Transient intermediate species active during the Fenton-mediated degradation of quinoline in oxidative media: pulsed laser spectroscopy

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Accepted 20 May 1997

Abstract

The transient kinetics for the species observed owing to the application of a pulsed ruby laser to quinoline (Q), quinoline and Fe^{3+}, and quinoline solutions in the presence of the Fenton reagent are reported in detail. The intermediates are seen to be affected by a number of factors such as reagent concentration, oxidant concentration, pH and the energy of the laser pulse. The short time delay laser transient was assigned to the Q^+-radical since it was not affected by O_2 or paramagnetic Fe^{3+}-ions added to the solution. The transient lifetime was observed to be ~ 4 μs. Biphotonic ionization was involved in the generation of the Q^+-radical. A linear dependence was observed between the amplitude of the transient and the energy of the applied pulse. A strong interaction was observed by laser spectroscopy for quinoline reacting with the Fenton reagent but not with H_2O_2 or Fe^{3+}-ions added separately. The effects of H_2O_2 and pH on the optical density of the transient at $\lambda = 490$ nm are seen to be independent. The effect of H_2O_2 was completely eliminated with ter-butyl alcohol when Fenton reagent was reacted with quinoline. This shows the presence of $^.OH$ radicals induced by the laser pulse in addition to intermediate complex formation in solution. © 1997 Elsevier Science S.A.

Keywords: Quinoline; Excited states; Transient kinetics; $^.OH$ scavengers

1. Introduction

Useful applications of photochemical reactions in the field of environmental abatement of toxic recalcitrant industrial pollutants have attracted considerable attention during the last decade [1–3]. The photo-assisted Fenton reaction in which a powerful oxidizing agent is generated, e.g. the $^.OH$ radical, has been widely reported. This radical attacks and degrades organic pollutants by hydrogen abstraction or addition to the double bond. In many cases this leads to complete abatement of the organic compound.

Partial degradation of quinoline has been reported via sewage bacteria [4], undergoing slow biodegradation in rivers [5] and in creosote mixtures [6]. Complete abatement has been reported during dark H_2O_2 oxidation [7] and ozonization [8].

The present study addresses six aspects related to the nature of the transients occurring during quinoline degradation. The details related to the nature of these transients allow us to describe the following: (a) the spectral and kinetic features of the excited state of quinoline (denoted Q hereafter) in solution; (b) the distinction between the triplet and the Q^+-radical after the pulse; (c) the interaction of the ecological oxidant H_2O_2 with the transient; (d) the interaction of the transient with added Fe^{3+}-ions; (f) the spectroscopy of the complete system of Q in the presence of H_2O_2 and Fe^{3+}-ions; finally (e) the effect of the intensity of the applied light on the generated transients.

In this study we investigated the details of the fast kinetics of Q decay following ruby laser pulse excitation. The new findings presented here are important for understanding the photodegradation in the steady state. This is reported in the second part of this study [9].

2. Experimental section

2.1. Materials employed

$FeCl_3 \cdot H_2O$, ter-butyl alcohol, Q and H_2O_2 were Fluka p.a. and used as received.

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2.2. Laser photolysis and spectrophotometric observations

Laser photolysis was carried out using the second harmonic ($\lambda = 347$ nm) of a JK-2000 ruby laser operated in the Q-switched mode. The pulse width was about 15 ns and the highest energy per pulse was ~ 15 mJ. During the laser studies the pulse energy was monitored and the experimental results normalized according to these measured energies. The mean average of the laser beam surface was 0.5 cm^2. The transient absorption changes were detected via an EG&G photomultiplier with a rise time of about 5 ns. Further details of the laser system have been reported elsewhere [10]. The pre-amplifier full band-width at 125 MHz was used to register the signals in the nanosecond range and up to 2 μs. At longer times the bandwidth was narrowed to 5 MHz. All solutions were used only once to avoid accumulation of the irradiated products and irreversible decomposition during laser photolysis. Decomposition of Q was prevented in two ways: (a) the solutions were stored in the dark before use and (b) the monitoring Xe-light used for detection of the intermediates was narrowed by Schott SKF pass band filters. These filters allowed light to come through in a region of $\Delta\lambda \approx 20$ nm and were centered each time at the appropriate λ of interest. All experiments were performed in 1 cm quartz cells in aerated solutions at room temperature.

