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# Kinetic and spectral properties of rhodamine 6G free radicals: a pulse radiolysis study

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## Abstract

Using the pulse radiolysis technique $Br_2^{\bullet -}$ has been shown to react with the laser dye, rhodamine 6G ($RhH^+$) to produce cation radicals. At pH 4, the species designated $RhH^{2\bullet +}$ is produced which was shown to deprotonate with a p$K_a$ of 5.7 yielding $Rh^{\bullet +}$. Both forms of the radical have characteristic transient difference absorption spectra with distinct maxima at 470 nm.

The cation radicals are relatively long-lived and can be observed for up to 1 s after the pulse. At the end of the reaction(s) of $Rh^{\bullet +}$, significant increases in absorption relative to the ground state area were observed in the dye laser output region, 555–620 nm. Oxygen had no effect on the decay of these radicals; however, it was demonstrated that $O_2^{\bullet -}$ could regenerate the dye ground state in a redox process. At high concentrations of rhodamine 6G, it appears that only monomeric cation radicals are formed on reaction with $Br_2^{\bullet -}$, suggesting that any dimer cation radicals formed initially are short-lived ($k[\text{dissociation}] > 5 \times 10^6\ s^{-1}$). The relevance of cation radical formation to the efficiency and photostability of rhodamine dye laser systems in both liquid and solid state is discussed. It is proposed that the formation of such radicals, particularly in the solid state, may account for the loss of efficiency and photostability and so provide an alternative mechanism to one involving the dye triplet state.

*Keywords:* Rhodamine 6G; Pulse radiolysis; Free radicals; Lasers

## 1. Introduction

The development of solid-state dye lasers to replace the conventional liquid dye lasers is motivated by their performance, robustness and low cost and particularly for their inherent versatility as a multiwavelength source for a variety of applications including photodynamic therapy and remote sensing. Such solid-state systems include a variety of dye classes (coumarins, xanthenes, pyrromethenes and perylenes) which have been incorporated into glasses, [1–3] acrylic polymers [4,5] and sol–gels [6,7] and pumped using both lasers and flashlamps [8]. The performances of solid-state dye lasers in various host media have been reviewed recently [9]. One of the most important and fundamental problems with dye lasers is the photochemical degradation of the dye in the gain region. This may arise from photochemical reactions of the first excited singlet state, the triplet state and through multiphoton absorption, all of which may be influenced by oxygen, reactive hydrocarbons or other impurities. The effect of the absence of oxygen together with the effect of DABCO on photodegradation have already implicated singlet oxygen as a possible intermediary in the photodegradation of both pyrromethene and rhodamine dyes [8,10,11].

Studies on the photophysical and photochemical properties of rhodamine dyes in our laboratories have been directed towards making quantitative assessments of the potential role of excited singlet state absorption, the triplet state and multiphoton processes in the degradative process [12–15]. In our most recent work on rhodamine 123 [15], it was concluded that the dye underwent photoionisation by both mono- and biphotonic processes when excited at 355 nm in aqueous solution. The resultant cationic and anionic free radicals were relatively long-lived and exhibited absorption spectra extending into the laser output region. The possibility that such free radicals can lead to dye degradation is clear. It is therefore the goal of this study to use the fast reaction technique of pulse radiolysis to generate the cationic free radicals of rhodamine 6G and to investigate their spectral and kinetic properties with the overall aim of assessing the potential for the participation of such free radical species in photodegradation processes occurring in rhodamine dye laser systems.

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## 2. Experimental

Rhodamine 6G was purchased from Sigma and used as supplied. Solutions were made up in triply distilled water and buffered with phosphate and NaOH (pH 4–9) at an ionic strength equivalent to 10 mM phosphate. All solutions were saturated with either nitrous oxide or nitrous oxide/oxygen (4:1 v/v mixtures).

The pulse radiolysis has been described in detail elsewhere [16]. The optical detection system consisted of a 500 W xenon lamp, a Kratos GM252 monochromator, an RCA IP28, or Hamamatsu R728 photomultiplier and a Tetronix 7612 Digitizer. Either a 1 or 2.5 cm cell was used, the former being used at high rhodamine dye concentrations. All spectra in the figures were normalised for a path length of 2.5 cm. A nitrous oxide saturated aqueous solution of KSCN ($10^{-2}$ mol dm$^{-3}$) was used for dosimetry. Radiation doses were calculated from the transient absorption of $(SCN)_2^{\bullet -}$ assuming $G\,[(SCN)_2^{\bullet -}]\,\varepsilon = 2.23 \times 10^{-4}$ m$^2$ J$^{-1}$ where $G$ and $\varepsilon$ represent the radiolytic yield (mol J$^{-1}$) and molar absorption coefficient of $(SCN)_2^{\bullet -}$ respectively [17]. The yield of the bromide anion radical ($Br_2^{\bullet -}$) was calculated from the radiation dose, assuming a radiolytic yield of 0.58 μmol J$^{-1}$.

## 3. Results and discussion

### 3.1. The reaction of $Br_2^{\bullet -}$ radicals—kinetic measurements

Pulse radiolysis techniques were used to produce the powerful one-electron oxidant, $Br_2^{\bullet -}$ ($E^0 = 1.65$ v) [18] by irradiating nitrous oxide saturated solutions of $10^{-2}$ mol dm$^{-3}$ potassium bromide. Under these conditions, $Br_2^{\bullet -}$ is produced as follows:

$$H_2O \rightsquigarrow e^-_{aq},\quad H^\bullet,\quad {}^\bullet OH,\quad H_2O_2,\quad H_2,\quad H_3O^+ \tag{1}$$

$$e^-_{aq} + N_2O \rightarrow {}^\bullet OH + OH^- + N_2 \tag{2}$$

$${}^\bullet OH + Br^- \rightarrow Br^\bullet + OH^- \tag{3}$$

$$Br^\bullet + Br^- \rightarrow Br_2^{\bullet -} \tag{4}$$

Under such conditions $Br_2^{\bullet -}$ is produced in a yield 0.58 μmol J$^{-1}$ within 100 ns following the pulse. In the presence of micromolar concentrations of rhodamine 6G, therefore, $Br_2^{\bullet -}$ would be expected to react over much longer timescales. As indicated in an earlier study carried out in these laboratories [13], both $N_3^\bullet$ and $Br_2^{\bullet -}$ were found to react to produce identical transient absorption spectra at the end of their reactions with rhodamine 6G, confirming the likelihood of a common electron transfer reaction to produce one-electron oxidised species of rhodamine. However, difficulties were encountered using azide radicals near the p$K_a$ for dissociation of $HN_3$ which gave spurious and non-reproducible kinetic data. It was decided therefore to use $Br_2^{\bullet -}$ as the oxidant. In contrast to the earlier preliminary study [13], the study presented here focusses on the effects of dye concentrations and pH on the one-electron oxidation process.

