

Oxidation of crystal violet and malachite green in aqueous solutions — a kinetic spectrophotometric study

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Abstract

The reactions of two triphenyl methane (TPM) dyes — crystal violet (CV^+) and malachite green (MG^+) — with $N_3^{\cdot-}$ and OH^{\cdot} radicals were studied by pulse radiolytic kinetic spectrophotometry. The rate constants for the reaction of the cationic dyes (D^+) with $N_3^{\cdot-}$ are $(9.0 \pm 0.6) \times 10^9$ and $(3.0 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively and those for the reaction with OH^{\cdot} are obtained as $(8.0 \pm 0.6) \times 10^9$ and $(1.1 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. The transient spectra resulting from the oxidation of the dyes were characterized. The time-resolved spectra indicate that the reaction with OH^{\cdot} radicals initially generates an adduct which subsequently dissociates to form the radical dication $D^{\cdot 2+}$. The $D^{\cdot 2+}$ species decay by further reaction with the parent dye.

Keywords: Oxidation; Crystal violet; Malachite green; Kinetic spectrophotometry; Radicals; Pulse radiolysis

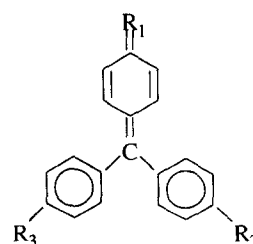
1. Introduction

Reduction and oxidation reactions of triphenyl methane (TPM) dyes incorporated in polymers, fibres and polyelectrolytes have been increasingly studied in recent years with a view to understanding the photodegradation of this class of dyes [1–7]. Apart from their use in dyeing textiles, TPM dyes find wide application as saturable absorbers [8], laser dyes [9], biological stains and in cosmetics and stationery [10]. The mechanism of photofading of these dyes is far from clearly understood. Reduction reactions involving electron transfer from suitable donors have been studied by photochemical techniques [4,6,11]. Using the technique of pulse radiolysis, we have recently reported a time-resolved study on the reduction of four TPM dyes, namely brilliant green, malachite green, crystal violet and methyl green, by diphenyl ketyl radicals and hydrated electrons (e_{aq}^-) [12]. A recent photobleaching study by Jockusch et al. on the 532 nm excitation of crystal violet in aqueous polymeric solutions has provided evidence for the formation of semioxidized and semireduced species [6]. In the context of effluent water treatment, oxidative degradation of TPM dyes by ozone and UV irradiation has been investigated [13,14]. It is clear that degradation of the dyes, photochemical or otherwise, in various media will involve both reduction as well as oxidation.

However, little work is available on the intermediate stages of dye oxidation as compared with reduction.

Pulse radiolysis has been the technique of choice for studying oxidation reactions, since, using suitable conditions, one-electron oxidants such as OH^{\cdot} and $N_3^{\cdot-}$ can be conveniently generated [15]. In the present work, employing pulse radiolysis of aqueous medium, the oxidation of two widely used TPM dyes, namely crystal violet and malachite green, by $N_3^{\cdot-}$ and OH^{\cdot} radicals has been studied. The reactivities of the dye molecules towards the oxidant radicals were estimated. The transient spectra arising from the radical reactions with the dyes were obtained. The decay kinetics of the oxidized dye species were also evaluated.

The structures of the dyes are given below:



Dye	R ₁	R ₂	R ₃
CV ⁺	N(CH ₃) ₂	N(CH ₃) ₂	N(CH ₃) ₂
MG ⁺	N(CH ₃) ₂	N(CH ₃) ₂	H

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2. Experimental details

The dyes employed in this work were in the cationic form (D^+). Crystal violet in the chloride form (Sigma Chemical Co.) was used as received. Malachite green oxalate (Qualigens, Bombay) was used after repeated crystallization from ethanol–water mixture. NaN_3 (Fluka, Purris) was used as received. All aqueous solutions were prepared in nanopure water obtained from a Barnstead system (resistivity $18.3 \text{ M}\Omega \text{ cm}$) and irradiated at their natural pH. The aqueous solutions were deaerated and saturated with N_2O (Indian Oxygen Iolar grade, purity better than 99.8%) before carrying out irradiations. Pulse radiolysis experiments were carried out using 50 ns electron pulses from a 7 MeV linear electron accelerator (Ray Technology, UK). The detailed experimental set-up for pulse radiolysis and kinetic spectrophotometry was described earlier [12,16]. Solutions in Suprasil cuvettes of 1 cm path length were irradiated at a radiation dose of 7 Gy per pulse or less as measured by an air-saturated 0.05 mol dm^{-3} KCNS dosimeter, taking $G\epsilon$ for $(\text{CNS})_2^{2-}$ as $21\,522 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 500 nm, G being defined as the number of molecules formed per 100 eV of energy absorbed [15]. At the highest dose of 7 Gy, about $5 \times 10^{-6} \text{ mol dm}^{-3}$ OH^\cdot radicals were formed per pulse in N_2O -saturated solution, where all the e_{aq}^- would be converted into OH^\cdot radicals.

In the concentration range studied, both the dyes were present in their monomeric form, as seen by the proportionality between absorbance and concentration.

3. Results and discussion

Both the TPM dyes used have good reactivity towards e_{aq}^- . The rate constants for the reaction of e_{aq}^- with CV^+ and MG^+ are 4.0×10^{10} and $9.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respec-

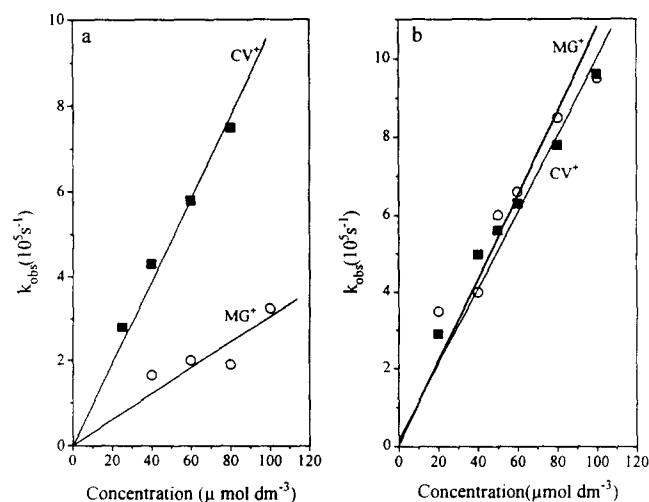
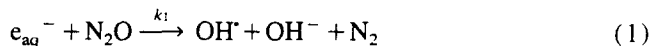


Fig. 1. (a) Plots of pseudo-first-order rate constant vs. [dye] for dye + N_3^\cdot reaction in N_2O -purged dye solutions containing $5 \times 10^{-3} \text{ mol dm}^{-3}$ NaN_3 . (b) Plots of pseudo-first-order rate constant vs. [dye] for dye + OH^\cdot reaction in N_2O -purged solutions.

tively [12]. However, in the dye solutions employed here, the e_{aq}^- produced by the electron pulses were nearly quantitatively replaced by OH^\cdot radicals by prior purging and saturation of the solutions with N_2O :



$$(k_1 = 9.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [17])$$

In the dye solutions to which NaN_3 was also added, the oxidant radical N_3^\cdot could be generated subsequently by nearly exclusive reaction of OH^\cdot with azide:



$$(k_2 = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [17])$$

Following the generation of the oxidant radicals N_3^\cdot and OH^\cdot , a growth of transient absorption that could be attributed to the radical encounter with the dye was observed in each case.