Spectrophotometric analysis for the absorbance of the solutions was carried out by means of a Hewlett Packard 8452 diode array. The absorption spectra of Q in relatively dilute solutions extend up to 360 nm, depending slightly on the concentration of Q used. The maximum extinction coefficient for Q absorption ϵ was found to be at $\lambda = 315$ nm (3650

M^{-1} cm^{-1}). At the ruby laser excitation wavelength of $\lambda = 347$ nm the value was $\epsilon = 330$ M^{-1} cm^{-1} and laser studies had to be carried out at concentrations of 2.4–3 mM to attain optical densities D between 0.8 and 1.0. The decomposition of Q was observed to be negligible when Q was mixed with the Fenton reagent immediately before use.

3. Results and discussion

3.1. Photo-ionization of aqueous quinoline by pulse ruby laser

The transient absorption spectra of Q after the laser pulse are shown in Fig. 1 in the time range 3–100 μs. It is readily seen that the broad differential optical absorption D for the Q spectrum at different λ values after the laser pulse conserves its shape, decreasing monotonically between 3 and 100 μs (0.01 ms). This transient could be attributed to the triplet excited state or to ionic forms of Q. Triplet π–$\pi*$ excited states are usually quenched by O_2 with diffusion controlled rate constants of ~ 10^9 to 6×10^9 M^{-1} s^{-1} in aqueous solutions. The expected lifetime for the transient in Fig. 1 should be ~ 2 μs. The lifetime for the observed transients was seen not to depend on the presence of oxygen since the lifetime of the transient was the same in Ar purged or O_2 purged solutions. The transient at $\lambda = 490$ nm follows a one-exponential fit with a lifetime of 4 μs. The presence of a long lived transient is observed after the initial decay up to 25 μs but the nature of this transient could not be clarified. The lack of effect of O_2 on the transient lifetime suggests the presence
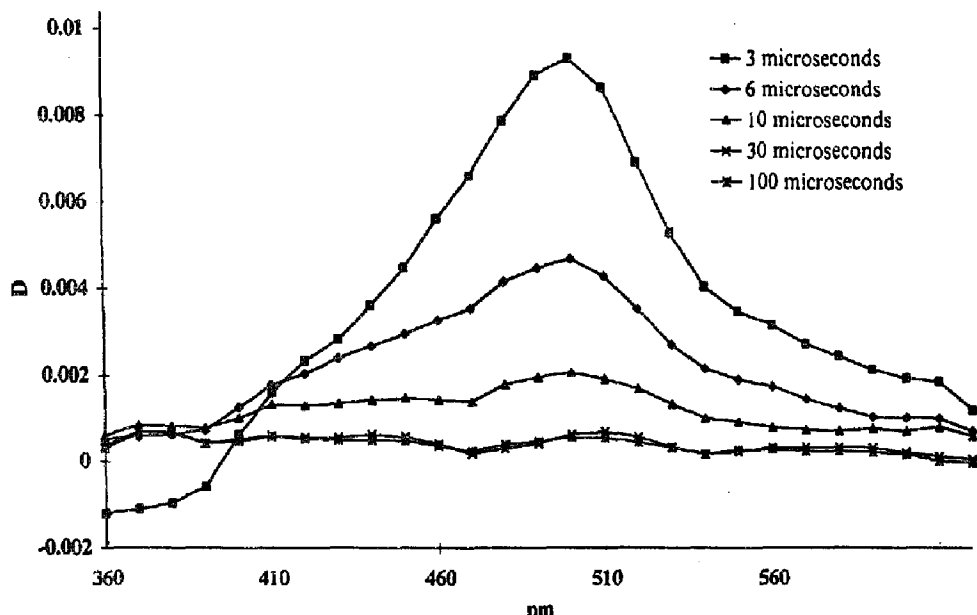