The aggregative properties of rhodamine 6G have been the subject of several studies [19–27] from which it is clear that rhodamine 6G aggregates relatively easily in aqueous solution to form dimers, trimers, etc. Hence, at $10^{-6}$ and $10^{-5}$ mol dm$^{-3}$ rhodamine 6G concentration at pH 7, it has been calculated that the proportions of dimers present are 2% and about 4%, respectively. Hence, in this study, the reactions of $Br_2^{\bullet -}$ radicals with monomeric rhodamine 6G were therefore carried out at dye concentrations of $10^{-5}$ mol dm$^{-3}$ or less.

On pulse irradiating nitrous oxide saturated solutions containing $10^{-2}$ mol dm$^{-3}$ bromide at pH 5.05 and dye concentrations of $5 \times 10^{-6}$ mol dm$^{-3}$, a pseudo first-order growth in transient absorption due to a rhodamine free radical at 470 nm could be observed easily. The rate of growth was relatively fast and was complete within 300 μs yielding a pseudo first-order rate constant of $(1.7 \pm 0.2) \times 10^4$ s$^{-1}$.

Within the restricted dye concentration range, $(5–10) \times 10^{-6}$ mol dm$^{-3}$, it was also clear that the rate of decay of the $Br_2^{\bullet -}$ absorption at 360 nm and the rate of growth of the dye transient absorption at 470 nm were the same and directly proportional to the dye concentration.

In the absence of dye, the decay of the $Br_2^{\bullet -}$ absorption at its maximum at 360 nm was much slower and was not complete within 1 ms following the pulse. Despite this relatively slow process, allowance for a contribution of $Br_2^{\bullet -}$ self-reaction to the overall reaction processes of $Br_2^{\bullet -}$ in the presence of dye was nevertheless made by kinetic simulation of the decay of transient absorption at 360 nm due to $Br_2^{\bullet -}$, assuming the following reactions:

$$Br_2^{\bullet -} + Br_2^{\bullet -} \rightarrow \text{products} \tag{5}$$

$$Br_2^{\bullet -} + RhH^+ \rightarrow \text{products} \tag{6}$$

where $RhH^+$ represents rhodamine 6G.

The self-reaction rate constant for reaction (5) was measured experimentally at the same radiation dose per pulse of 2.0 Gy and found to be $2k/\varepsilon = (1.7 \pm 0.2) \times 10^5$ s$^{-1}$ cm. On this basis, a good kinetic fit for the decay of $Br_2^{\bullet -}$ using $5 \times 10^{-6}$ mol dm$^{-3}$ rhodamine 6G was found using a first-order rate constant of $1.1 \times 10^4$ s$^{-1}$, for reaction (6) indicating a bimolecular rate constant of $(2.2 \pm 0.5) \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.

Similar kinetic experiments, making observations at both 360 nm (for the decay of $Br_2^{\bullet -}$) and 470 nm (for the growth of a rhodamine free radical product), were made for pH values between 2.9 and 8.5. Fig. 1 shows, in fact, the lack of an effect of pH on the observed first-order rate constant for the growth of the transient absorbance at 470 nm—all rate constants being the same within experimental error. This kinetic data suggests that there are no protolytic changes in rhodamine 6G itself in the pH range 2.9–8.5. This suggestion

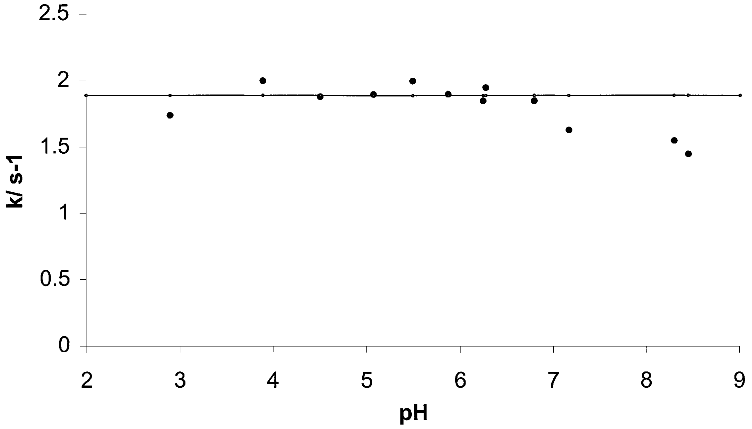
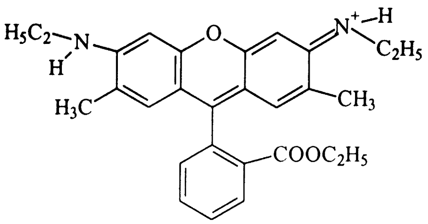


Fig. 1. Effect of pH on the first-order rate constant for the growth of transient absorbance at 470 nm measured following the pulse irradiation of a nitrious oxide saturated solution of $10^{-2}$ mol dm$^{-3}$ potassium bromide containing $5 \times 10^{-6}$ mol dm$^{-3}$ rhodamine 6G (dose = 5 Gy).

is consistent with the literature where no evidence has been found for protonation or deprotonation within this pH range [19–25]. In order to confirm that this was also the case when dimers or trimers of the rhodamine 6G are present, measurements of the visible absorption spectra of the dye were made over the same pH range and at dye concentrations in the range $(1–200) \times 10^{-6}$ mol dm$^{-3}$. No discernable effect of pH on the spectra of these dyes at any dye concentration could be observed. It would appear therefore that the possible protonation of nitrogen in the secondary amine group of the xanthene ring must occur at a pH significantly lower than 2.9.