Owing to the intense optical absorption of the parent dyes throughout the visible region, the apparent transient changes in absorbance were either positive or negative depending upon the monitoring wavelength. However, knowing the values of the molar extinction coefficients of the parent dyes for the various wavelengths, the extinction values of the species responsible for the transient spectra have been evaluated as

$$\epsilon_{\text{R}} = \epsilon_{\text{p}} + \frac{21\,522 \times \Delta(\text{OD})}{\text{OD}_{\text{D}} \times G(-\text{dye})} \quad (\text{A})$$

where ϵ_{R} and ϵ_{p} are the molar extinction coefficients of the transient and the parent dye respectively at a particular wavelength and OD_{D} is the optical density of $(\text{CNS})_2^{2-}$ at 500 nm obtained for the KCNS dosimeter solution. It was apparent that at all the wavelengths monitored, both the formation of the transient species and the depletion of the parent dye contributed to the observed absorbance and hence the value for $G(-\text{dye})$ could not be estimated independently. However, at the highest dye concentrations employed for obtaining the ϵ values, the reaction of the oxidant radical with the dye was quantitative. Therefore in the case of such solutions it could be assumed that $G(-\text{dye}) = G(\text{oxidant}) = 6.0$ for estimating the values of ϵ using relation (A).

3.1. Reaction of CV^+ with azide radical

A build-up of transient absorbance that could be attributed to the reaction between CV^+ and N_3^\cdot was readily observed at 380 nm. At this wavelength the ϵ value for CV^+ is low and any contribution to the absorbance from dye bleaching could be neglected. The rates of absorbance growth fitted a first-order kinetics dependent upon the dye concentration. By varying $[\text{CV}^+]$ in the range $(2-8) \times 10^{-5} \text{ mol dm}^{-3}$ and employing an appropriate dose per pulse, the corresponding pseudo-first-order constant k_{obs} (s^{-1}) was evaluated. The linear plot of k_{obs} vs. $[\text{CV}^+]$ thus obtained is shown in Fig.

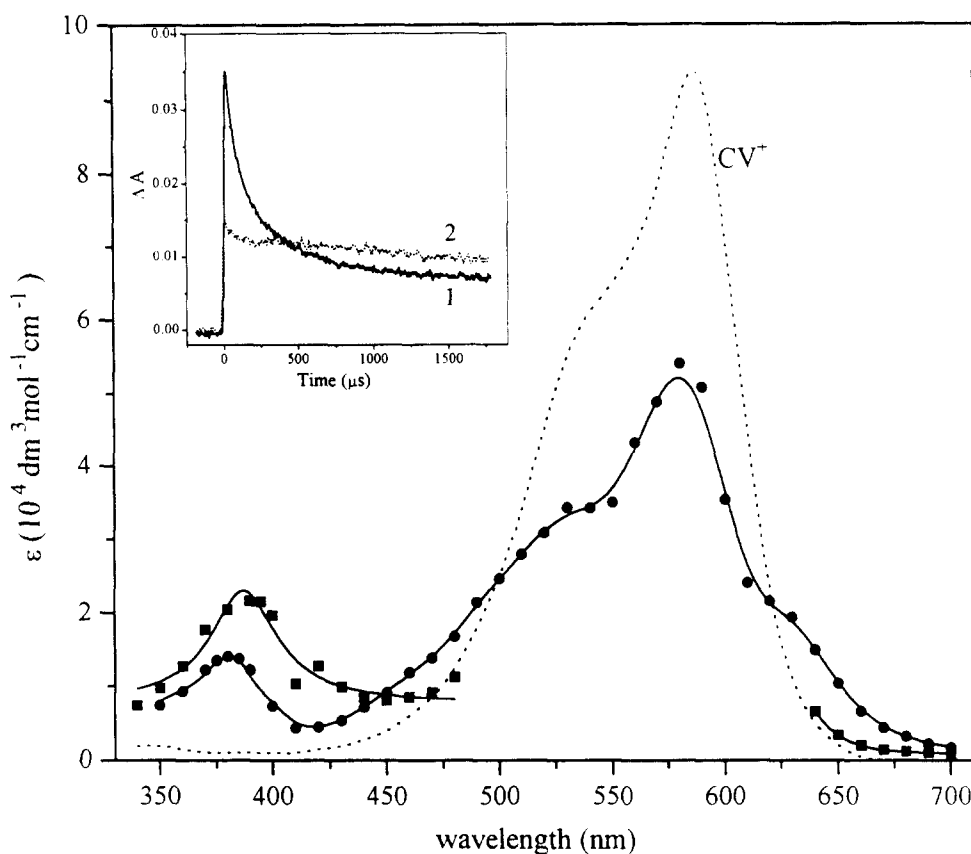
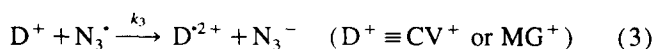