Fig. 1. Transient absorption spectra of quinoline solutions (3 mM) at pH 2.7 at different times after the laser pulse as a function of λ.
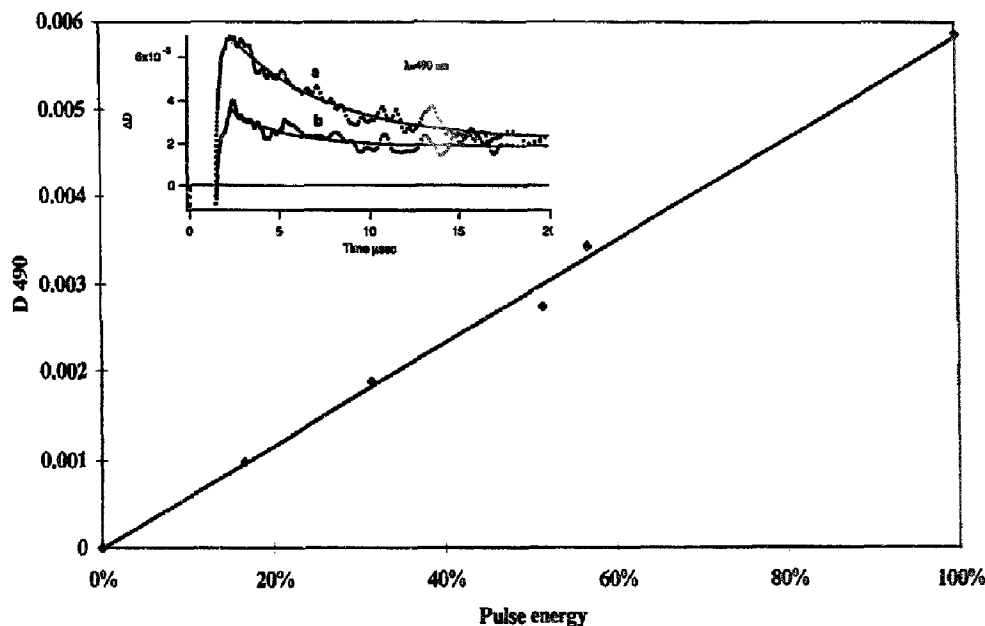
Fig. 2. Dependence of the transient absorption at $\lambda = 490$ nm on the energy of the ruby laser pulse ($\lambda = 347$ nm) for quinoline solutions (3 mM) at pH 3 and 3 μs after the laser pulse. The inset shows the decay of the transient at two different energies at $\lambda = 490$ nm.

of a Q^+-radical. The ionic intermediate found in our work is therefore different from results reported by a previous study of Q in methanol–water (4:1) at low temperature (77 K), where a triplet state with a peak at 470 nm was reported [11].

Next the details of ion-radical formation will be explored. The dependence of the transient absorption at 490 nm on the energy of the laser pulse (15 mJ/pulse = 100%) is shown in Fig. 2. This figure shows a linear dependence between the amplitude of the transient signal and the laser energy applied. The formation of ions

$$Q + nh\nu \rightarrow (QS_1)^* \rightarrow Q^+ + e^- (aq) \tag{1}$$
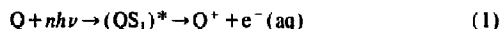
due to photo-ionization occurs via a process involving a number n of photons. A value of 2.32 can be estimated from the relation

$$n = IP/(hc/\lambda) \tag{2}$$

since the ionization potential (IP) of Q is 8.3 eV, and 3.57 eV corresponds to the energy of the ruby laser. A value of $n = 2.32$ can be estimated for the number of photons intervening in Eq. (1). Therefore, biphotonic ionization is observed in Fig. 2. The linear dependence observed in Fig. 2 could only occur if the ionization proceeds through excitation of the S_1 state as the intermediate state in the photo-ionization. The inset in Fig. 2 shows second-order decay for the transient in trace (a) when the full laser dose is applied and in trace (b) when 60% of the full laser dose is applied. The lifetime at lower energies was observed to be 30% longer than when the full laser dose was applied, as would be expected for a bimolecular reaction. This is an argument in favor of ion-

radical formation in a biphotonic ionization [10,11] process as stated above. This is shown below in Eq. (3):

$$Q + nh\nu \rightarrow (Q^*S_1) \rightarrow Q^- + Q^+ \tag{3}$$
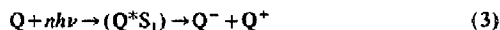
Eq. (1) suggests that the intermediate leading to the Q^+-cation also produces electrons. These electrons would then attach subsequently to Q with concomitant anion formation.

