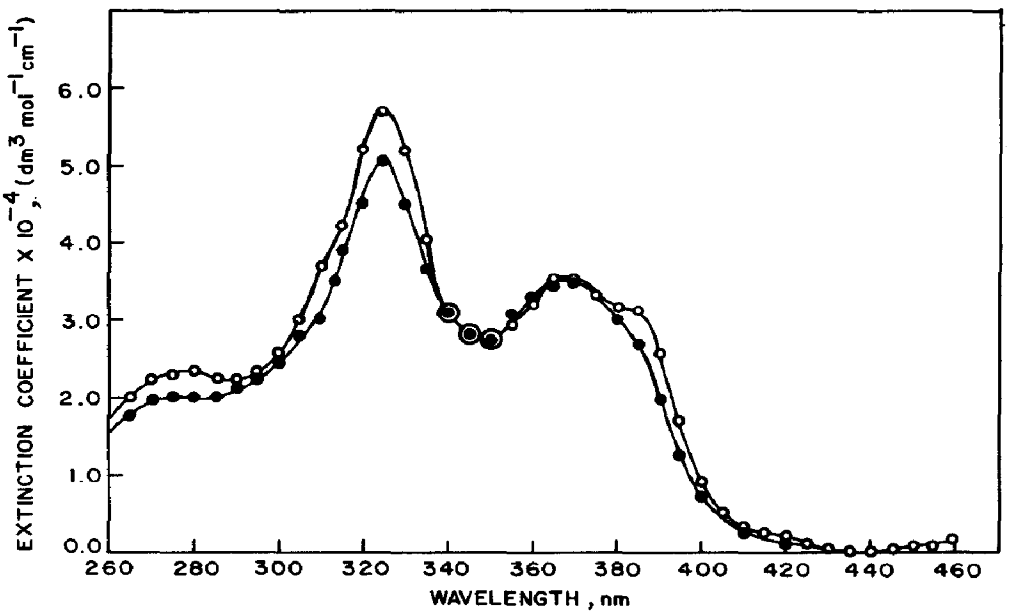


Fig. 7. Corrected T–T absorption spectra of juglone in cyclohexane (—○—) and in methanol (—●—).

3.5. *Quantum yield of juglone semiquinone production*

The interaction of excited states of juglone is different with each different solvent. In methanol and isopropanol, after the disappearance of the initially formed juglone triplets, a long-lived slow-decaying transient contributed to the absorption, and this was attributed to semiquinone free radical, $JH_2^{\cdot}$. Since the absorption spectra of juglone triplet and semiquinone free radical overlap and the peaks are also very close to each other, it was not possible to follow the rise of the absorption due to the formation of the semiquinone free radical in place of juglone triplet; we obtained a very complicated decay profile at 370 nm which made accurate kinetic analysis impossible. Hence, to estimate the quantum yield of formation of this radical, an assumption was made that the extinction coefficients of $JH_2^{\cdot}$ in water, methanol and isopropanol are equal within the acceptable limits of error associated with such measurements. This is a reasonably valid assumption since the absorption maximum is at or around 370 nm in each of the three solvents. The extinction coefficient at 370 nm was thus assumed to be $(1.25 \pm 0.05) \times 10^4$ dm^3 mol^{-1} cm^{-1} [3]. Knowing this extinction coefficient, we can now determine the quantum yield of $JH_2^{\cdot}$ formation, by a method comparable with that used for the triplet. The transient OD at 370 nm is measured at $t = 0$ (this results from ^3JH only) and after the decay of ^3JH (at $t = 3.6$ μs and $t = 9$ μs for methanol and isopropanol respectively), when it will be due to $JH_2^{\cdot}$, neglecting any decay of the radical,

$$\phi(JH_2^{\cdot}) = \frac{OD(JH_2^{\cdot})}{\epsilon(JH_2^{\cdot})} \frac{\epsilon(^3JH)}{OD(^3JH)} \phi_T(^3JH) \qquad (10)$$

The quantum yields for radical formation in methanol and isopropanol were thus estimated to be 0.25 and 0.31 respectively.