The bimolecular rate constant for the reaction of $\mathrm{Br_2}^{\bullet-}$ with rhodamine 6G, $(2.2 \pm 0.5) \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$, can be compared with the value of $1.4 \times 10^{8}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ obtained in an earlier study on the related dye, rhodamine 123. The significant difference in the structures of these two dyes is found in the amino groups of the xanthene ring; in rhodamine 6G, both are monoethylated (there being no ethylation in rhodamine 123). The stronger electron donor capacity of the monoethylated dye [24] presumably has a significant effect on the ease of oxidation by $\mathrm{Br_2}^{\bullet-}$.

### 3.2. The reaction of $\mathrm{Br_2}^{\bullet-}$, $\mathrm{(SCN)_2}^{\bullet-}$ and $^{\bullet}$OH radicals—spectral measurements

The transient difference absorption spectra observed at the end of the reaction of $\mathrm{Br_2}^{\bullet-}$ with rhodamine 6G were also measured at pH values between 3.9 and 8.3. Fig. 2 shows the spectra so obtained at pH values 3.9 and 8.3. The spectra are self-evidently different, with the spectrum at pH 3.9 showing a relatively intense absorption maximum at 470 nm ($\Delta\varepsilon = 21{,}600 \pm 3500$ dm$^{3}$ mol$^{-1}$ cm$^{-1}$) compared to pH 8.3 ($\Delta\varepsilon = 7700 \pm 900$ dm$^{3}$ mol$^{-1}$ cm$^{-1}$). In addition, the spectrum at pH 8.3 also shows a distinct maximum at 380 nm ($\Delta\varepsilon = 3100 \pm 400$ dm$^{3}$ mol$^{-1}$ cm$^{-1}$).

Spectra (not shown), identical in shape but with lower yields, were obtained using another one-electron oxidant, $\mathrm{(SCN)_2}^{\bullet-}$ ($E^{\theta}(\mathrm{(SCN)_2}^{\bullet-}/2\mathrm{SCN}^{-}) = 1310$ mV) [28]. $\mathrm{(SCN)_2}^{\bullet-}$ is formed by the pulse irradiation of nitrous oxide saturated solutions of $10^{-2}$ mol dm$^{-3}$ potassium thiocyanate in which $^{\bullet}$OH, formed in reactions (1) and (2), reacts as follows:

$$^{\bullet}\mathrm{OH} + \mathrm{SCN}^{-} \rightarrow \mathrm{SCN}^{\bullet} \tag{7}$$

$$\mathrm{SCN}^{\bullet} + \mathrm{SCN}^{-} \rightarrow \mathrm{(SCN)_2}^{\bullet-} \tag{8}$$

At both pH 4.1 and 8.5, $\mathrm{(SCN)_2}^{\bullet-}$ was also observed to react rapidly with rhodamine 6G. However, the dye radicals so produced were not as stable as in the bromide experiments and hence there was significant decay of the rhodamine species competing with their production making accurate determination of both the rate constants and full yield (equivalent to the concentration of $\mathrm{(SCN)_2}^{\bullet-}$) difficult to attain. Given this constraint, the bimolecular rate constant for the reaction of $\mathrm{(SCN)_2}^{\bullet-}$ with rhodamine 6G was estimated, from a simulation of the kinetic traces obtained in this experiment, to be approximately $(1.0 \pm 0.5) \times 10^{9}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ at both pH values. The differences in the yields obtained using $\mathrm{Br_2}^{\bullet-}$ and $\mathrm{(SCN)_2}^{\bullet-}$ could therefore be accounted for by the lower rate of reaction of $\mathrm{(SCN)_2}^{\bullet-}$ as well as by the faster self-reaction processes of $\mathrm{(SCN)_2}^{\bullet-}$ compared to $\mathrm{Br_2}^{\bullet-}$.

The reaction of $^{\bullet}$OH radicals with rhodamine 6G has been studied previously at neutral pH where a transient absorbance having a maximum at 475 nm was observed [29,30]. This experiment was extended in the present study by carrying out the reaction at pH 4.0. The spectrum so