The effect of pH on the transient absorption of Q after the laser pulse at $\lambda = 490$ nm is shown in Fig. 3. In the pH range used almost all Q is in protonated form (pK 4.7–4.9) [12]. However, the optical density at $\lambda = 490$ is seen to increase in Fig. 3 when the pH moves to more acidic values. The shape of the absorption spectrum of Q^+ is not significantly affected by pH, as seen in the inset to Fig. 3. It is difficult to suggest that deprotonation of Q^+ is taking place because only one species is observed in the transient spectra. Also the optical density at $\lambda = 490$ nm does not fall to zero with increasing pH. It is suggested that at pH < 3 protonation of the singlet excited state of Q occurs. The protonation leads to changes in the singlet–singlet absorption and would affect the Q photo-ionization yield. No experiments were performed at higher pH than 4, because the aim of the work was to explore the conditions suitable for Fenton degradation.

3.2. Interaction of quinoline with H_2O_2

Fig. 4 presents the transient spectra at different times after the laser pulse as a function of λ for Q solutions when H_2O_2 has been added in different concentrations. It is readily seen that the differential transient absorption changes little with
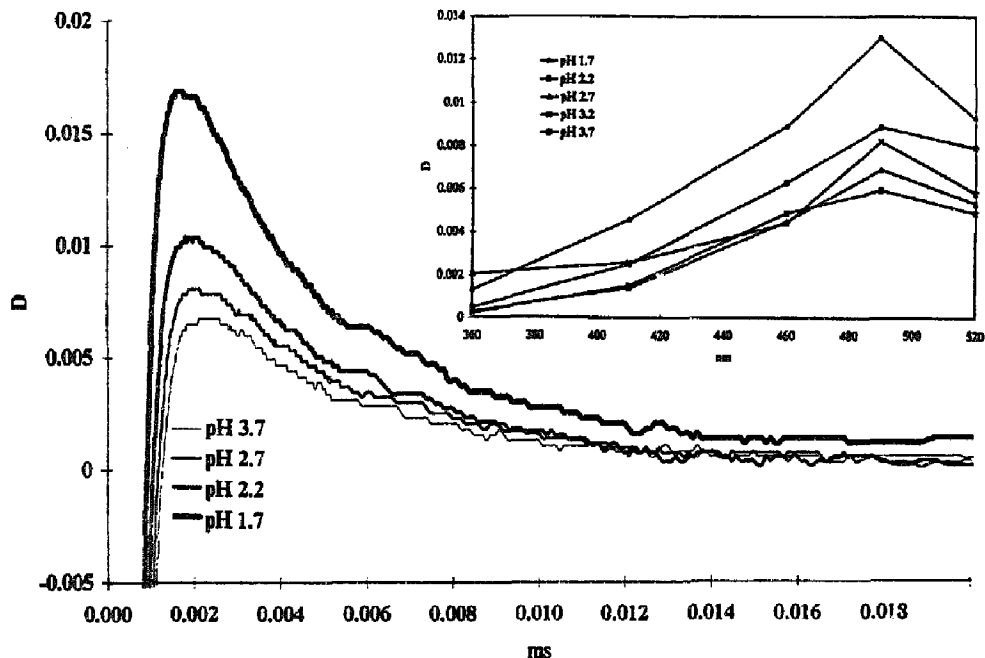
Fig. 3. The dependence of the optical absorption on the pH of quinoline solutions (3 mM) as a function of decay time. The inset shows the optical absorption as a function of λ for different pH values.
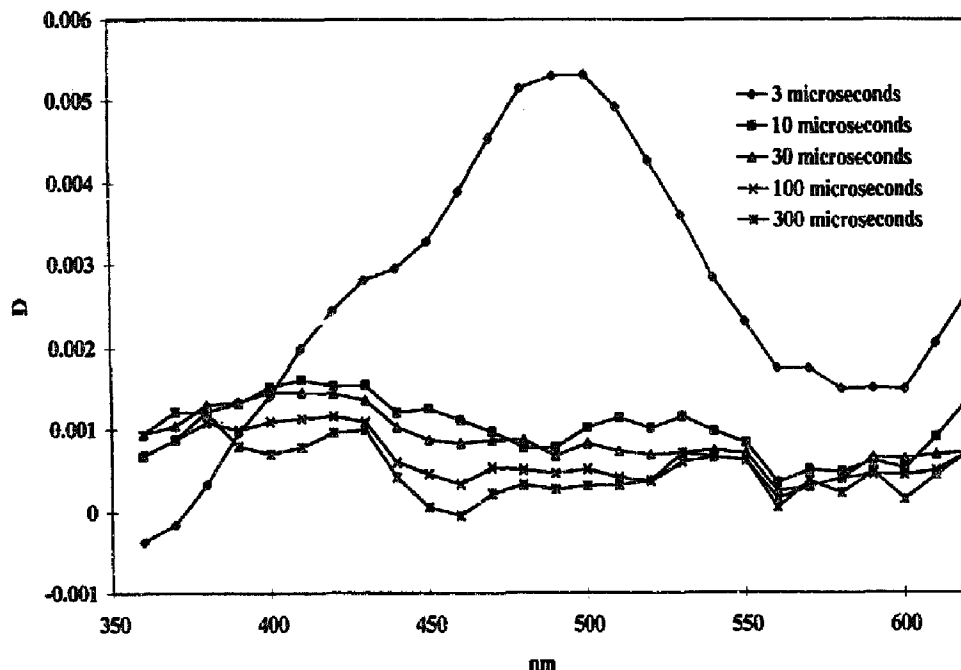