Fig. 2. (●) Transient absorption spectrum (corrected) from N_2O -purged CV^+ solutions containing $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaN}_3$. The spectrum in the 340–460 and 640–700 nm regions was evaluated at $8 \mu\text{s}$ delay employing $6 \times 10^{-5} \text{ mol dm}^{-3} \text{ CV}^+$. The 470–630 nm region was covered with $35 \mu\text{s}$ delay or less and $2 \times 10^{-5} \text{ mol dm}^{-3} \text{ CV}^+$ or less and appropriate normalization to about 100% reaction (see text). (■) Transient absorption spectrum (corrected) from N_2O -purged $6 \times 10^{-5} \text{ mol dm}^{-3} \text{ CV}^+$ solutions evaluated at $6 \mu\text{s}$ delay. (...) Ground state absorption spectrum of CV^+ in water. Inset: decay of transient absorbance in N_2O -purged solutions containing $6 \times 10^{-5} \text{ mol dm}^{-3} \text{ CV}^+$ and $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaN}_3$ — 1, $\lambda = 380 \text{ nm}$; 2, $\lambda = 670 \text{ nm}$.

1a. Since the azide radical is a well-known one-electron oxidant, we attribute the observed transient absorption at 380 nm to the generation of the oxidized form of the dye, CV^{2+} :



From the slope of the linear plot the bimolecular rate constant was evaluated as $k_3 = (9.0 \pm 0.6) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction of N_3^{\cdot} with CV^+ .

The absorption spectrum of CV^{2+} between 340 and 700 nm was obtained by recording the fully developed transient absorbance. Taking into account the ground state absorption of CV^+ , an appropriate dye concentration was employed for the various spectral regions. The 340–460 and 640–700 nm regions could be covered with $6.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ CV}^+$. At this concentration almost all the N_3^{\cdot} reacted according to reaction (3). Lower concentrations of the dye ($2 \times 10^{-5} \text{ mol dm}^{-3}$ or less) were used to obtain the transient spectrum in the 470–630 nm region. The absorbance values recorded in this region were normalized to 100% reaction of N_3^{\cdot} with the dye molecules. This was done by noting the ratio of maximum absorbance values for $6 \times 10^{-5} \text{ mol dm}^{-3}$ and the lower dye concentration at 380 nm, which was a convenient window in the ground state absorption spectrum of the parent dye. The

complete spectrum of CV^{2+} obtained, with estimated values of ϵ , is shown in Fig. 2.

It was interesting to note that in separate experiments on the laser flash photolysis of aqueous CV^+ solutions, following the excitation of CV^+ by a 248 nm laser (KrF excimer laser, 10 ns, 100 mJ), an e_{aq}^- absorption band in the 650–750 nm region and another band centred at 380 nm have been observed [18]. The latter band, which was attributed to CV^{2+} species, was very similar to that shown in Fig. 2.

The slower decay of CV^{2+} could be conveniently monitored at 380 nm on a 100 μs –millisecond time scale. The decay kinetics deviated significantly from second order and conformed to first order, with a dependence on $[\text{CV}^+]$. The decay rates were unaffected by a variation in azide concentration ($(2-5) \times 10^{-3} \text{ mol dm}^{-3}$).