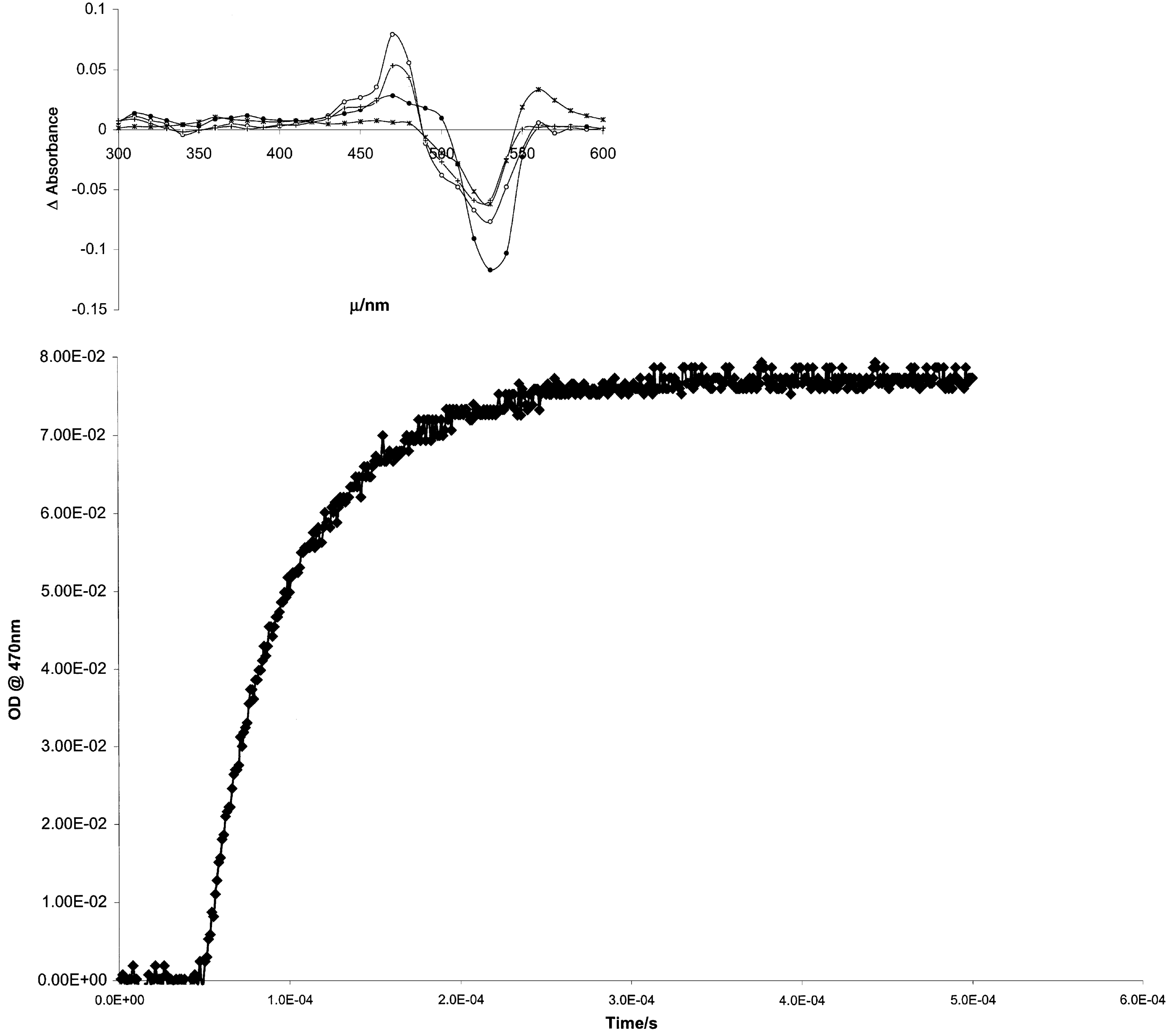


Fig. 2. Transient absorption spectra measured on pulse irradiation of a nitrous oxide saturated solution of $10^{-2}$ mol dm$^{-3}$ potassium bromide containing $5 \times 10^{-6}$ mol dm$^{-3}$ rhodamine 6G (○) at 250 μs and pH 3.9; (●) at 250 μs and pH 8.3; (+) at 450 ms and pH 3.9; and (✖) at 80 μs and pH 8.3; (dose = 2.3 Gy). (The insert shows the kinetic trace at 470 nm.)

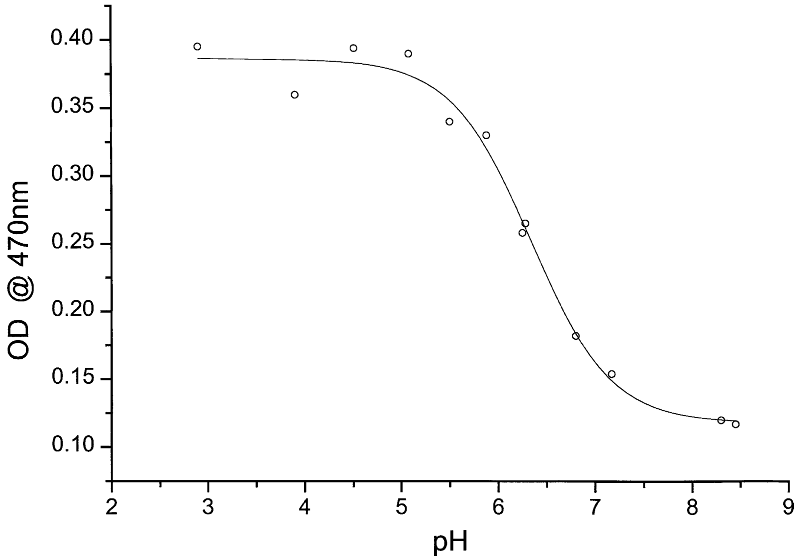


Fig. 3. Effect of pH on the absorbance at 470 nm measured at the end of the reactions $Br_2^{\bullet -}$ with rhodamine 6G (dose = 11.5 Gy).

obtained on the pulse irradiation of a nitrous oxide saturated solution of $6 \times 10^{-6}$ mol dm$^{-3}$ rhodamine 6G is identical in both shape and intensity to that obtained in the reaction of $Br_2^{\bullet -}$ with the dye (Fig. 2).

It is thus clear that all three oxidants, $Br_2^{\bullet -}$, $(SCN)_2^{\bullet -}$ and $^{\bullet}OH$, react with rhodamine 6G to produce identical transient species presumably by one-electron oxidation of the dye. It is also apparent that there is an effect of pH on the absorption spectra of the transient species. Fig. 3 shows the effect of pH on the transient absorbance at 470 nm measured at the end of the reaction of $Br_2^{\bullet -}$ with rhodamine 6G, from which a p$K_a$ of 6.3 is indicated for the species so produced.

A similar effect of pH was also found in our recent study on rhodamine 123 [15]. In that work, at low pH (2.5) the species formed on one-electron oxidation of the dye exhibited an intense difference absorption maximum at 450 nm ($\Delta\varepsilon = 42{,}000$ dm$^3$ mol$^{-1}$ cm$^{-1}$). At pH 7.0, a much less intense difference absorption maximum at 450 nm ($\Delta\varepsilon = 13{,}000$ dm$^3$ mol$^{-1}$ cm$^{-1}$) was observed. From these observations, it was concluded in that study that at low pH, the radical cation ($RhH^{2\bullet +}$) which is formed can deprotonate to form $Rh^{\bullet +}$, the p$K_a$ for the dissociation being 5.7. It is therefore proposed that a similar explanation may be offered for Fig. 3 and is represented by the following equation:

$$RhH^{2\bullet +} \leftrightarrow Rh^{\bullet +} + H^+ \tag{9}$$

where the ground state of the dye is $RhH^+$ and the p$K_a$ of dissociation is 6.3.

## 4. Reactions of the rhodamine 6G free radicals

In order to study the subsequent reactions of the cationic rhodamine free radicals following their formation through oxidation of the dye by $Br_2^{\bullet -}$, their decay kinetics were monitored at 470 nm for up to 400 ms. Since it is clear that two distinct species are formed depending upon the pH (see Fig. 3), experiments were conducted at either pH values around 3.9–4.2 or around 8.3–8.5.