Fig. 4. Transient absorption for quinoline solutions (3 mM) containing H_2O_2 (50 mM) at pH 2.7 as a function of λ at different times after the laser pulse.

respect to the spectra of Q already reported in Fig. 1. The transient decay was also similar to that observed in Fig. 1. These two observations show that only a very weak interac-

tion takes place between Q and H_2O_2. This is an important consideration for the design of future experiments, presented below in the text.
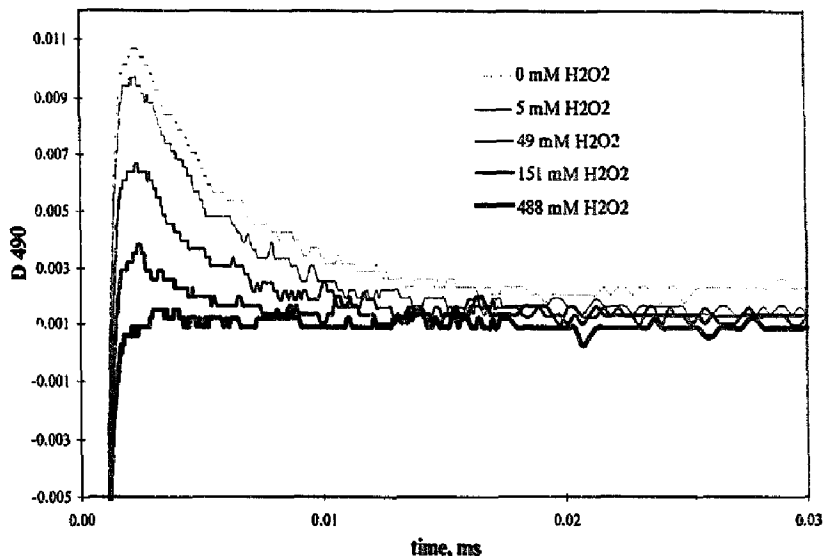
Fig. 5. Decay of quinoline transients in quinoline solutions (3 mM) as a function of added H_2O_2 concentration at $\lambda = 490$ nm.

Fig. 5 shows that the transient absorption band at $\lambda = 490$ nm is quenched when higher concentrations of H_2O_2 are used but the lifetime of the transient was only marginally affected by the addition of the oxidant. A concentration of 0.1 M H_2O_2 was seen to decrease the amplitude of the transient at $\lambda = 490$ nm by a factor of two. This suggests (a) that the concentration of excited molecules is affected by the addition of H_2O_2 and (b) the photoionized Q undergoes static quenching with H_2O_2.

In separate experiments, it was observed that the dependence between the concentration of H_2O_2 and the reciprocal value of the transient optical density at $\lambda = 490$ nm followed a linear relation. This observation suggests that the interaction of Q with H_2O_2 occurs prior to the photo-ionization of Q. Since no effect of H_2O_2 was observed on the absorption spectrum of Q in the ground state, it is possible that Q interacts with the oxidant through the singlet excited state as suggested previously in Eqs. (1) and (3).