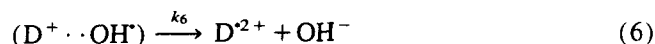
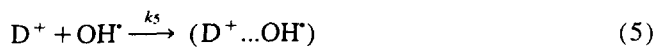


From the absorbance changes at 380 nm, k_4 was evaluated in a similar manner to k_3 and found to be $(9.0 \pm 0.5) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It was noted that the relative changes in absorbance occurring as a result of reaction (4) were different in the different spectral regions. The inset of Fig. 2 shows the absorbance values at 380 and 670 nm, where the absorbance changes due to parent dye bleaching would be negligible. The

apparently small changes in absorbance values at 670 nm as compared with those at 380 nm would mean that the ϵ values for the decaying CV^{2+} and for the product from reaction (4) were comparable at 670 nm.

3.2. Reaction of CV^+ with hydroxyl radical

The reaction of OH^\cdot with CV^+ also gave rise to an initial development of an absorption band centred at 380 nm. However, it was noted that the spectral features of the band were significantly different from those obtained for the oxidation of CV^+ by N_3^\cdot (reaction (3)). The band was broader and the estimated value of ϵ at 380 nm was much higher. Moreover, the absorbance decay at 380 nm displayed a faster and a slower component. These observations and the features of the time-resolved spectra in the 340–700 nm region, covered by appropriate variation in the CV^+ concentration, showed the consecutive occurrence of the reactions



The value of k_5 for OH^\cdot adduct formation was obtained by following the growth of initial absorbance in the $(4\text{--}10) \times 10^{-5} \text{ mol dm}^{-3}$ range of $[\text{CV}^+]$ at 380 nm. The growth followed a pseudo-first-order kinetics and from the slope of the linear plot of pseudo-first-order rate constant k_{obs} vs. $[\text{CV}^+]$ (Fig. 1b) the bimolecular rate constant k_5 was obtained as $(8.0 \pm 0.9) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The decay traces at 380 nm corresponded to two first-order components and were analysed in detail. The slower component showed a dependence of the rates on $[\text{CV}^+]$, as could be expected according to reaction (4) following the formation of CV^{2+} from the adduct species. The corresponding bimolecular rate constant was estimated as about $5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in fair agreement with the value for k_4 obtained from the oxidation of CV^+ by N_3^\cdot . The initial faster decay component was found to be independent of CV^+ concentration and would correspond to the formation of CV^{2+} from the OH^\cdot adduct according to reaction (6). From the analysis of the initial portion of the decay traces we estimated $k_6 \approx 10^4 \text{ s}^{-1}$.

The initial absorption spectrum recorded in the 340–460 and 640–700 nm regions by employing $6 \times 10^{-5} \text{ mol dm}^{-3}$ CV^+ and at 6 μs delay after the electron pulse is also shown in Fig. 2. The spectrum could be attributed to the adduct ($\text{CV}^+ \cdots \text{OH}^\cdot$) proposed in reaction (5). The ϵ values in the spectrum were estimated after due correction for dye bleaching as mentioned earlier (Eq. (A)), since at 6 μs the reaction of OH^\cdot with CV^+ would be essentially complete and the extent of reaction (6) could be neglected.

The time-resolved spectra in the 440–670 nm region, evolving at 25 and 170 μs delay from $2 \times 10^{-5} \text{ mol dm}^{-3}$ CV^+ solutions, are shown in Fig. 3. It may be noted that in contrast with the absorbance decay at 380 nm, the absorbance value at λ_{max} (590 nm) increased between the two time