In nitrous oxide saturated solutions, at pH 3.9 and low dye concentrations of $6 \times 10^{-6}$ mol dm$^{-3}$, the absorbance of the rhodamine free radicals was very stable—even at 450 ms after the pulse, only 30% of the absorbance had decayed, presumably via reaction (10).

$$2RhH^{2\bullet +} \rightarrow \text{products} \tag{10}$$

The spectrum measured after 450 ms in this reaction is also shown in Fig. 2. It is difficult to establish from such spectral changes whether rhodamine 6G itself is regenerated in reaction (10) via a disproportionation reaction. However, in view of the fact that there are significant absorbance changes at 470 and at 560 nm, while the rest of the spectrum remains unchanged this possibility seems unlikely. It thus seems that relative to the rhodamine ground state that the product(s) of reaction (10) have larger extinction coefficients in the range 400–490 nm and smaller extinction coefficients in the 500–530 nm region. If reaction (10) were a simple disproportionation or dimerisation, the extinction coefficient of the new product(s) could be as much as 24,000 dm$^3$ mol$^{-1}$ cm$^{-1}$ greater than the ground state of the dye at 470 nm, with a corresponding reduction of 32,000 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 530 nm. If reaction (10) were a simple first-order process (A → B), the respective changes in extinction coefficient would be 12,000 and 16,000 dm$^3$ mol$^{-1}$ cm$^{-1}$.

At pH 8.3, using nitrous oxide saturated solutions containing $6 \times 10^{-6}$ mol dm$^{-3}$ rhodamine 6G, the dye radicals formed in the reaction with $Br_2^{\bullet -}$ were observed to decay more rapidly than was the case for the radicals formed at pH 4. Thus, under typical dose per pulses of about 2 Gy, the absorbance at 470 nm decayed over 20 ms at which time a residual stable absorbance was evident.

The spectrum measured after 80 ms in the decay process is also shown in Fig. 2. It can be seen that there is some recovery of absorbance at 530 nm, the maximum of the ground state of the dye. It is possible therefore, that some of the ground state dye is regenerated in the decay process. However, perhaps the most significant observation relevant to laser action efficiency is the appearance of significant increases in absorbance at the end of the decay process (relative to the dye in the ground state) over a wide range of wavelengths between 340 and 470 nm ($\Delta\varepsilon 1500 \pm 200\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ at 470 nm) and at 550–620 nm ($\Delta\varepsilon 8500 \pm 1000\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ at 560 nm). These increases are much more pronounced than those found at pH 4 in the equivalent wavelength region.

## 5. Effect of oxygen

In solutions of $10^{-2}\,\mathrm{mol\,dm^{-3}}$ potassium bromide containing rhodamine 6G which have been saturated with either air or oxygen, $e^-_{aq}$, formed as a primary radiolysis product, will react to yield $HO_2^{\bullet}$ or $O_2^{\bullet -}$ free radicals, as follows:

$$e^-_{aq} + H^+ \rightarrow H^{\bullet} \tag{11}$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{12}$$

$$e^-_{aq} + O_2 \rightarrow O_2^{\bullet -} \tag{13}$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+ \tag{14}$$

where the $\mathrm{p}K_a$ for reaction (14) is 4.75 [31].

Hydrogen atoms, formed as a primary radiolysis product in a relative small yield ($0.06\,\mu\mathrm{mol\,J^{-1}}$), also contribute to the yield of $HO_2^{\bullet}/O_2^{\bullet -}$ formed via reactions (12)–(14).

Under these aerobic conditions at pH 4.0, the absorbance changes were followed kinetically at 470 nm. The absorbance measured at the end of the reaction was consistent with that expected from the reaction of $Br_2^{\bullet -}$ with the dye. This indicated that $HO_2^{\bullet}/O_2^{\bullet -}$ either do not react with the dye (as may be anticipated from the lower oxidising ability of $HO_2^{\bullet}/O_2^{\bullet -}$) or do not produce a dye free radical with a significant absorbance at 470 nm. On the likely assumption therefore that only the one-electron oxidised species of the dye is produced, its kinetic fate was studied over the millisecond timescale. It was immediately apparent that the lifetime of this species is reduced dramatically relative to nitrous oxide solutions (where only about 30% of the absorbance at 470 nm was lost after 450 ms see Fig. 2). In these aerated solutions, the 470 nm absorbance decayed completely (>95%) via second-order kinetics over 10 ms. The second-order rate constant was found to be $2k/\varepsilon l = 2.7 \times 10^4\,\mathrm{cm\,s^{-1}}$. Using a value of 35,000 for the extinction coefficient of the cation radical ($RhH^{2\bullet +}$) at 470 nm the second-order rate constant ($2k$) for the decay of the radical was calculated to be $2.36 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Confirmation that second-order kinetics were being observed was obtained by varying the dose per pulse from about 2 to 14 Gy which produced much more rapid decay processes as the dose per pulse increased and identical (within experimental error) second-order rate constants.

The most likely reaction occurring here is the reduction of the dye radical by either $HO_2^{\bullet}$ or its deprotonated form $O_2^{\bullet -}$, as shown in reaction (15):

$$RhH^{2\bullet +} + \frac{HO_2^{\bullet}}{O_2^{\bullet -}} \rightarrow RhH^+ + O_2 + H^+ \tag{15}$$

The regeneration of the dye ground state was confirmed by simultaneous observation of changes in absorbance at 520 nm (the maximum of the dye ground state) where over 80% of the ground state absorbance was recovered over the timescale of reaction (15).

At pH 5, where $RhH^{2\bullet +}$ is still the predominant species (see Fig. 3), a similar second-order process also occurred over the same timescales. However, only about 40% of the absorbance at 470 nm disappeared rapidly (within about 3 ms) with the remaining absorbance decaying more slowly over 200 ms. This observation is also consistent with reaction (15) since at pH 5, the rate of reaction between $HO_2^{\bullet}$ and $O_2^{\bullet -}$ (reaction 16) increases by a factor of approximately 10 relative to that of the self-reaction at pH 4.0 [31], thus ensuring that there is insufficient $HO_2^{\bullet}$ or $O_2^{\bullet -}$ to react with all $RhH^{2\bullet +}$ in reaction (15):

$$HO_2^{\bullet} + O_2^{\bullet -} \xrightarrow{H^+} H_2O_2 + O_2 \tag{16}$$

Similar kinetic observations were made in argon-saturated solutions at pH 4.0. In such experiments, hydrogen atoms are formed instead of $HO_2^{\bullet}/O_2^{\bullet -}$. In this case, the absorbance at 470 nm was found to disappear over 10 ms via mixed order kinetics. H atoms may also regenerate $RhH^+$ by acting as a reducing agent as $O_2^{\bullet -}$ does in reaction (15).