3.3. Study of the complete system $Q–H_2O_2–Fe^{3+}$

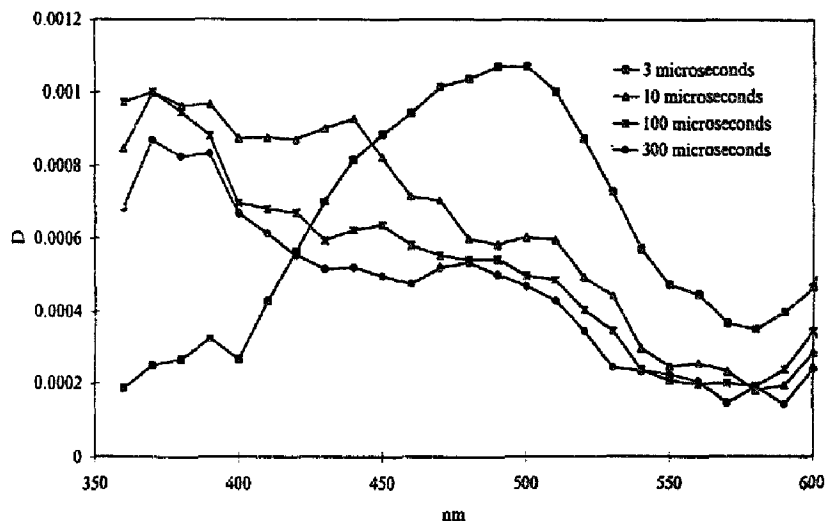Fig. 6 presents the differential optical spectra for a solution containing the complete system: Q, Fe^{3+} and H_2O_2. A high

Fig. 6. Transient absorption spectra for a quinoline solution (2.4 mM) in the presence of Fenton reagent ($FeCl_3$ 0.24 mM and H_2O_2 300 mM) at different times after the laser pulse as a function of λ.
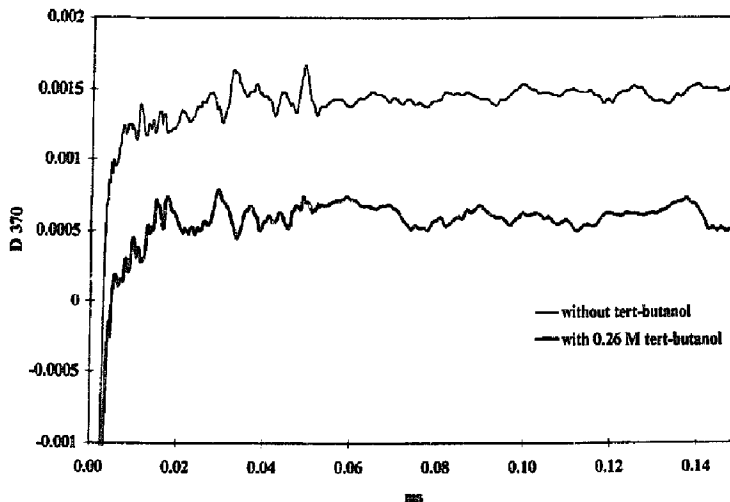
Fig. 7. Photobleaching at $\lambda = 370$ nm for a quinoline solution (2.4 mM) in the presence of $FeCl_3$ (0.24 mM) and H_2O_2 (300 mM) at pH 2.7 with and without radical scavenger.

concentration of Q is used since the interaction between Q and H_2O_2 was previously observed to be weak (see Section 3.2). The spectral decay resembles Fig. 1 at $\lambda > 510$ nm, but new intermediates appear at the left-hand side of the spectrum rising up to $\lambda = 350$ nm. These optical intermediates become more important at longer delay times and at $\lambda < 450$ nm. The $Fe^{3+}*(aq)$ reacts in solution

$$Fe^{3+}*(aq) + H_2O_2 \rightarrow Fe^{3+}(aq) + 2^{\cdot}OH \qquad (4)$$

$$^{\cdot}OH + Q \longrightarrow \qquad (5)$$
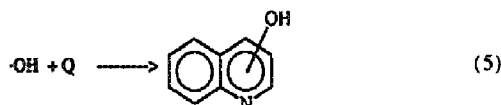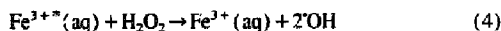
Previously during this study we have seen that no new intermediates were observed when Q reacts with H_2O_2 or Fe^{3+} respectively. However, in the case of the complete system as shown in Fig. 6, new bands appear reflecting new intermediates formed in solution. This could explained by the formation of