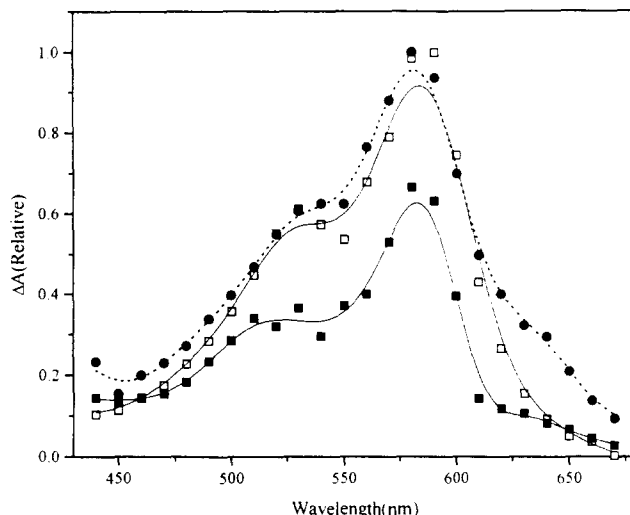


Fig. 3. Transient absorption spectra (corrected for dye depletion with $G = 6.0$) from N_2O -purged $2 \times 10^{-5} \text{ mol dm}^{-3}$ CV^+ solutions evaluated at 25 μs (■) and 170 μs (●) delay. (●) Comparative spectrum at 170 μs delay obtained from solutions which also contained $5 \times 10^{-3} \text{ mol dm}^{-3}$ NaN_3 (see text).

delays. It can be estimated from the values of k_5 and k_6 that the spectrum at 25 μs would correspond to the formation of the OH^\cdot adduct and its partial decay (reaction (6)). However, the spectrum at 170 μs was very similar to that obtained from the reaction of N_3^\cdot with $2 \times 10^{-5} \text{ mol dm}^{-3}$ CV^+ at the same delay. The spectrum at longer delay thus represents the presence of largely one species, i.e. CV^{2+} , corroborating the decay of the OH^\cdot adduct according to reaction (6).

3.3. Oxidation of MG^+

The processes observed for the N_3^\cdot - and OH^\cdot -radical-induced oxidation of malachite green and crystal violet were similar and the individual steps could be represented by reactions (3)–(6).

Fig. 4 shows the corrected transient spectrum arising as a result of the reaction of N_3^\cdot with MG^+ . The absorbances in the 330–540 and 650–690 nm spectral regions were obtained by employing $5 \times 10^{-5} \text{ mol dm}^{-3}$ MG^+ . The intermediate region (550–640 nm) was covered with a lower concentration ($2 \times 10^{-5} \text{ mol dm}^{-3}$) of MG^+ and the absorbances were normalized for approximately 100% reaction by reference to $5 \times 10^{-5} \text{ mol dm}^{-3}$ MG^+ . The relative values of the maximum absorption build-up at 350 nm as well as at 480 nm were used for the normalization procedure, since any contribution to the observed absorbance from bleaching of the dye could be neglected at either of the above wavelengths. The spectrum with discernible λ_{max} at 425, 540 and 610 nm could be attributed to the dication MG^{2+} formed according to reaction (3).

The plots of pseudo-first-order rate constant vs. dye concentration for the growth of MG^{2+} (reaction (3), Fig. 1a) as well as its slower decay (reaction (4)), both monitored at 350 and 480 nm, were linear. From the slopes of the plots

Table 1
Spectral and kinetic parameters for the oxidation of CV⁺ and MG⁺ by N₃[•] and OH[•] radicals

Parameter	Dye	
	CV ⁺	MG ⁺
$k_3(D^+ + N_3^{\bullet})$ (dm ³ mol ⁻¹ s ⁻¹)	$(9.0 \pm 0.6) \times 10^9$	$(3.0 \pm 0.2) \times 10^9$
$\lambda_{\max}(D^{2+})$ (nm)	380, 580	425, 540, 610
$\epsilon_{\max}(D^{2+})$ (dm ³ mol ⁻¹ cm ⁻¹)	1.4×10^4 (380 nm) 5.4×10^4 (580 nm)	1.4×10^4 (425 nm) 2.2×10^4 (540 nm) 3.5×10^4 (610 nm)
$k_4(D^{2+} + D^+)$ (dm ³ mol ⁻¹ s ⁻¹)	$(9.0 \pm 0.5) \times 10^7$	$(3.2 \pm 0.4) \times 10^7$
$k_5(D^+ + OH^{\bullet})$ (dm ³ mol ⁻¹ s ⁻¹)	$(8.0 \pm 0.9) \times 10^9$	$(1.1 \pm 0.1) \times 10^{10}$
$\lambda_{\max}(D^+ \cdots OH^{\bullet})$ (nm)	385	400
$\epsilon_{\max}(D^+ \cdots OH^{\bullet})$ (dm ³ mol ⁻¹ cm ⁻¹)	2.3×10^4	1.35×10^4
$k_6(D^+ \cdots OH^{\bullet})$ (s ⁻¹)	$\approx 10^4$	$(4.8 \pm 0.6) \times 10^3$