In order to exclude the possibility that the direct reaction of oxygen with $RhH^{2\bullet +}$ can account for the above kinetic observations in aerated solutions at pH 4, similar experiments were conducted using solutions saturated with both nitrous oxide and oxygen. In such solutions, the yield of $HO_2^{\bullet}/O_2^{\bullet -}$ is relatively small (about 10% of the yield of $Br_2^{\bullet -}$ radicals ($0.06\,\mu\mathrm{mol\,J^{-1}}$)) and hence any reaction of $RhH^{2\bullet +}$ with oxygen can be observed more easily. Under such conditions, about 10% of the 470 nm absorbance disappeared rapidly over 2–3 ms consistent with reaction (15). The majority of the absorbance decayed much more slowly (up to 400 ms after the pulse) i.e. over similar timescales to those observed in nitrous oxide solutions. However, the decay process was distinctly irreproducible and appeared to be affected by photolysis caused by the analysing light. This apparent photosensitivity of a laser dye under these conditions was somewhat surprising but was not investigated further here.

From these observations, therefore it does not seem likely that there is a direct reaction between $RhH^{2\bullet +}$ and oxygen. In confirmation of this, it was found that the spectrum measured at the end of this decay process (at 280 ms) in $N_2O/O_2$ solution was the same as that measured in solutions saturated with nitrous oxide only.

At pH 8.55 in $N_2O/O_2$ saturated solutions, $Br_2^{\bullet -}$ was found to react with rhodamine 6G to produce, as anticipated, the same species that is produced in $N_2O$-saturated solutions i.e. with a maximum in the difference absorption spectrum at 470 nm. By monitoring at this wavelength, no discernible change in kinetics could be observed in the $N_2O/O_2$ saturated solutions compared to the $N_2O$-saturated solutions, again indicating that the oxidised dye species does not appear to react directly with oxygen. In confirmation of this, the spectrum (not shown) measured at the end of the decay process (e.g. at 80 ms) was the same as that shown in Fig. 2 for nitrous oxide saturated solutions at pH 8.55.

## 6. High concentrations of rhodamine 6G

At concentrations of rhodamine 6G in excess of $10^{-5}$ mol dm$^{-3}$, dimers of the dye are known to form [25,27]. Thus, at $5 \times 10^{-5}$ mol dm$^{-3}$, it can be calculated that 15.1% of the total dye concentration exists as dimers. In order to investigate the effect of dimers, therefore, on the free radical chemistry, solutions containing dye concentrations in the range $7.6 \times 10^{-5}$–$1.9 \times 10^{-4}$ mol dm$^{-3}$ were pulsed irradiated under similar conditions to those used for dilute solutions above.

As with the dilute solutions at pH values close to 4, characteristic transient difference spectra similar to that observed in Fig. 2 were observed having absorption maxima at 470 nm (450 nm at the highest dye concentration of $1.9 \times 10^{-4}$ mol dm$^{-3}$). The transient difference spectrum measured at the end of the $Br_2^{\bullet -}$ reaction is shown in Fig. 4 for the dye concentration of $1.0 \times 10^{-4}$ mol dm$^{-3}$ (similar spectra were obtained for all three concentrations used but not shown).

It was observed that both the decay rate of $Br_2^{\bullet -}$ absorbance at 360 nm and growth rate of the 470 nm absorbance were the same, within experimental error, for each experimental condition. Fig. 5 is a plot of the average of these first-order rate constants measured over a range of dye concentrations, $5 \times 10^{-6}$–$1.9 \times 10^{-4}$ mol dm$^{-3}$.

As at low dye concentrations at pH values around 4, the decays of absorbance at 470 nm were relatively slow at all these dye concentrations showing a loss of only 50% after some 200 ms.

At pH values 8.3–8.4 in nitrous oxide saturated solutions, $Br_2^{\bullet -}$ was found to react with rhodamine 6G at concentrations of $1.0 \times 10^{-4}$ and $1.9 \times 10^{-4}$ mol dm$^{-3}$ with first-order rate constants which were the same, within experimental error, to those measured at pH values around 4.0 (also shown in Fig. 5). Similar transient spectra were obtained at the end of $Br_2^{\bullet -}$ reaction under the above conditions. A representative spectrum (for $1.0 \times 10^{-4}$) is also shown in Fig. 4.

Over longer timescales, the transient species formed at $1.0 \times 10^{-4}$ and $1.9 \times 10^{-4}$ mol dm$^{-3}$ dye concentrations were found to decay at a much faster rate than was observed at pH 4.0 as was also the case at low dye concentrations at this pH. Fig. 4 shows the spectrum for $1.0 \times 10^{-4}$ mol dm$^{-3}$ measured at 4 ms after the pulse, at which time about 70% of the initial absorbance had disappeared. This spectrum is significantly different to that observed at the end of the decay of the 470 nm transient at low dye concentrations (see Fig. 2). It seems likely therefore that the decay product at high dye concentrations many also associate with ground state dye molecules to form a species with a relatively strong absorption ($\Delta\varepsilon = 6600$ dm$^3$ mol$^{-1}$ cm$^{-1}$) at 570–580 nm.