$$[Q\cdots Fe^{3+}] \xrightarrow{H_2O_2} [Q\cdots Fe^{3+}\cdots H_2O_2] \xrightarrow{h\nu}$$
$$[\text{intermediate complex}]^* \qquad (6)$$
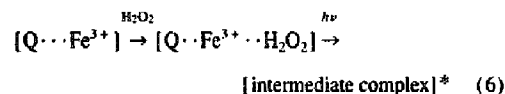
The photobleaching signal of Q in the system $Q-H_2O_2-Fe^{3+}$ at $\lambda = 370$ nm is shown in Fig. 7. This is consistent with the photobleaching observed for Q after the laser pulse in Fig. 1 at $\lambda < 390$ nm and also in Fig. 4 for $Q-H_2O_2$. Our experimental results show that H_2O_2 led to the growth of the signals observed at $\lambda = 370$ nm while quenching at the same time the amplitude of the signal observed at $\lambda = 490$ nm. The effect of H_2O_2 was eliminated by addition of the well known radical scavenger ter-butyl alcohol (0.26 M). The action of

this scavenger on the $^{\cdot}OH$ radicals is seen in Fig. 7. It seems that the formation of an intermediate complex involving $^{\cdot}OH$ radicals takes place. The intermediate is probably a complex comprising $Fe^{3+}-Q$-derived species resulting from $^{\cdot}OH$ radical attack. Because the signal to noise ratio was poor the results were averaged over four measurements.

A linear proportionality is observed for the increase in photobleaching at $\lambda = 370$ nm as a function of H_2O_2 concentration. Therefore, the concentration of the intermediate is seen to depend on the oxidant concentration added. This is shown in Fig. 8. The inset in Fig. 8 shows the change in optical absorption of the transients at a delay time of 300 μs after the laser pulse. This points to different transients occurring at more advanced reaction stages.

The transient responsible for the effect of the pH variation in Fig. 8 is shown in Fig. 9. The effect of pH in oxidative media proceeds through the formation of MLCT bands. $Fe^{3+}*(aq)$ protonates at low pH (pK_a 2.7). This species deprotonates rapidly above pH 2.7 [13,14]. The Fe^{3+}-ion reacts associatively with H_2O_2 in acid media owing to its highly oxidative character (Fe^{3+}/Fe^{2+} 0.77 V) but it does not lead to well defined Fe^{3+}-peroxides in solution [15]. Unstable peroxo-complexes have been suggested to decompose in solution, producing the superoxide radical [16]:

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \qquad (7)$$

The Fe^{2+}-ion has been reported to coordinate with the superoxide prior to electron transfer leading to $^{\cdot}OH$ radical formation [17]. The back reaction of Eq. (7) leads to