the estimated values of bimolecular rate constants were $k_3 = (3.0 \pm 0.2) \times 10^9$ dm³ mol⁻¹ s⁻¹ and $k_4 = (3.2 \pm 0.4) \times 10^7$ dm³ mol⁻¹ s⁻¹.

The rates of absorbance build-up as a result of the reaction of OH[•] with MG⁺ were followed at 350 nm. The linear plot of k_{obs} vs. [MG⁺] (Fig. 1b) gave the value $k_5 = (1.1 \pm 0.1) \times 10^{10}$ dm³ mol⁻¹ s⁻¹. The corrected spectrum due to the OH[•] adduct arising from reaction (5) was obtained at 6 μs delay from 5×10^{-5} mol dm⁻³ MG⁺ solutions and is shown in Fig. 4.

The two components observed for the absorbance decay at 340–360 nm could be attributed to processes (6) and (4).

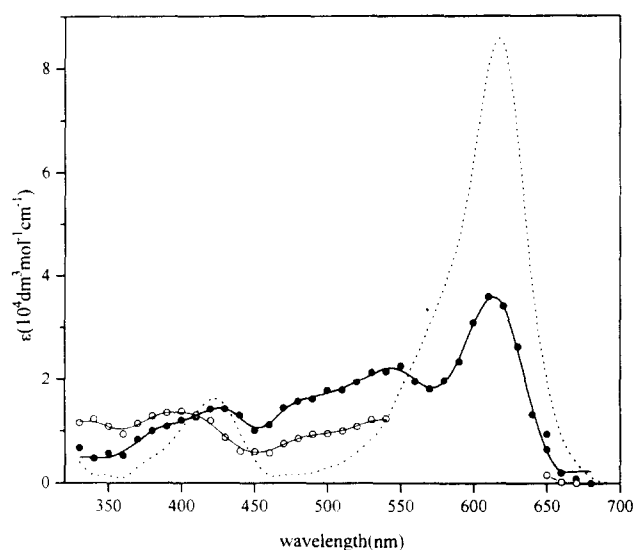


Fig. 4. (●) Transient absorption spectrum (corrected) from N₂O-purged MG⁺ solutions containing 5×10^{-3} mol dm⁻³ NaN₃; [MG⁺] = 5×10^{-5} mol dm⁻³ for the 330–540 and 650–690 nm regions, delay 15 μs; [MG⁺] = 2×10^{-5} mol dm⁻³ for the 550–640 nm region, delay = 30 μs (absorbances were normalized w.r.t. 5×10^{-5} mol dm⁻³). (○) Transient spectrum (corrected) from N₂O-purged solutions obtained at 6 μs delay. (...) Ground state spectrum of MG⁺ in water.

From the analysis of the faster component of the decay trace the rate constant for the formation of MG²⁺ from the adduct (MG⁺...OH[•]) was estimated to be about $(4.8 \pm 0.6) \times 10^3$ s⁻¹.

The various spectral and kinetic parameters evaluated in the present study are summarized in Table 1.

4. Conclusions

The oxidation of two triphenylmethane dyes (crystal violet and malachite green) was studied by the pulse radiolysis technique. Absorption spectra of the transient species and the rate constants for their formation and decay were obtained. The transient spectrum arising from the reaction between the dyes and the N₃[•] radical could be attributed to the radical dication D²⁺. Time-resolved spectra show that the OH[•] radical reaction with the dyes initially forms an adduct which dissociates in a first-order process to generate D²⁺. The radical dication decays by a pseudo-first-order process via reaction with the parent dye.

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