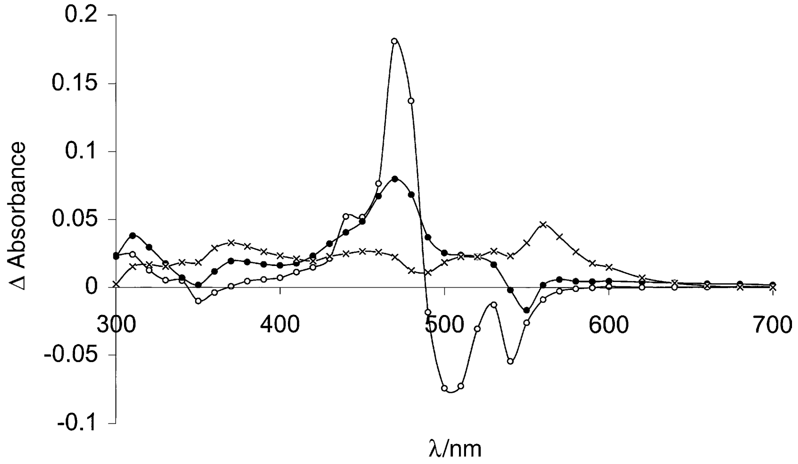


Fig. 4. Transient absorption spectra measured on pulse irradiation of nitrous oxide saturated solution of $10^{-2}$ mol dm$^{-3}$ potassium bromide containing $1.0 \times 10^{-4}$ mol dm$^{-3}$ rhodamine 6G at pH 4.0 and 8.3. Dose = 3.7 Gy; normalised to 2.5 cm path length. ((●) 80 μs; pH 4), ((○) 130 μs; pH 8.3) and ((×) 4 ms; pH 8.3).

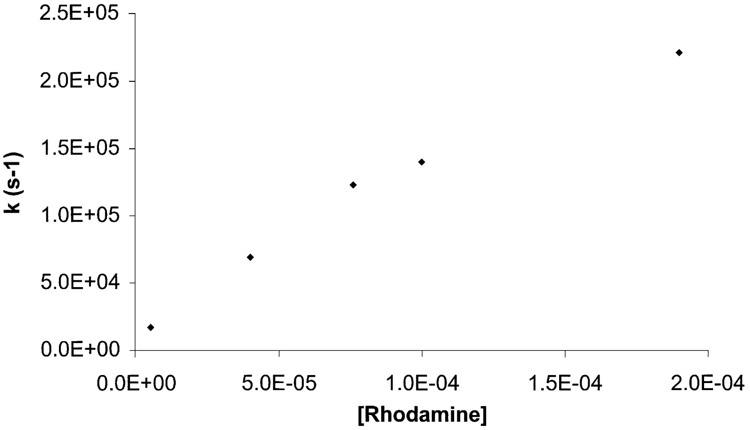


Fig. 5. The effect of total rhodamine 6G concentration on the first-order rate constants for the formation of the 470 nm absorption in nitrous oxide saturated solutions of $10^{-2}$ mol dm$^{-3}$ potassium bromide.

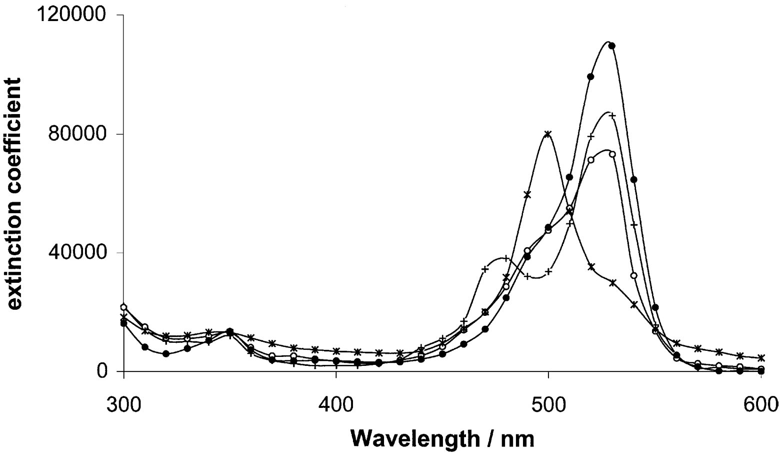


Fig. 6. Spectra of rhodamine 6G species: ground state monomer (●); ground state dimer (✱); cation radical at pH 3.9 (from data in Fig. 2 (+)); cation radical at pH 8.3 (from data in Fig. 2 (○)).

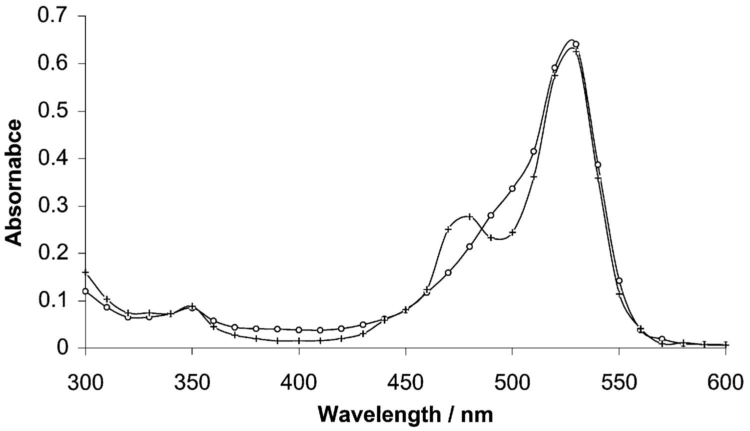


Fig. 7. Corrected absorption spectra obtained from Fig. 4 at pH 4 ((+) $1.0 \times 10^{-4}$ mol dm$^{-3}$ rhodamine 6G) and at pH 8.3 ((○) $1.0 \times 10^{-4}$ mol dm$^{-3}$ rhodamine 6G).

In order to interpret the spectral changes observed in Fig. 4 which represent rhodamine dye free radicals formed at the end of the $Br_2^{\bullet -}$ reactions, it is necessary to estimate the proportions of $Br_2^{\bullet -}$ which react with dye monomers and dimers. To do this, the kinetic data in Fig. 5 can be analysed to produce a rate constant for the reaction of $Br_2^{\bullet -}$ with dye dimers assuming that the observed rate constants ($k_{obs}$) in the figure can be fitted to the equation:

$$k_{obs} = k_1[\text{monomer}] + k_2[\text{dimer}] \quad (17)$$

where [monomer] and [dimer] can be calculated from $K_d = (1-x)/2cx^2$ ($x$: molar fraction of monomer, $c$: total dye concentration, $K_d = 5000\,dm^3\,mol^{-1}$). This value is a little different to that measured in an earlier study where $K_d$ was found to be $6200\,dm^3\,mol^{-1}$ [25] and arises from experiments carried out in this work under the conditions which apply here. The monomer and dimer spectra so obtained are shown in Fig. 6. Using $k_1 = 2.2 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$, $k_2$ is thus estimated to be $3.6 \pm 0.5 \times 10^8\,dm^3\,mol^{-1}\,s^{-1}$.