$$HO_2^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + ^{\cdot}HO_2^{-} \qquad (8)$$
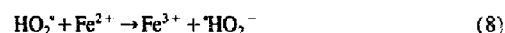
Therefore the Fenton system is at the origin of an extremely corrosive system in solution containing Fe^{3+}/Fe^{2+}, $HO_2^{\cdot}$, $^{\cdot}OH$ and Cl–Fe-hydrated complexes [14–17].
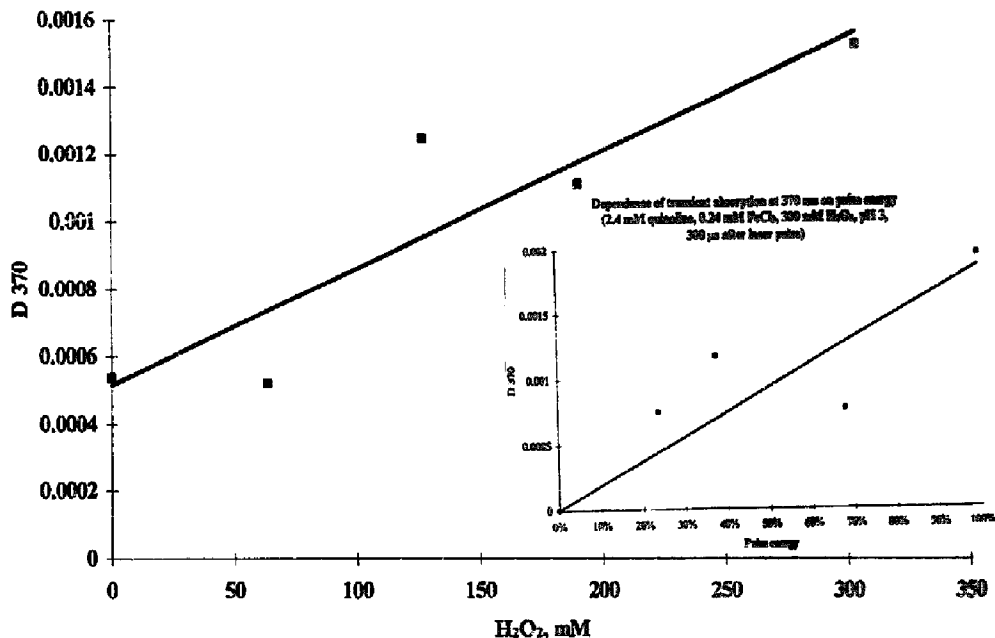
Fig. 8. Effect of the concentration of H_2O_2 on the transient absorption of a quinoline solution (2.4 mM) with added $FeCl_3$ (0.24 mM) at 370 nm and at 100 μs after the pulse. The inset shows the same effect but at 300 μs after the laser pulse. For other details see text.
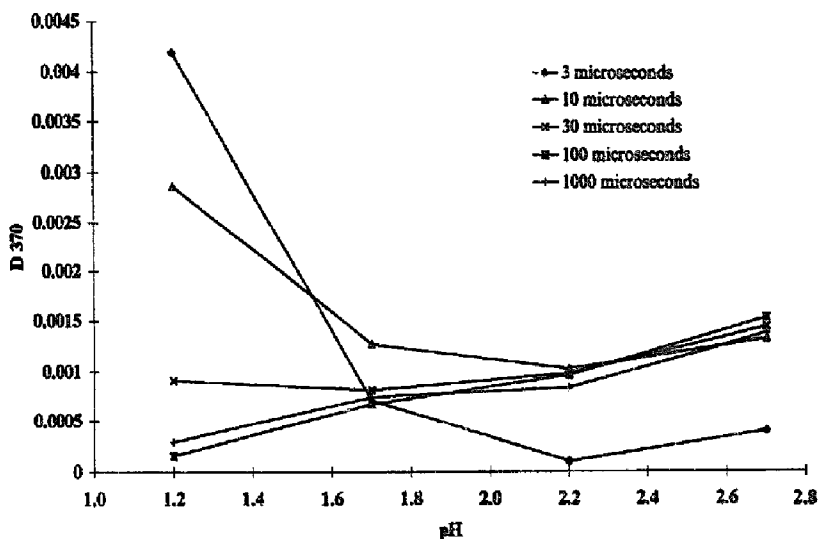

Fig. 9. Effects of pH on transient absorption at λ = 370 nm for a quinoline solution (2.4 mM) in the presence of the Fenton reagent.

4. Conclusions

This study reports on the decay time of excited Q, the effect of pH and applied pulse energy. At λ = 347 nm Q is the main photo-receptor but this is changed in the presence of Fenton reagent. The effects of H_2O_2 and pH on the transient absorption are observed to be independent. When Fe^{3+}-ion is added to Q solutions no difference is observed for the decay time of the excited state and optical density as a function of λ. This is indicative of a weak interaction between the excited state and the d^6 electron orbitals of the transition metal. The rise-times reported for the signals at 370 nm coincide with the decay times observed for the intermediate at 490 nm. The latter observation strongly suggests that the excited state

responsible for the absorption at $\lambda = 490$ nm is the precursor of the intermediate growing at 370 nm. Q solutions in the presence of the Fenton reagent reveal precursor bands for intermediate(s) at $\lambda < 500$ nm found only when $Fe^{3+} + H_2O_2$ were added together to the Q in solution.

Acknowledgements

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