3.6. *Triplet–triplet reaction*

Both the rate of triplet decay in cyclohexane and the concentration of initial triplets formed were determined for different juglone concentrations in the range (1×10^{-5}) - (1×10^{-4}) mol dm^{-3} and at different laser intensities. The experiments were repeated in other solvents. Some of the results are shown in Fig. 8 and are discussed below.

(a) The maximum concentration $[^3\text{JH}]_0$ of the juglone triplets formed after the laser flash is proportional to the initial ground state concentration, for each laser intensity used (Fig. 8(a)). Thus in all cases, the exciting light absorbed is proportional to the incident light intensity and the distribution of the transient species is homogeneous in the cross-section (1 mm × 1 cm) of the sample observed.

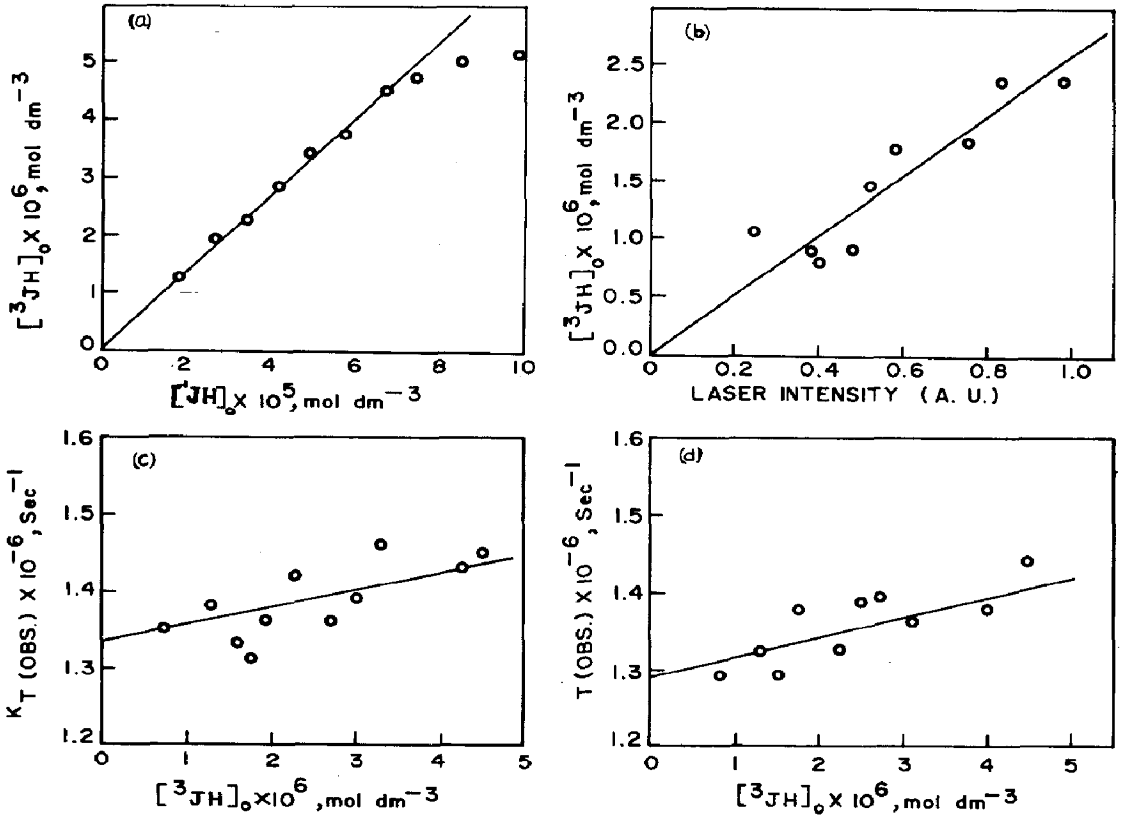


Fig. 8. (a) Maximum concentration $[^3\text{JH}]_0$ of juglone triplet formed as a function of ground state concentration of juglone in cyclohexane. (b) Maximum concentration of triplet formed in cyclohexane as a function of laser intensity. (c) Observed unimolecular decay rate constant k_T(obs) of T–T absorption in cyclohexane as a function of maximum concentration $[^3\text{JH}]_0$ of triplet formed. (d) k_T(obs) as a function of $[^3\text{JH}]_0$ in acetonitrile. For all four cases the monitoring wavelength was 325 nm.