Using this kinetic data together with known spectra of the ground state monomeric and dimeric forms of rhodamine 6G, it is possible to correct the difference spectra in Fig. 4 by calculating the amount of the dye ground state absorption lost due to reactions of $Br_2^{\bullet -}$ with the monomers and dimers. To do this, the ground state spectra for the monomer and dimer shown in Fig. 6 were used. The corrected spectra of the rhodamine 6G free radicals so obtained are shown in Fig. 7 for both pH 4.2 (at $1 \times 10^{-4}\,mol\,dm^{-3}$ dye, 9.2% dimer) and pH 8.4 (identical corrected spectra were obtained at both $1.0 \times 10^{-4}$ (9.2% dimer) and $1.9 \times 10^{-4}\,mol\,dm^{-3}$ (18% dimer) dye, the figure shows only the spectrum obtained at $1.0 \times 10^{-4}\,mol\,dm^{-3}$ dye).

Also shown in Fig. 6 are the corrected cation radical spectra obtained from reactions of $Br_2^{\bullet -}$ at low dye concentrations where only the dye monomers are present. Comparison of the free radical spectra shown in Figs. 6 and 7 show that they are very similar in shape at the respective pH values, with relatively small differences in extinction coefficient which can be attributed to both experimental and other errors.

## 7. Conclusions

These studies have demonstrated that $Br_2^{\bullet -}$ reacts at near diffusion-controlled rates with rhodamine 6G to produce the cation radicals, $RhH^{2\bullet +}$ and $Rh^{\bullet +}$ (the deprotonated form). The p$K_a$ value of 5.7 for dissociation of $RhH^{2\bullet +}$ is close to that determined for the corresponding cation radical of rhodamine 123 [15]. Both forms of the cation radical have characteristic difference absorption spectra, with maxima at around 470 nm, with the protonated form, $RhH^{2\bullet +}$ absorbing more intensely than the deprotonated form.

Both $RhH^{2\bullet +}$ and $Rh^{\bullet +}$ are relatively long-lived, the former species being easily detected up to 1 s after the pulse. Interestingly, at the end of the decay of $Rh^{\bullet +}$, significant increases (relative to the dye ground state) in absorption in the typical rhodamine dye laser output wavelength range (555–620 nm) were observed. The increase in extinction coefficient was about 30,000–35,000 $dm^3\,mol^{-1}\,cm^{-1}$ at 560 nm and about 8000–12,000 $dm^3\,mol^{-1}\,cm^{-1}$ at 590 nm.

Oxygen did not react with either of the cation radicals. However, the peroxy radicals, $O_2^{\bullet -}$ (or its protonated form, $HO_2^{\bullet}$) were found to react with these dye radicals. It seems likely that this reaction regenerates the ground state of the dye, although the percentage regeneration is pH dependent, being in competition with the pH dependent dismutation of $O_2^{\bullet -}/HO_2^{\bullet}$.

From experiments at high concentrations of rhodamine 6G, $Br_2^{\bullet -}$ reacts about six times as fast with the monomer compared to the dimer. Although the transient difference spectra measured at high dye concentrations are complicated by changes in absorption of the ground state due to the differing spectra of dye monomers and dimers, the evidence presented here shows that the monomeric forms of the cation radical are still produced. This may not be surprising since it may be expected that any dimeric cation radicals produced initially ($RhH^{2\bullet +} \cdots RhH^{+}$ and $Rh^{\bullet +} \cdots RhH^{+}$) are likely to dissociate rapidly facilitated by solvation of these highly polar species. To be consistent with the kinetic data, the dissociation rates would have to be greater than $5 \times 10^6\,s^{-1}$.

It has been shown earlier that rhodamine 123 can also form cation radicals through photoionisation in aqueous solution, probably by both mono- and biphotonic processes [15]. The yield for the monophotonic process was found to be low (<0.001). Although no similar study has been carried out on rhodamine 6G, it would be surprising if photoionisation did not also occur. It may also be surmised that either photoionisation and/or photodissociation (to give similar dye free radical species) would be likely in the polar solvents (e.g. methanol) used in dye laser systems.

The efficiency and lifetimes of rhodamine laser systems depend both on the inherent energy loss mechanisms and the photostability of the dye. For liquid dye lasers which usually involve flow, lack of photostability arising from photodegradation is not a significant problem. In solid-state dye lasers, however, there is no mechanism for removing photodegradation products. In such lasers, the efficiency appears to reach a limiting value of about 50% and is not dependent on the nature of the solid matrix, indicating that phtodegradation may occur spontaneously from higher excited singlet states via excited state absorption (ESA) [9]. Our earlier picosecond studies showed that ESA is significant for rhodamines throughout the ‘pumping’ wavelength range [14]. For liquid rhodamine systems, it appears that the production of the triplet state, although of very low yield, is the main mechanism for photodegradation [32].

In view of our previous work on the photoionisation of rhodamine 123 and also the work presented here, it seems likely that there are at least two processes by which the ‘pumping’ process in laser action can cause photodegradation i.e. via either intersystem crossing from the lowest excited singlet state of the dye or by photoionisation in a mono- or biphotonic process to produce dye cation radicals. Both processes can be minimised in flow systems. However, in solid-state dye lasers, cation radicals of the dye, already long-lived in solution, will be even longer-lived in the solid state leading to photodegradation unlike dye triplet states which can still be readily quenched by the rapidly diffusing oxygen molecule. Probably more significant, however, is the ability of such long-lived species or their reaction products to absorb the laser output itself i.e. in the region of 555–620 nm. It can be seen from this work that the reaction product of the decay of the dye free radical, $Rh^{\bullet +}$, absorbs relatively strongly at these wavelengths at all dye concentrations and it may be this species which has a significant effect on the limited lifetimes of solid-state dye laser systems based on rhodamines.

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