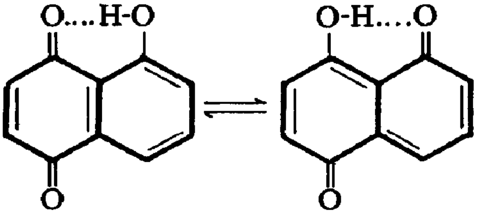
(b) For a fixed ground state concentration of juglone, the maximum concentration of the initial triplet formed after the laser flash is proportional to the laser intensity, indicating that the formation of the transient is a monophotonic process (Fig. 8(b)).

(c) As the initial concentration of the triplets formed after the laser flash becomes higher, the deviation of the decay rate from simple first-order kinetics becomes more pronounced and results in the observed initial decay rate constant becoming higher; this is due to the T–T reaction and not to the reaction of ^{3}JH with ^{1}JH, because the decay rate constant was seen to be independent of ground state concentration. Thus it is possible to determine a rate constant k_{TT} defined as the slope of the straight line obtained by plotting the initial observed rate constant of the triplet decay *vs.* the initial triplet concentration $[^3\text{JH}]_0$ [15]:

$$-\frac{\mathrm{d}}{\mathrm{d}t}\log[^3\text{JH}]_0 = (k_4 + k_5[\text{SH}]) + k_{TT}[^3\text{JH}]_0 \qquad (11)$$

4. Conclusions

Introduction of a hydroxyl group into the non-quinonoid phenyl ring of a simple quinone drastically alters the spectroscopic properties of the triplet state of the molecule. The main T–T absorption peak is at about 325 nm, with other peaks at about 285 nm, 365 nm and 385 nm, whereas for simple quinones one peak is found around 300 nm but the main visible absorption lies around 450 - 500 nm. Of course, the major differences between these cases are the values of the quantum yields and extinction coefficients. The extinction coefficient for T–T absorption in simple quinones is of the order of 5×10^3 dm^3 mol^{-1} cm^{-1}, while for juglone it is 5.7×10^4 dm^3 mol^{-1} cm^{-1}. The quantum yield of triplet formation in simple quinones is about unity [8], but for juglone the estimated value in the solvents studied is only about 0.2. Since the fluorescence quantum yield of juglone is 0.077 in cyclohexane and 0.085 in methanol [10], it can be safely concluded that internal conversion from $S_1 \rightarrow S_0$ has a quantum yield of about 0.7, *i.e.* internal conversion is the most dominant process in the photophysics of juglone. This is probably because the $S_1 \rightarrow S_0$ transition is a highly allowed transition because of the ground symmetry of the quinone. This conclusion is fully consistent with our previous results [10]. Since the phosphorescence from juglone is extremely weak [10] the forbidden $T_1 \rightarrow S_0$ transition is also quite predominant. This further strengthens our hypothesis [10] of photoenolization in the excited state [16]:



This is further supported by two other observations: (1) juglone has an extremely weak phosphorescence in 3-methylpentane, a non-polar solvent favouring only intramolecular hydrogen bonding, whereas the phosphorescence is stronger in an alcohol matrix where the more polar environment favours breakage of the intramolecular hydrogen bond [17], and (2) excited 1-hydroxy-9,10-anthraquinone undergoes fast radiationless decay in 3-methylpentane, but shows a weak phosphorescence in diethyl ether–ethanol because of breakage of the intramolecular hydrogen bonds [18].

Acknowledgments

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